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Recent Advances and Perspectives in Catalyst Design for Converting Syngas to Higher Alcohols

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Cite This: *Energy Fuels* 2024, 38, 14769−14796 Read Online

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ABSTRACT: Higher alcohol synthesis (HAS) has attracted much attention owing to the wide use of $C_{2+}OH$ as a synthetic fuel, an alternative fuel additive, a hydrogen carrier, and a versatile platform molecule. Using homogeneous and heterogeneous catalysts, HAS can be produced from syngas (H_2 and CO) derived from nonfood-based lignocellulosic biomass, oil residues, coal, natural gas, and solid or liquid carbonaceous waste products. Although much effort has been devoted to maximizing the yield of $C_{2+}OH$ using noble- and non-noble-metal catalysts, significant challenges remain in terms of large-scale industrial production. In the past decade, the development of solid catalysts for the efficient production of higher alcohols, from carbon feedstocks, has attracted much interest. In this Review, we focus on the developments in the past decade that have focused on the use of heterogeneous catalysts in HAS. We have reviewed the developments regarding the effect of supports, promoters, Rh-based catalysts, modified methanol synthesis catalysts, modified Fischer−Tropsch (FT) synthesis catalysts, Mo/MoS_2-based catalysts, and the generic structural design of catalysts on their catalytic performances in HAS. We have also summarized the use of tandem catalysts that have been used in HAS. Catalyst stability, reaction mechanisms, and density functional theory (DFT) calculations used in HAS studies have also been briefly discussed. Finally, we provide our insights and perspectives on the topic to encourage further exploration in this emerging field.



1. INTRODUCTION

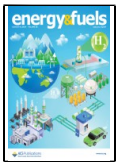
A society's development requires energy and chemicals, and modern society is based on access to carbon-based sources to fulfill these requirements. Traditionally, carbon energy and carbon-based chemicals come from fossil fuels (coal, petroleum, and natural gas), which are not renewable. Therefore, the integrated utilization of coal and natural gas with renewable energy sources has received increasing attention. One of the key strategies to achieve this integration will be to use CO as a primary building block to make chemicals and fuels. CO together with H_2 is called syngas. Syngas, depending on factors such as the catalyst, reaction conditions, and reactor type, can be converted into a range of chemicals/fuels which include methanol, ethanol, $C_{2+}OH$, alkanes, alkenes, etc.[1] Until recently, most studies on making alcohols from syngas focused on making ethanol and methanol. However, the higher alcohols ($>C_{2+}$) have high added-value and thus have become a product of importance. This Review focuses on methods for making future "O" containing fuels and chemicals of the type $C_{2+}OH$, called higher alcohols.

In the past, the abundance of coal and natural gas reserves on earth was the main source of carbon that was converted into syngas. Indeed, Germany and China, and certain other countries that were lacking petroleum, developed technology for the gasification of coal (and later natural gas) to produce CO that was used to make chemicals and fuels.[2] Low-temperature (900 °C) and high-temperature (>1300 °C) gasification processes were used for direct gasification.[3]

Syngas (CO/H_2) can also be obtained from CO_2 by means of dry reforming with CH_4 and by use of the reverse water gas shift (RWGS) reaction. Syngas can also be produced from renewable biomass and some solid and liquid carbonaceous waste products.[4] Large reserves of nonfood-based lignocellulose materials can also be converted into CO/H_2 through gasification processes.[5] Therefore, syngas is an important platform matrix that can be derived from renewable and nonrenewable sources for downstream energy applications and making chemicals.

Indeed, the industrial production of alcohols, in particular, methanol, has been in place worldwide for decades and uses Cu-ZnO catalysts at ∼250 °C and ∼10 MPa.[6] The Fischer−Tropsch (FT) synthesis reaction can also make some alcohols, including methanol. Once made, methanol can be transformed

Received: March 25, 2024
Revised: July 10, 2024
Accepted: July 10, 2024
Published: July 25, 2024



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https://doi.org/10.1021/acs.energyfuels.4c01419
Energy Fuels 2024, 38, 14769−14796

to various valuable chemicals, such as dimethyl ether (DME) and lower hydrocarbons. $C_{2+}OH$ products have also been obtained from syngas streams.

Compared with alkane products obtained using the conventional FTS process, $C_{2+}OH$ is a much more versatile product. These alcohols have different properties compared with those of methanol and thus produce many products used in different environments (Figure 1). For example, $C_{2+}OH$ can

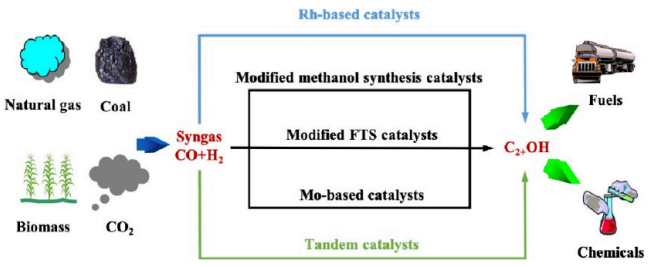


Figure 1. Five types of representative catalysts for the synthesis of $C_{2+}OH$ in heterogeneous catalysis.

be added to gasoline as a fuel additive to improve the octane value of an engine.[7] Also, steam reforming of ethanol can offer H_2 for fuel cells and some chemical processes.[8,9]

It is necessary to consider the activity/selectivity of $C_{2+}OH$ and the cost of the catalysts for commercial application. In order to ensure economic viability, the required alcohol productivity should be as high as about 0.5 g/(g_{cat}·h).[10] Since the 1980s, some companies and institutes have filed many patents related to CO/H_2 conversion to $C_{2+}OH$.[7,11] So far, commercial success in this field has not been achieved due to the low yield of $C_{2+}OH$. However, with increasing concern about the depletion of oil reserves and possible price fluctuations in the future, higher alcohol synthesis (HAS) has become a frontier area of research again.[7,12,13] For example, it is reported that the production of $C_{3+}OH$ is more favorable after the addition of a small amount of methanol and/or ethanol to the syngas feed, especially when using Cu-based catalysts in HAS.[14]

This Review has been written to summarize the research that has been undertaken in the area of HAS. The focus is on the role of the catalyst in HAS. The Review commences with a short discussion of homogeneous catalysts and then considers the important work that has been performed using heterogeneous catalysts.

1.1. Homogeneous Catalysts. Higher alcohols can be produced through homogeneous processes, directly from CO/H_2, or via CH_3OH homologation. CO hydrogenation using homogeneous catalysts can be realized at low temperatures (usually less than 220 °C) with the reaction exhibiting high selectivity toward higher alcohols. Fe-, Ru-, Co-, Ir-, and Rh-based organometallic complexes have been reported for use in the reaction.[15,16] In order to enhance the catalytic performance of HAS, halide promoters were added to homogeneous catalysts.[17,18] With most homogeneous catalysts, a high reaction pressure (~100 MPa) is required.[18] However, it was shown that $[Bu_4P]Br$ promoted Ru catalyst exhibited higher turnover frequency of ethanol at lower reaction pressure (10 MPa).[19] A study found that $Rh/P\text{-}i\text{-}Pr_3$ and $Rh/P\text{-}n\text{-}Bu_3$ catalysts showed high yield of ethylene glycol (EG).[20]

Since the 1950s, the use of Co-, Ru-, or Cu/Ru-containing complexes to synthesize ethanol from methanol has been widely studied.[7] A report exhibited that the space-time yield (STY) of ethanol could be 0.26 g/(g_{cat}·h) at the reaction conditions of 220 °C and 8.5 MPa, with very small amounts of other compounds.[21] Recently, Krause et al. has reported a strategy of the combination of homogeneous catalyst and heterogeneous catalyst for ethanol synthesis.[22] First, methanol was produced over the $Cu/ZnO/Al_2O_3$ catalysts. Then, ethanol was formed over the $Mn_2(CO)_{10}$ catalysts.

Homogeneous catalysts have high selectivity for $C_{2+}OH$ synthesis. However, there are also significant challenges, such as requiring very high reaction pressure and dealing with the toxic catalysts.[22] Homogeneous catalysts for $C_{2+}OH$ synthesis have been rarely reported recently, and no commercially viable process has been developed using homogeneous catalysts.[18] Therefore, the rest of this Review will focus on recent advances made with heterogeneous catalysts for the HAS reaction.

1.2. Heterogeneous Catalysts. As shown in Figure 1, five types of heterogeneous catalysts have been extensively studied in the $C_{2+}OH$ synthesis reaction: (a) Rh-based catalysts, (b) modified methanol synthesis catalysts, (c) modified FT synthesis catalysts, (d) Mo-/MoS_2-based catalysts, and (e) tandem catalysts. In Table 1, we summarize a comparison of the five types of catalysts.

Table 1. Comparison of Five Types of Heterogeneous Catalysts

Catalysts	Reactions	Advantages	Disadvantages
Rh-based	$2CO + 4H_2 = C_2H_5OH + H_2O$ $CO + 3H_2 = CH_4 + H_2O$	High $C_{2+}OH$ selectivity	High cost; low yield of $C_{2+}OH$
Modified methanol synthesis catalysts	$CO + 2H_2 = CH_3OH$ $nCO + 2nH_2 = C_nH_{2n+1}OH + (n-1)H_2O$[a] $CO + H_2O = CO_2 + H_2$	Low cost; high $C_{2+}OH$ yield	Large amount of methanol
Modified FT	$nCO + (2n+1)H_2 = C_nH_{2n+2} + nH_2O$[b] $nCO + 2nH_2 = C_nH_{2n+1}OH + (n-1)H_2O$[c]	Low cost	Large amount of alkanes
Mo-/MoS_2-based	$CO + 3H_2 = CH_4 + H_2O$ $nCO + 2nH_2 = C_nH_{2n+1}OH + (n-1)H_2O$[c] $CO + H_2O = CO_2 + H_2$	Low cost; high yield; sulfur-resistance	Large amount of alkanes and CO_2
Tandem	$CO + 2H_2 = CH_3OH$ $CH_3OH + CO = CH_3COOH$ $CH_3COOH + H_2 = C_2H_5OH$	Low cost; very high ethanol selectivity	Regulation of different carbon number products

[a] $C_nH_{2n+1}OH$ = Ethanol, propanol, and 2-methyl branched alcohols. [b] C_nH_{2n+2} = Linear alkanes. [c] $C_nH_{2n+2}OH$ = Linear primary alcohols.

https://doi.org/10.1021/acs.energyfuels.4c01419
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Although the reaction of synthesizing higher alcohols from syngas is thermodynamically favorable, there are many byproducts produced during the reaction process.[23] Regardless of the catalyst type, or whether the catalysts were investigated separately or in combination, numerous different chemical reactions exist in these reaction systems.[24] Thus, formation of $C_{2+}OH$ will be under kinetic control.[25,26]

Lower alkanes and CO_2 are two of the primary undesirable products, and their production varies with the catalyst used. According to literature results, alkanes are the main undesirable products when using Rh-based catalysts, modified FT catalysts, and Mo-/MoS_2 based catalysts. This is different from the byproducts seen when using modified methanol synthesis catalysts, as shown in Table 1.[14,27−30] A large amount of undesired CO_2 is formed when using methanol synthesis catalysts or Mo-/MoS_2 based catalysts, due to the dominance of the water gas shift (WGS) reaction.[26,29,31] The advantage of tandem catalysis is that it can complete multiple reaction steps in one reactor, allowing for extremely high ethanol selectivity, but with formation of some acetic acid.

To enhance the positive attributes and reduce the disadvantages of the catalysts listed in Table 1, much research has been undertaken in the past decade to make $C_{2+}OH$ in high yield with high selectivity. Thus, recent developments in new strategies for heterogeneous catalyst preparation have shown improved catalytic performance toward $C_{2+}OH$ synthesis. There are several review articles that have appeared in the past decade.[32−34] However, most reviews focus on metallic catalysts. For example, Ao et al.[32] reviewed the synergistic effect between active centers over multimetallic catalysts. More recently, a review article has also highlighted the progress in this area on the development of bimetallic active centers.[33] The present Review not only includes the recent progress on metallic catalysts, e.g., Cu-, Rh-, Co-, and Mo-based catalysts, but also tries to shed light on the recent developments on the rational design of new types of heterogeneous catalysts such as tandem catalysts, potentially having industrial application in this chemical process in the future.

2. RH-BASED CATALYSTS

Extensive studies showed that Rh-based catalysts have high selectivity toward C_{2+} oxygenates as shown in Figure 1.[14,35,36] With Rh-based catalysts, CO hydrogenation to CH_x species and CO insertion into the chain of the CH_x species have been considered as the two critical steps for C_{2+} oxygenate synthesis.[14] Hydrogenation of CH_x leads to CH_4 and coupling of CH_x results in the formation of C_{2+} alkanes.[37] Early study has showed that Rh-based catalysts without any promoters gave very little $C_{2+}OH$ products, owing to the CO dissociating completely and then hydrogenation to alkanes.[38]

To improve the production of $C_{2+}OH$, recent studies focus on the development of many new support materials and promoters for HAS from syngas. These catalysts contain only a small amount of Rh but exhibit high activity and selectivity toward $C_{2+}OH$ formation. The following sections review the recent studies on Rh-based catalysts and emphasize the different types of supports and promoters that have been used.

2.1. Supports. The textural properties of the support can influence the dispersion of active sites on the support surface and the interaction between the active site and support, thereby affecting the catalytic performance. Currently, many supports (e.g., Al_2O_3, ZrO_2, SiO_2, TiO_2, MgO and carbon-based materials) have been investigated for CO hydrogenation to $C_{2+}OH$.[35,39−42]

A series of Rh/Mn/Li/SiO_2 catalysts with different amounts of Si−OH have been synthesized. The results show that the Si−OH amount on the catalysts have the positive relationship with the dispersion of Rh and the CO adsorption. More Si−OH leads to better catalytic performance for HAS.[43] Moreover, the calcination of SiO_2 at 350 °C led to a moderate interaction between Rh and Mn, which facilitated the insertion reaction between CO and CH_x, thus increasing the selectivity to C_{2+} oxygenates. The STY of the C_{2+} oxygenates reached 274.1 g/(kg_{cat}·h), with a corresponding selectivity of 55.4 at 290 °C, 3 MPa, and $H_2/CO = 2$.

Han and co-workers examined SiO_2 and ZrO_2 supports separately, and in combination, to study the effect of the support on a series of Rh−Mn−Li catalysts.[44] The combination of SiO_2 and ZrO_2 supported Rn/Mn/Li catalyst showed a high dispersion of Rh and a high concentration of Rh^+, which led to a higher rate of CO conversion and the selectivity of C_{2+} oxygenates. In addition, the strong interaction between Rh and Mn supported on SiO_2 could be weakened by the addition of ZrO_2, which was critical for the C_{2+} oxygenate formation.

Some new composite materials are also used as supports for the HAS. These types of supports can facilitate the formation of $C_{2+}OH$, such as lanthanum zirconate pyrochlores ($La_2Zr_2O_7$).[45] Two catalysts that have Rh species doped into $La_2Zr_2O_7$ lattice and supported on the $La_2Zr_2O_7$ surface by a modified Pechini method were synthesized, respectively. The results showed that the catalyst with surface Rh species exhibited better CO conversion and selectivity to $C_{2+}OH$, due to the large amount of Rh^+/Rh^0 active sites. Zhong et al. investigated the difference between La_2O_3 modified $LaFeO_3$ (La_2O_3−$LaFeO_3$) and SiO_2 as supports for HAS. They found that Rh nanoparticles (NPs) supported on La_2O_3−$LaFeO_3$ showed a better catalytic performance compared to Rh NPs/SiO_2, owing to a well-matched ratio of Rh^+/Rh^0 and oxygen vacancies.[46] In addition, the same researchers synthesized a new catalyst of $La_{1-x}Ce_xFe_{0.5}Rh_{0.5}O_3/SiO_2$.[47] They found that La−O−Ce modified $LaFeO_3$ increased oxygen vacancies on the $LaFeO_3$ surface, which could improve CO conversion and $C_{2+}OH$ selectivity. Rh/$Ce_xTi_{1-x}O_2$ catalysts were investigated in HAS.[48] A series of Rh/$Ce_xTi_{1-x}O_2$ (x = 0, 0.25, 0.5, 0.75, and 1) catalysts were synthesized by a co-precipitation method, and it was found that Rh/$Ce_{0.75}Ti_{0.25}O_2$ exhibited a better catalytic performance for HAS, which was attributed to the higher Rh^+ ion concentration compared to Rh supported on pure TiO_2.

Rh/Mn/Li/Fe catalysts supported on carbon-based materials, such as nanotubes (CNTs), mesoporous CMK-3, carbon black (CB), and activated carbon (AC), were investigated by Fan et al.[39] Rh/Mn/Li/Fe supported on CNT showed higher activity and yield of $C_{2+}OH$ for HAS, due to the highly dispersed Rh species and optimal particle size. The same group also found that the $Rh_1/Mn_1/Li_{0.075}/Fe_{0.05}$ particles, mainly deposited inside of CNTs, exhibited very high STY (84.4 mol·mol^{-1}_{Rh}·h^{-1}) toward $C_{2+}OH$, with 76% ethanol selectivity.[49] The excellent catalytic performance was attributed to two reasons: the first one is that the electron-deficient interior surface of CNTs promoted CO activation, and the second one is that the confined structure of CNTs caused a high concentration of syngas on encapsulated particles' surface.[50,51] Other carbon-based materials were also investigated as

https://doi.org/10.1021/acs.energyfuels.4c01419
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Table 2. Catalytic Performance of MnO_2, Fe_2O_3, and V_2O_5 Promoted Rh-Based Catalysts for HAS

Catalyst (wt %)	T (°C)	P (MPa)	Syngas H_2/CO	GHSV ($L/(L_{Cat.}·h)$)	Conversion CO (%)	Selectivity (%) CH_4	CO_2	HC_{2+}	MeOH	EtOH	C_{3+} Oxy.	ref.
2%Mn/3%Rh/CNTs	290	2.0	2:1		4.0	48.9	0	2.9	6.5	35.2		62
5.56%Rh/1.69%Mn/SiO_2	277	8.3	1.9	7,500	20.8	31.7		16.2	0.5		51.6	63
	302			11,000	20.5	47.1		12.4	0.9		39.6	
2% Rh/5% Fe/TiO_2	270	2.0	1	8,000	6.2	35.3		7.0	4.8	37.2	15.6	64
1.5%Rh/2.6%La/1.5%V/SiO_2	270	1.4	2	9,000	7.9	15.4	3.1		5.0	51.8	19.1	38

supports for improving the catalytic performance of Rh-based catalysts; these supports include ordered mesoporous carbons (OMCs),[52,53] graphitic mesoporous carbon (GMC),[54] and carbon spheres.[55]

2.2. Promoters. The effect of promoters on Rh catalysts has been studied. Their effects can be summarized as follows: (1) creation of new active sites through metal-promoter interfaces; (2) suppression of the chemisorption and hydrogenation ability of Rh by partially covering the surface of the Rh; and (3) provision of metal cation and/or oxygen vacancies by the partially reduced promoters and facilitation of the chemisorption, dissociation, and insertion reactions of CO.[56,57] Various promoters have been extensively employed in studies to improve the C_{2+} oxygenate yield and suppress the formation of byproducts (e.g., lower alkanes). Generally, there are three types of promoters that have been used in the studies: (1) rare earth oxides (REOs),[56,58] e.g., La_2O_3, CeO_2, Sm_2O_3, and ThO_2; (2) some first row transition metals/metal oxides, e.g., Fe_2O_3, MnO_2, and V_2O_5;[41,59,60] and (3) alkali promoters, e.g., Li, Na, and K.[61]

Rh dispersion can be improved, and the physicochemical properties of Rh can be affected to some extent by these promoters. Better dispersion of Rh nanoparticles, represented by a small (usually less than 5 nm), uniform size, has been found to favor higher catalytic activity. Changes in the physicochemical properties of Rh help to provide active sites for the insertion reaction of CO into the CH_x species. For instance, the Rh^+ species can be stabilized by the promoters, which leads to a suitable Rh^+/Rh^0 ratio which is considered to be vitally important for synthesizing $C_{2+}OH$.[44,45]

Five kinds of rare earth oxide promoters (La_2O_3, CeO_2, Pr_6O_{11}, Nd_2O_3, and Sm_2O_3) were examined by Du et al. using Rh/SiO_2 catalysts.[56] The promoted catalysts that were reduced at a higher temperature (500 °C) exhibited much higher selectivity toward ethanol than the catalysts reduced at 350 °C, probably because of the benefit of a stronger metal−promoter interaction. According to the study of Du et al.,[56] partial reduction of REO promoters resulted in the formation of suboxides, which then created the Rh-REO interfaces for active sites. Rh^+ centers and the oxygen vacancies formed on the partial reduction interface of Rh-REO are important for chemisorption and activation of CO and the insertion reaction of CO with CH_x.

First row transition metal promoters (MnO_2, Fe_2O_3, and V_2O_5) have received much attention in recent years. We have summarized some of these catalysts for HAS in Table 2. Liu et al. investigated Rh/CNT catalysts with different amount of Mn for HAS.[62] The selectivity toward ethanol increased from 10.2% over 3%Rh/CNTs to 35.2% over 2%Mn3%Rh/CNTs at 290 °C, 2.0 MPa, and H_2/CO of 2 (Table 2). It was reported that the significant improvement in ethanol synthesis was ascribed to the intimate interaction between the Mn promoter and Rh active sites. However, in the study done by Mei et al., a Rh/Mn alloy was shown to be generated over SiO_2 supported Rh/Mn catalysts using a combined experimental and theoretical study.[63] The catalyst with Rh/Mn alloy exhibited a higher selectivity to C_{2+} oxygenates and an improved catalyst stability, which was attributed to the lower activation barrier of CO insertion into the CH_x (x = 1−3) reaction. The authors hypothesized that the promotional effect of Mn on $C_{2+}OH$ synthesis correlated with the electronegativity difference between the Rh metal and the Mn promoter. The partially *in situ* reduced $Mn^{\delta+}$ embedded in the Rh matrix induced a Lewis acidic center that facilitated the adsorption and insertion reaction of CO.

To verify increasing the interaction between promoter and Rh active sites can improve $C_{2+}OH$ selectivity for HAS, Liu et al. synthesized $Rh/Mn/SiO_2$ catalysts using a strong electrostatic adsorption (SEA) method.[65] The SEA synthesis method is based on the spontaneous protonation or deprotonation reaction of surface hydroxyl groups (−OH) by tuning the pH of the contacting solution. By control of the pH between the point of zero charge of Rh_2O_3 (∼8.5) and the SiO_2 support (∼4), the MnO_4^- anion was selectively adsorbed on the surface of Rh_2O_3 through the electrostatic interaction between the MnO_4^- anion in the solution and the $-OH_2^+$ sites on the Rh_2O_3 surface. Compared with the catalyst prepared by the traditional IWI method, the catalyst prepared using the SEA method showed a much higher Rh−Mn interaction (Figure 2) and showed ∼3−4 times higher ethanol selectivity.

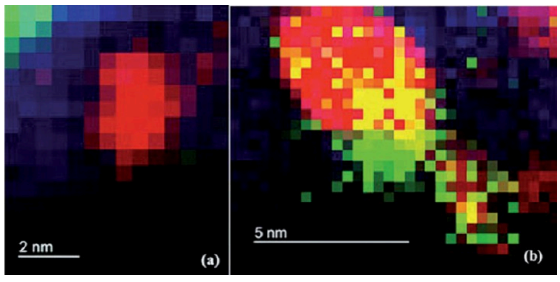


Figure 2. EELS elemental mapping of Rh catalysts prepared by different methods: (a) the $1\%Mn_{IWI}3\%Rh/SiO_2$ catalyst; (b) the $1\%Mn_{SEA}3\%Rh/SiO_2$ catalyst. (Color code: green, Mn; red, Rh; blue, silica.) Reproduced from ref 65 with permission of Wiley-VCH Verlag GmbH & Co. KGaA, copyright 2013.

A kinetic study by Mao et al. showed that the apparent activation energy (AAE) for HAS was only slightly influenced by MnO_x placed on Rh/SiO_2 catalysts. However, the AAE required for the formation of alkanes showed a significant increase.[66] Moreover, DRIFT studies indicated that CO adsorbed on the Rh surface gave new CO sites (as seen by CO IR bands at 2110, 1714, and 1586 cm^{-1}), caused by MnO_x, which suggested that the surface properties of Rh were altered after the modification using Mn promoters. Yang et

https://doi.org/10.1021/acs.energyfuels.4c01419
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al.[67] synthesized Rh-MnO catalysts by atomic layer deposition (ALD) method to investigated the function of Mn promoter. The researchers claimed that surface modification by MnO delivered significant enhancement in catalytic performance for HAS, which was attributed to the Rh-MnO interface promoting the CO dissociation.

Recently, Rh−Mn supported on Zr-based metal−organic frameworks (MOFs) catalysts were prepare by coimpregnation for HAS.[68,69] The structural and textural properties of the catalysts clearly showed that Rh and Mn were highly dispersed in the pores of the MOFs. It was claimed that the highly dispersed Rh and Mn active sites promoted the CO hydrogenation, which resulted in a high yield of C_{2+} oxygenates, 197.3 g $(kg\ h)^{-1}$. Similarly, Wang et al.[70] proposed that RhMn@S-1 catalyst with a core−shell structure exhibited high $C_{2+}OH$ selectivity of 40.3% under a CO conversion of 42.4% (Figure 3). The authors claimed that the structure of MOFs can stabilize $Mn-O-Rh^{\delta+}$ sites, which played an important role in $C_{2+}OH$ formation.

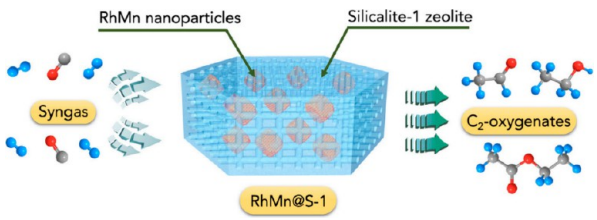


Figure 3. Schematic illustration of syngas conversion to $C_{2+}OH$ over a RhMn@S-1 catalyst. Reproduced from ref 70 with permission from Elsevier, copyright 2020.

In a study performed by Burch and co-workers to optimize the Rh−Fe interaction, an Al_2O_3 support was decorated with Fe oxide particles using iron nitrate and/or $NH_4[Fe(EDTA)]$ as precursors, prior to loading the Rh metal.[71] With a 10 wt % Fe/2 wt %Rh/Al_2O_3 catalyst, selectivity toward ethanol was enhanced up to 50% at 270 °C and 1 MPa. The researchers concluded that adding Fe to the Al_2O_3 support led to a Rh−Fe interface that prevented the Rh from migrating into the support and thus suppressed the interaction between the Rh and the Al_2O_3 support. Moreover, it was shown that the Rh moiety could facilitate the reduction of Fe oxides, as verified by the temperature-programmed reduction (TPR) results. This was probably because the hydrogen atoms that formed on the reduced Rh metal spilt over to the Fe oxides, which led to the relatively lower reduction temperature.

ZrO_2, SBA-15, and CeO_2 were also used as supports for Rh−Fe bimetallic catalysts.[32] However, it was shown that it was difficult to form the Rh−Fe alloy after reduction on these supports. Han et al.[72] synthesized a $YRh_{0.5}Fe_{0.5}O_3$ catalyst with perovskite supported on ZrO_2 using an impregnation method. The catalyst with Rh−Fe alloy exhibited a high CO conversion and selectivity to $C_{2+}OH$. In addition, Carrillo et al.[73] also indicated that Rh/Fe_2O_3 catalyst with FeRh nanoalloy exhibited high $C_{2+}OH$ selectivity for HAS.

The combination of Vanadia promoters and lanthana promoters were used to improve the catalytic performance for HAS.[14,27] Gao et al.[14] reported that the activity of the doubly promoted $Rh/La/V/SiO_2$ catalysts was three times higher than that of the singly promoted $Rh/La/SiO_2$ and $Rh/V/SiO_2$ catalysts. In addition, the selectivity of C_{2+} oxygenates over the doubly promoted catalysts was higher than 30% at 230 °C at a low pressure of 0.18 MPa. This was attributed to intimate interaction between the promoters (La and V) and Rh, which contributed to the chemisorption of CO on the surface. However, no further details of the synergistic effect in that study were provided. Subramanian et al.[38] extended the study to optimize the reaction conditions. They reported that the selectivity of ethanol was as high as 51.8%, with a CO conversion of 7.9% at 270 °C and H_2/CO = 2 and 1.4 MPa.

Adding alkali promoters to Rh-based catalysts facilitated the formation of C_{2+} oxygenates and suppressed the production of alkanes, e.g., methane. It is widely accepted that the main role of alkali promoters is to suppress the dissociation of adsorbed CO by blocking the Rh sites or by creating new active sites at the Rh−alkali interface, thus keeping the surface CH_x and undissociated CO/CHO species in balance.[26,74] It was reported that when using the 1.5 wt % Rh/Al_2O_3 catalyst, the selectivity of C_{2+} oxygenates was increased in the following order: unpromoted < Li < Na < K ≤ Cs.[75] However, the addition of alkali promoters usually decreased the overall activity, owing to the physical blockage of Rh surface sites, as reported by Chuang and co-workers, where the activity decreased following the order unpromoted > Li > K > Cs.[74]

There is still controversy about whether the electronic state of the Rh metal surface is altered by alkali promoters or not. The chemisorption of CO might be influenced by the electronic state of Rh, as reported by Kusama et al.[76] They argued that, in the presence of a Li promoter, the in situ IR bands due to linear and bridged CO species (at 2040 and 1860 cm^{-1}) shifted toward lower wave numbers (2032 and 1841 cm^{-1}), respectively. It was suggested that the C−O bond in CO was weakened because there were more back-donated electrons from the Rh metal nanoparticles. However, Egbebi et al. reported that the frequency of linearly adsorbed CO on both Rh/TiO_2 and $Rh-Li/TiO_2$ catalysts was almost the same, which suggested that the electronic structure of Rh was unchanged when using a Li promoter.[61] Additionally, although the gem-dicarbonyl species were more stable in the presence of Li at room temperature, they were not detected at the reaction temperature (270 °C). This indicated that there was no cationic Rh present under the reaction conditions, despite Rh being more difficult to reduce in the presence of the Li promoter. Therefore, the authors concluded that the effect of Li was due to structural rather than electronic effects. Consistent with the work performed by Egbebi et al. above, no cationic Rh was observed by Schwartz and co-workers.[77] However, they suggested that the lower reducibility of Rh might influence the CO insertion reaction and lead to an increase in the selectivity for the C_{2+} oxygenates.

It was reported that achieving monodispersed Rh particles on Rh-based catalysts is challenging, when introducing one or more promoters.[78] To overcome this challenge, Huang et al. synthesized a new Rh catalyst with highly dispersed Rh particles, modified by manganese and stabilized by mesoporous SiO_2. It was found that the Mn promoted Rh/SiO_2 catalyst exhibited high catalytic activity and $C_{2+}OH$ selectivity of 75.4%.[79]

2.3. Reaction Mechanisms. Various reaction pathways and a range of intermediates have been postulated and extensively discussed to explain the reaction mechanism. Ketene ($H_2C=C=O$) and acetyl ($H_3C-C=O$) were widely assumed to be the initial C_2 intermediates.[80] The former is considered to be generated from the insertion of CO into CH_2,

https://doi.org/10.1021/acs.energyfuels.4c01419
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while the latter is considered to be generated through the combination of CO with CH_3.[79,81,82]

As indicated above, various promoters were added to the Rh to improve the $C_{2+}OH$ yield and suppress the formation of byproducts.[42,60,64] It was found that promoters can inhibit complete dissociation of CO and that there was an increase in formation of their nondissociative counterparts, which enhanced the insertion reaction of CO into CH_x species.[54,79] It is speculated that the active site involves both the Rh center and promoters.

Acetate was reported to be one of the crucial intermediates on Mn promoted Rh-based catalysts for HAS.[83] Wang et al. proposed a geometrical structure for the active site, $Rh^0_xRh^+_y$)-O-M^{n+} ($x \gg y$), based on computational studies. As shown in Figure 4, with the existence of promoter ions (M^{n+}), the CO

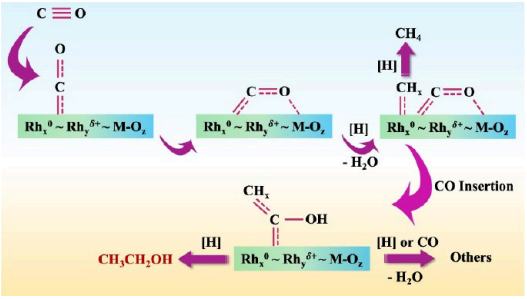


Figure 4. Simplified reaction path of M (M = promoters) promoted Rh-based catalysts. Modified and reproduced from ref 79 with permission from Elsevier, copyright 2000.

was activated and can be hydrogenated readily to form H_xCO, which facilitated the subsequent insertion of CO and/or CH_x to generate the C_{2+} oxygenates.

As indicated, promoters can enhance the insertion reaction of CO into CH_x species for Rh-based catalysts, thereby suppressing the production of the undesired methane.[42,65,83] The CH_x hydrogenation to CH_4 inhibits the insertion reaction.[84] Zhang et al.[85] clarified that the appropriate combination of support and promoters is important for high ethanol productivity. Specifically, as shown in Figure 5, the result of projected density of state (PDOS) data indicated that the d-band energy of $FeRh_6/TiO_2$ catalyst (−1.70 eV) is

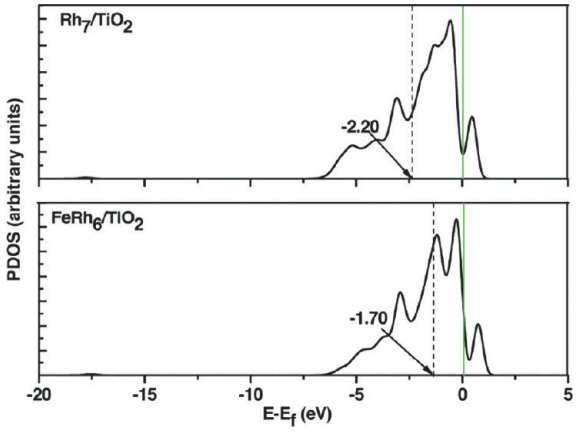


Figure 5. PDOS for the Rh atoms of the Rh_7/TiO_2 and $FeRh_6/TiO_2$ model catalysts. Reproduced from ref 85 with permission from the Royal Society of Chemistry, copyright 2017.

higher than that of Rh_7/TiO_2 catalyst (−2.20 eV). This indicates that the $FeRh_6/TiO_2$ catalyst is active for insertion of CO into CH_3 and less active for CH_4 formation.

The reactions on the Rh catalysts for HAS are quite complex, including many intermediates and reaction pathways. Gu et al.[86] provided a method that can be used to automatically identify preferential reaction pathways in a complex reaction. For example, when using the Rh(111) catalyst for HAS, the occurrence frequency of possible reaction pathways indicated that CHCO was a crucial intermediate. This methodology could be used to evaluate the Rh catalysts enhanced by the promoters used in HAS.

3. MODIFIED METHANOL SYNTHESIS CATALYSTS

Modified methanol synthesis catalysts include high-temperature catalysts (Cr/ZnO catalysts) and low-temperature methanol synthesis catalysts (Cu-based catalysts). The Cr/ZnO-based catalysts have higher yield of iso-butanol production at high reaction temperature and pressure. Li and co-workers[87] synthesized four different alkali metal (Na, K, Cs, and Li) modified Cr/ZnO catalysts to study the effect of alkali metals on iso-butanol synthesis. They found that Na, K, and Cs can improve iso-butanol selectivity and CO conversion, and the results indicated that the active sites were associated with the nonstochiometric spinel of $Zn_xCr_{2/3(1-x)}O$. The same group also studied the effect of excess ZnO phase on Cr/ZnO based catalysts, prepared by different methods.[88] Cr/ZnO catalysts prepared by fractional precipitation exhibited the highest selectivity to iso-butanol with the highest CO conversion, which was attributed to the small particle size of ZnO promoting the nonstochiometric spinel of ZnCrO formation. Gao and co-workers[89] synthesized a series of ZnO/ZnCr catalysts by the sol−gel method and studied the effect of hydroxyl groups on the catalysts for iso-butanol synthesis from syngas. They found that a lower calcination temperature was helpful for keeping hydroxyl groups on the catalyst surface and the hydroxyl groups could be consumed by CO during the reaction, resulting in more oxygen vacancies (the active sites for CO activation). The oxygen vacancies were beneficial for enhancing the catalytic performance. Moreover, the synergistic effect between ZnO and $ZnCr_2O_4$ for iso-butanol synthesis from syngas was also studied by Wang.[90] They found that the strong synergistic function of ZnO and $ZnCr_2O_4$ phases improved the formation of C1 species, which is a crucial intermediate in iso-butanol synthesis.

Cu-based catalysts ($Cu/ZnO/Al_2O_3$) have been used industrially for decades to produce methanol from synthesis gas.[6] It was found that traces of alkali residuals remained in Cu-based catalysts prepared by a coprecipitation method.[91] The presence of alkali facilitated the generation of $C_{2+}OH$, which has attracted attention to the study of promoted Cu-based catalysts for HAS.[92,93] Compared with the other types of catalysts, Cu-based catalysts have less hydrocarbon formation (such as methane and higher alkanes) and have a superior cost advantage compared to Rh.[94,95] Consequently, modified Cu-based methanol synthesis catalysts have been extensively explored for higher alcohol synthesis.[96]

In addition to alkali metals, transition metals and rare earth metals were also used for modified Cu-based catalysts to improve the catalytic performance for HAS.[97] Both high-temperature and low-temperature methanol synthesis catalysts for HAS have been studied extensively.[98−100] Liu et al.[101] prepared CuZnO catalysts using different methods and

https://doi.org/10.1021/acs.energyfuels.4c01419
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investigated the effect of preparation method on $C_{2+}OH$ selectivity. The results showed that the CuZnO catalyst synthesized by the sol−gel method exhibited higher $C_{2+}OH$ selectivity of 47.8%, compared with the CuZnO catalyst synthesized by precipitation. The preparation method greatly affected the crystallinity of the CuZnO catalyst. The reason was assumed to be the fact that the former catalyst had higher crystallinity which was beneficial for CO adsorption, thus improving $C_{2+}OH$ synthesis. In addition, the CuZnO modified with K_2O exhibited high iso-butanol selectivity at the reaction conditions of 420−480 °C and 5.0−30.0 MPa. However, there were many byproducts.[102]

Recently, modified Cu-based catalysts were investigated extensively.[103] Therefore, in this section, promoted Cu-based catalysts and CuZnM (M = Cr, Al, and Mn) catalysts for HAS are discussed.

3.1. Alkali Promoters. It was found that the reaction conditions played an important role in modified Cu-based catalysts for higher alcohol synthesis.[91,99,104] Temperature appears to be the most important parameter affecting the product distributions.[99,105,106] Nunan et al. claimed that Cs promoted Cu/ZnO catalyst could improve the selectivity of CH_3OH at 250 °C; however, the selectivity of $C_{2+}OH$ was not significantly increased.[107]

The range of 270−310 °C was considered to be the optimal temperatures for higher alcohol synthesis, while temperatures above 310 °C led to large amounts of undesired CO_2 and higher alkanes.[108] Different alkali metal promoted Cu/ZnO catalysts were prepared for HAS, and the addition methods of promoters were also investigated.[109] The yield of $C_{2+}OH$ increased in the order of Li < Na < K < Rb < Cs.[110] Among these alkali promoters, Cs has received much more attention, as it remarkably enhances the yield of $C_{2+}OH$.[97]

Calverley et al. claimed that 2-methyl branched aliphatic alcohols were the main $C_{2+}OH$ formed over K_2O-promoted $Cu/ZnO/Cr_2O_3$ catalysts.[99] The kinetics of $C_{2+}OH$ synthesis over K promoted $CuO/ZnO/Al_2O_3$ catalysts was investigated, and the results showed that the addition of 0.5 wt % K_2O greatly improved the yield of iso-butanol. This agrees with the results reported by Anderson et al.[92,93,104] Vedage et al. synthesized alkali hydroxides and Ba hydroxide modified Cu/ZnO catalysts for HAS.[110] It was found that the selectivities of $C_{2+}OH$ and CH_3OH were improved, in which it was assumed that the CsOH moiety better accelerated the βC addition reaction to generate branched $C_{2+}OH$, in comparison to unmodified Cu/ZnO.

Combing experiments and DFT calculations, Sun et al.[111] investigated the promotion of Cs promoter in HAS from syngas over Cs_2O−$Cu/ZnO/Al_2O_3$ catalysts. They found that the Cs promoter was helpful for the reaction of initial C−C bond formation, resulting in a high yield of $C_{2+}OH$. DFT calculations indicated that the HCO + HCO coupling was the main reaction of C−C bond formation. It was found that Cs promoted catalysts had lower activation barriers for HCO + HCO coupling, leading to a high selectivity of $C_{2+}OH$.

The addition of the structural promoter Cr or Al to $Cu/ZnO/M_2O_3$ (M = Al or Cr) catalysts showed high selectivity of undesirable products (dimethyl ether and alkanes), which was attributed to the acidic sites of Cr_2O_3 and/or Al_2O_3.[112,113] Thus, in order to neutralize the acidity, the authors introduced alkali metals as promoters.[113] It was found that the Cs promoted $Cu/ZnO/Cr_2O_3$ catalyst exhibited enhanced selectivity of $C_{2+}OH$, compared to the unpromoted $Cu/ZnO/Cr_2O_3$ catalyst. In addition, Hilmen et al. also prepared Cs promoted $Cu/ZnO/Al_2O_3$ for higher alcohol synthesis. The results showed that an appropriate amount of Cs promoters could improve the selectivity of $C_{2+}OH$; however, excess Cs suppressed the formation of $C_{2+}OH$.[114]

3.2. Nonalkali Promoters. Transition metals (e.g., Fe, Co, and Ru) can be used as promoters to enhance C−C coupling in Fischer−Tropsch synthesis; they have also been introduced to Cu-based catalysts.[115−117] In a study of light alcohol synthesis from syngas, Lin et al. prepared Fe, Co, and Ni promoted $Cu/ZnO/Al_2O_3$ catalysts by a coprecipitation method.[117] The researchers claimed that the best promoter was Fe. When the ratio of Fe_2O_3/CuO was increased to >66.7%, the yield of C_2−C_5 alcohols decreased. In addition, Xu et al. also prepared Fe promoted $Cu/Mn/ZrO_2$ catalysts with coprecipitation and impregnation methods for higher alcohol synthesis.[116] The latter catalyst showed a higher selectivity of $C_{2+}OH$, which was attributed to the stronger interaction between Cu and Fe species.

Various other promoters of nonalkali metals have also been studied individually and in combination with alkali oxides, including La, Ce, Th, and Mn.[113,118,119] Mn or Ce promoted $Cu/ZnO/Al_2O_3$ catalysts for HAS were investigated by Slaa et al.[118] It was found that iso-butanol formation in the $C_{2+}OH$ product slate was improved by the Mn promoter. The Ce promoted catalyst showed a lower yield of $C_{2+}OH$. However, a higher yield of iso-butanol was observed when a 2 mol % Ce doped catalyst was made using the coprecipitation approach. La was a good promoter for improving the yield of $C_{2+}OH$ for the Cu/SiO_2 catalyst.[119] It was speculated that the presence of La_2O_3 was beneficial for the stability of Cu^+, which played an important role in the formation of CH_3O intermediates. The aforementioned role of Cu^+ was also observed in a study of nonalkali metals (such as Th, Cr, and Ga) promoted Cu-based catalysts for HAS.[120]

Introducing multiple nonalkali promoters to $Cu/ZnO/Al_2O_3$ catalysts may also alter the active sites for $C_{2+}OH$ synthesis. Co-modified $Cu/ZnO/Al_2O_3$ catalysts with subsequent Na modification were investigated by Anton et al.[121] It was suggested that at lower Na loading (less than 0.6 wt %), the active site for $C_{2+}OH$ synthesis was the Cu−Co surface alloy. However, an increase in Na loading (higher than 0.8 wt %) led to the formation of Co_2C via Co^0 carbonization. The generated Co_2C−Co^0 interfaces were the active sites for the $C_{2+}OH$ synthesis. It was noted that at the beginning of the reaction (first few hours) the addition of Na caused serious catalyst deactivation, presumably due to coking on the Co^0 sites. Although the Cu-based catalyst has become a promising candidate for HAS from syngas, all the best catalysts contain FT elements (e.g., Co and Fe) and alkali metals.

CuZnAl catalysts without promoters were also investigated for HAS from syngas. CuZnAlOOH catalysts with different ratio of Cu and Al were prepared by a liquid-phase method and investigated for HAS from syngas.[122] The results indicated that when the ratio of Cu/Al reached 2/0.8, the catalyst exhibited a high $C_{2+}OH$ selectivity of 65% under a CO conversion of 20%. This was attributed to the high surface area of Cu and the synergistic effect of the Cu^0−Cu^+ and AlOOH active sites. The study provided a new understanding for developing the carbon chain growth mechanism and serves as a reference for other related carbon chain growth reactions.

Liu et al.[123] investigated the particle size effect of Cu on the performance of high alcohol synthesis for a CuZnAl catalyst.

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They synthesized a series of CuZnAl catalysts with narrow Cu particle sizes ranging from 32 to 49 nm. It was found that the selectivity of higher alcohols increased sharply from 8.9% to 60.5% with the increase in Cu particle sizes from 11 to 38 nm, followed by a slight increase to 68.6% as the Cu particle size further increased. This was attributed to larger Cu particle size with more Cu(111) facets leading to the formation of a Cu(111)−ZnO interface, whcih was beneficial for the dissociation of the C−O bond for CH_x formation.

Core−shell structured CuZnAl catalysts were also used for high alcohol synthesis. Wang and co-workers[124] prepared CuZnAl@S-1, ZnAl@S-1, CuZn@S-1, and CuAl@S-1 catalysts by a solid-phase method and investigated them for high alcohol synthesis. They found that CuZnAl nanoparticles encapsulated S-1 (CuZnAl@S-1) exhibited better catalytic performance, and the $C_{2+}OH$/ROH and ROH selectivity reached 50.63% and 27.27%, respectively. The good catalytic performance is due to the electron transfer from CuZnAl species in the core−shell structure to the S-1 layer, which promotes the adsorption and dissociation of CO and enhances C−C coupling.

3.3. Reaction Mechanisms. Various promoter-promoted Cu-based catalysts for higher alcohol synthesis from syngas were investigated extensively. The initial C−C coupling reaction was assumed as a key for understanding the mechanism and is thus discussed in depth below. This section provides a summary of some of the widely accepted mechanisms used to explain the effect of promoters on Cu-based catalysts.[125−127]

$$2CH_3OH = C_2H_5OH + H_2O \quad (1)$$

$$CH_3OH + CO + 2H_2 = C_2H_5OH + H_2O \quad (2)$$

As seen in eqs 1 and 2, methanol condensation and homologation reactions were once considered as the formation pathway of ethanol.[109,126] Methyl ether and methyl formate were assumed to be the intermediates of higher alcohol synthesis from syngas. Graves and Frolich et al. claimed that the rearrangement of methyl ether can form $C_{2+}OH$.[128,129] However, Murrell et al. pointed out this pathway was suppressed because the rearrangement of methyl formate had a high activation energy barrier.[130]

Mazanec et al. indicated that the insertion of CO into H_xCO intermediate led to initial C−C coupling.[131] However, in another study using the isotope approach, the results showed that two labeled ^{13}C species were found in the product of CH_3CH_2OH, which indicated that the C−C coupling occurred between formyl species and formaldehyde (Figure 6).[109] Deluzarche et al. also found the existence of formyl via a CH_3I trapping reaction.[132]

Xu et al.[133] showed that a different mechanism, with initial C−C formation, can be detected when using different Cu-based catalysts. When using $K/Cu/Mg_5CeO_x$ catalysts and $^{13}CO/H_2/^{12}CH_3OH$ as the feedstock, the main route to ethanol was hydrogenolysis of methyl acetate; the product contained an unlabeled methyl group and a doubly labeled acetate group. Therefore, the initial C−C coupling was deemed to be derived from ^{13}CO instead of methanol. Subsequent chain growth was due to the increase of basic sites on $CuMgO_x$ surfaces by K and Ce_2O.[134] However, with Cs promoted $Cu/ZnO/Al_2O_3$ catalysts, the C−C coupling reaction involved two methanol-derived intermediates, as shown in Figure 6.

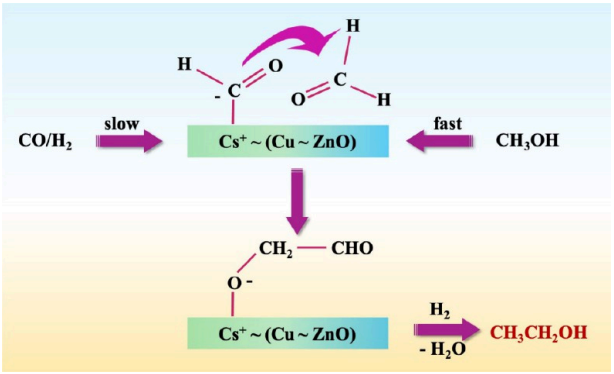


Figure 6. Mechanism for $C_{2+}OH$ synthesis over Cs promoted Cu/ZnO catalysts. Modified and reproduced from ref 109 with permission from Elsevier, copyright 1999.

The reaction pathways for the formation of C_{3+} alcohols are reported to be much more complicated. Various routes to enable chain growth are possible. In the work of Calverley et al., it was suggested that $C_{2+}OH$ was formed at the Cu and alkali metal interface.[99] It was also claimed that the promoter of alkali metals promoted the activation of CO and the aldol condensation reaction to synthesize $C_{3+}OH$.[126,135] In addition, an appropriate Cu^+/Cu^0 ratio can be achieved when adding an alkali, which played an important role in HAS from syngas.[104,136]

The reaction routes shown in Figure 7 were proposed by Hilmen et al. to explain the reaction mechanism. The routes

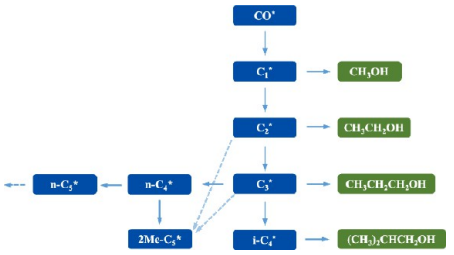


Figure 7. Reaction routes for HAS from syngas over alkali metal-promoted Cu-based catalysts. Reproduced from ref 114 with permission from Elsevier, copyright 1998.

are in agreement with suggestions made by many other researchers.[137] It was claimed that there were two routes for linear alcohol (C_nOH) formation. The first one is the insertion of a C_1 intermediate into $C_{n-1}OH$, and the second one is aldol condensation. In addition, branched alcohols were formed by the attack of the C_1 species on the βC of C_{2+} oxygenates or by an alternative reaction route. For instance, 2-methyl-1-butanol can be generated by attacking the C_1 intermediates on the βC of the linear C_4 oxygenates or by condensation of C_2 oxygenates with C_3 oxygenates.

As indicated in the study of Cu-based catalysts, C−C (C is CH_3OH or CO) coupling was assumed to be the rate-determining step for HAS from syngas.[25] In addition, $C_{3+}OH$ is mainly derived by means of the reaction of aldol condensation, which is faster than the C−C coupling reaction.[138] Given these conclusions, CH_3OH and CH_3CH_2OH were used to improve the productivity of higher alcohols.[91] The production of $C_{2+}OH$ reached 1027.2 $g/kg_{cat}/h$, as CH_3OH and CH_3CH_2OH were added to the syngas. This

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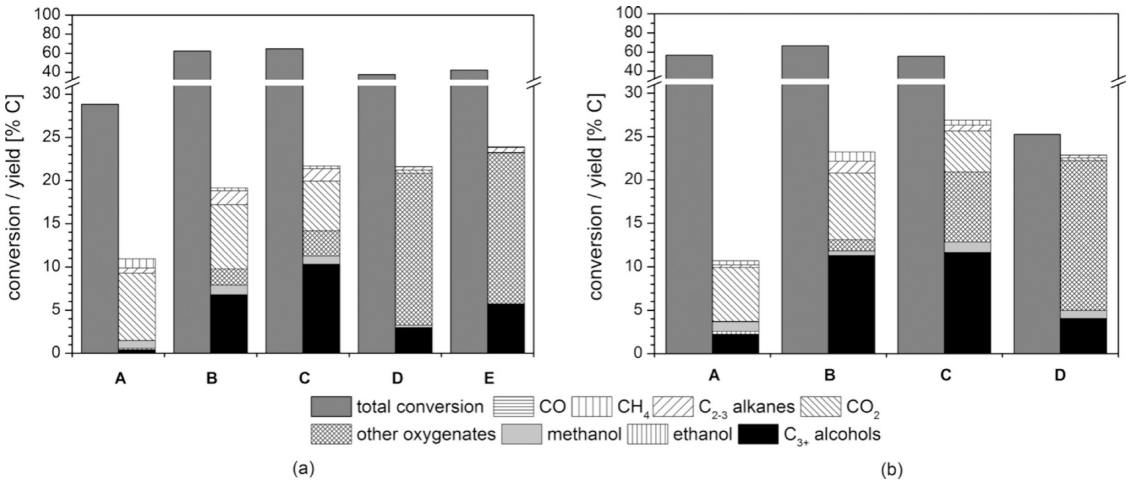


Figure 8. Catalytic performance of catalysts (a) CuO/ZnO and (b) Cs-CuO/ZnO. Reproduced from ref 13 with permission from the American Chemical Society, copyright 2015.

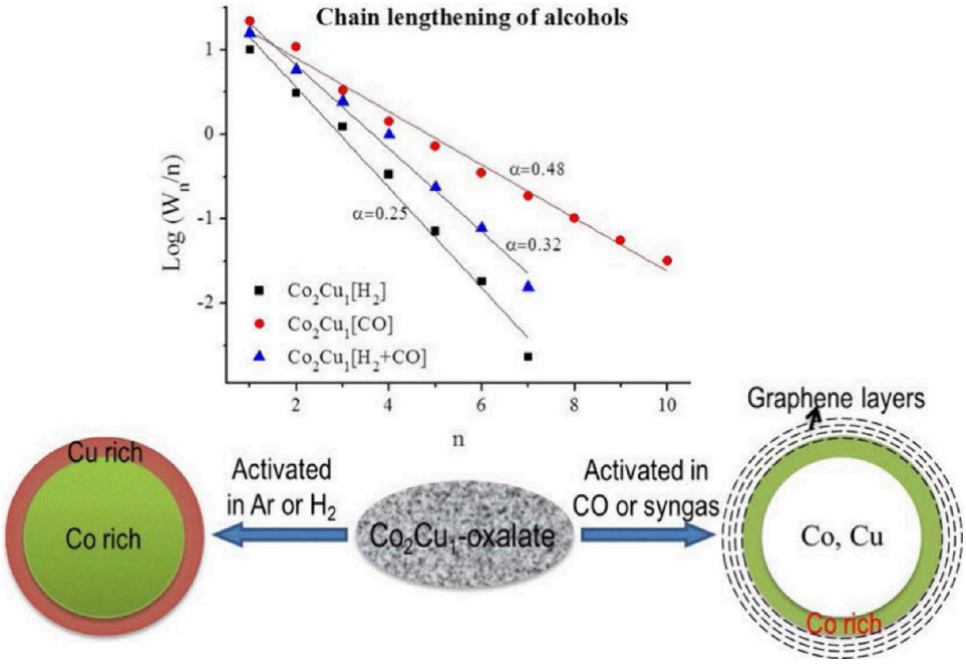


Figure 9. Effect of CuCo precursor activation on C_{2+}OH synthesis. Reproduced from ref 151 with permission from the American Chemical Society, copyright 2014.

suggests a potential methodology for use in industrial applications.[102]

The effect of adding ethanol to syngas in C_{2+}OH production in a batch reactor was recently studied by Walter et al.[13] The optimal ratio of n_{EtOH}:n_{CO} for C_{2+} oxygenate production was found to be ~0.9. The C_{2+} oxygenate yield was 20.1% with the Cs−Cu/ZnO catalysts, with modest formation of alkanes and CO_2 (Figure 8). Furthermore, it appeared that methanol formation was unaffected when ethanol was added, which suggested that methanol was generated solely from syngas.

4. CU-MODIFIED FT CATALYSTS

The FT synthesis for generating synthetic fuels directly from syngas has been known for almost a century. Fe, Co, Ni, and Ru are usually used in FT catalysis as the primary components with/and without a promoter.[139−141] When the metals (e.g., La, Cu, Ir, and Re) which are not active for CO dissociation were introduced,[142,143] FT catalysts exhibit some selectivity toward higher oxygenates, especially the linear C_1−C_6 terminal alcohols, and the product distribution of the alcohols complies with the ASF distribution.[143,144]

Various promoted Co−Cu catalysts have been developed for improving the yield of C_{2+}OH.[145,146] It was found that many promoters can affect the reducibility of the Co species. The addition of M (M = promoters) to Co led to the formation of the Co−M alloy, and studies have indicated a strong interaction between Co and M which is considered to play a pivotal role in C_{2+}OH production.

Cu-modified FT catalysts, Cu/M (M = Fe, Co, etc.), are of particular interest, owing to the efficient production of C_{2+}OH by these systems.[147] Cu additives are used to change the reducibility and dispersion of Co species and create active sites for C_{2+}OH synthesis.[148] The mechanism involved in higher alcohol synthesis involves two steps. First, CO/HCO is

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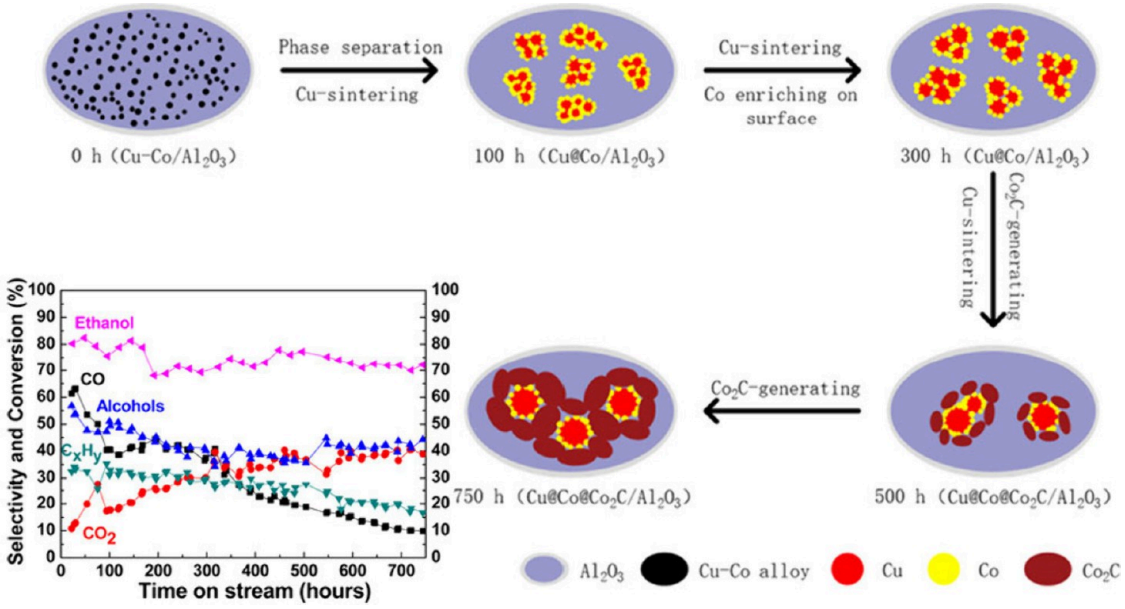


Figure 10. Structure variation and catalytic performance of $(Cu_1Co_2)_2$Al-LDHs with reaction time. Reproduced from ref 154 with permission from the American Chemical Society, copyright 2017.

inserted into CH_x to complete the C−C coupling reaction, followed by subsequent hydrogenation to form alcohols. The triple bonds in CO can be readily dissociated over FT metal catalysts, such as Fe, Co, Ru, etc., to give CH_x species. The introduction of Cu additives importantly can promote the insertion of nondissociative CO into CH_x to form C_{2+}OH.

The reactive sites on the modified F-T catalysts are still not fully understood. For example, with the Cu/Co catalysts, it is still controversial whether the alloy of Cu/Co[149] or interface of reduced Co particles and Cu^0 is an active site.[148,150] The differences were possibly related to the different preparation methods because different catalyst pretreatment conditions and reaction conditions (such as the H_2/CO ratio, which might cause the reconstruction of Cu/Co catalysts) were used by different researchers. It was shown that the surface structure of catalysts could be altered by activation procedures, which could change the catalytic performance.[151,152] For example, when a bimetallic CuCo catalyst (prepared from an oxalate catalyst precursor) was activated by CO, the catalyst exhibited higher activity and selectivity toward hydrocarbons and lower selectivity toward C_{2+}OH, when compared with the precursors reduced with H_2.[151] *In situ* XPS measurements showed that the Co/Cu ratio of the H_2-activated catalysts was 0.9, i.e., much lower than the 1.7 and 1.9 seen with the CO- and syngas-activated catalysts. Thus, the better catalytic performance of the CuCo catalyst activated by CO was attributed to the promotion of CO activation by more cobalt species. Interestingly, a carbon shell was detected on the CO-activated catalysts, which was probably caused by the Boudouard reaction, i.e., $2CO = C + CO_2$ (see Figure 9). Su et al. suggested that adding Cu to Co influenced the ensemble size of cobalt species and inhibited the dissociation of CO or HCO, which resulted in CH_x species formation.[153]

However, it was suggested that the good catalytic performance was attributed to the promotional role of Co_2C, which increased nondissociated CO adsorption. The catalytic performance of Cu−Co/Al_2O_3 was investigated by Yang and co-workers.[154] NPs were obtained after the reduction of a Cu−Co alloy supported on Al_2O_3. Co_2C appeared after a 300 h run, and Cu@Co@Co_2C supported on Al_2O_3 was found after a 500 h run. Between 500 and 750 h, the generated Co_2C inhibited the loss of Co species in the Cu@Co@Co_2C composite and prevented sintering of the Cu particles (Figure 10).

The structural evolution and the use of different reaction conditions over Co/Cu catalysts were investigated by Muhler et al.[155] In the first 2 h, it was found that metallic Cu^0 and Co^0 species were rapidly separated and sintered under the reaction conditions. The carbonization (and sintering) of metal Co to form Co_2C was achieved within 40 h of TOS. After reaction for 40 h, the mixture of Cu^0 and Co_2C was stable in the catalyst. The high selectivity to oxygenates was ascribed to the multifunctional properties of this Cu^0/Co_2C interface, which enabled the dissociative CO adsorption, hydrogenation, and CO insertion reactions.

Numerous studies have been conducted on Cu−Fe,[147] Cu−Co, and Cu−Ni binary catalysts in relation to synthesizing C_{2+}OH.[156−158] Xiao et al. studied the effect of Cu on different FT metal catalysts.[142] It was found that the Cu−Fe catalyst exhibited the highest catalytic activity, compared with Cu−Co and Cu−Ni catalysts. However, the selectivity to C_{2+}OH over Cu/Ni catalysts was below 10 wt %, i.e., much lower than that over Cu/Co and Cu/Fe catalysts.

Other additives such as oxides[159,160] (including La,[161] Mn,[162] Cr, Mo,[163] and Zn−Zr) have also been studied over Cu/Co catalyst to further enhance the yield of higher alcohols. Xiang et al. investigated a Co/Cu/Mn core−shell catalyst for HAS from syngas and found that the C_8∼C_{14} 1-alcohols were favored to form, rather than C_2∼C_6 alcohols.[162] The results of atom probe microscopy showed that the core of the catalyst was Co-rich Co/Cu/Mn components, while the shell of it was Cu-rich Co/Cu/Mn components (Figure 11), resulting in a high selectivity of long-chain alcohols (Figure 12). Huang et al.[164] synthesized ZnO/ZrO_2 modified CuCoAl catalysts with different ZnO-to-ZrO_2 ratios; they found that ZnO/ZrO_2−CuCoAl (ZnO/ZrO_2 = 4:1) showed higher selectivity of C_{2+}OH. The excellent catalytic performance of ZnO/ZrO_2−CuCoAl (ZnO/ZrO_2 = 4:1) catalyst was attributed to the

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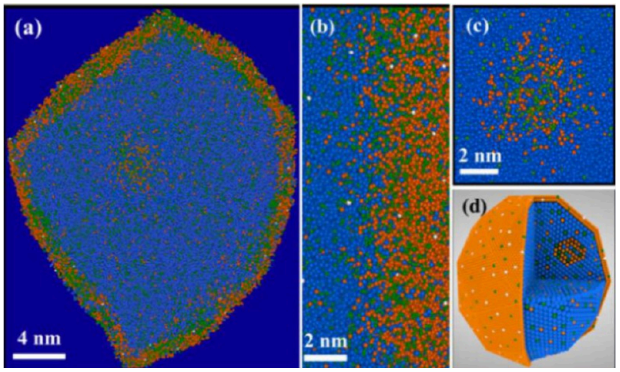


Figure 11. (a−e) Results of the atom probe microscopy done on the CoCuMn catalyst. (d) A 3D sectional view of the catalyst (Co = blue; Cu = orange; Mn = green; O = white.) Reproduced from ref 162 with permission from the American Chemical Society, copyright 2013.

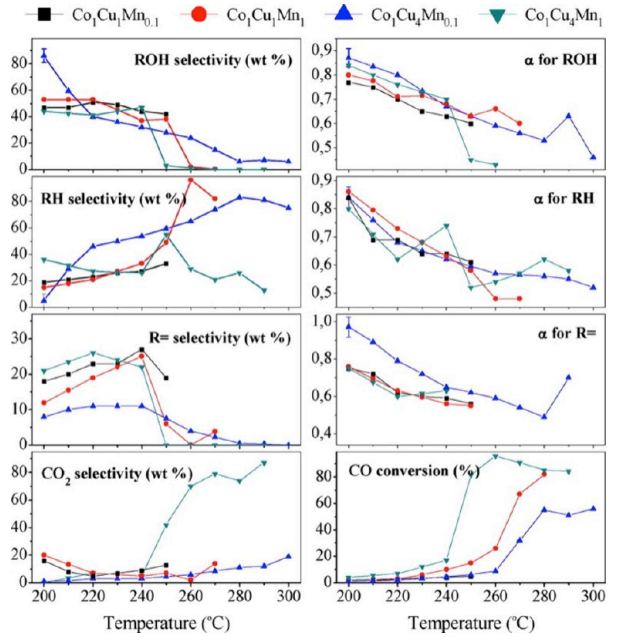


Figure 12. Detailed catalytic performance of Co/Cu/Mn catalysts. Reproduced from ref 162 with permission from the American Chemical Society, copyright 2013.

appropriate amount of CO* and CH_x* species, which was helpful for the initial C−C coupling reaction.

Sun et al.[165] synthesized a spherical-plate-like CuCoMn catalyst using a coprecipitation method, followed by a calcination-reduction process, and used it for HAS from syngas. The results showed that the catalyst included CuMn particles and a Co-rich nanosheet (Figure 13) and exhibited a high yield of $C_{2+}OH$. The good catalytic performance was due to the optimal ratio of surface Cu^+/Cu^0, which was helpful for the insertion of CO into CH_x to form higher alcohols.

Most of the Co-M catalysts that have been reported were prepared by means of coprecipitation or impregnation. Neither of these routes allows for precise control of the active center distribution. Tien-Thao et al.[166] prepared two different alkali metals (K and Na) promoted $La_{0.9}Sr_{0.1}Co_{0.8}Ni_{0.1}Cu_{0.1}O_3$ perovskite catalysts for HAS from syngas. The results showed that all the reduced catalysts were equipped with uniformly dispersed Co−Cu alloy, and the $C_{2+}OH$ productivity of the catalysts followed the order K promoted > Na promoted > unpromoted. The enhanced $C_{2+}OH$ productivity was attributed to the promoters facilitated the stable of Co_2C/Co ratio during reaction and increased catalyst basicity which promoted the chain growth of methanol to ethanol.

4.1. Influence of Supports. Various supports (e.g., SiO_2, Al_2O_3, CNTs, TiO_2, and KIT-6) have been studied for the preparation of Co−Cu catalysts. It is widely accepted that the strong interaction between Co−Cu and supports as well as the high surface area of supports play a crucial role in HAS from syngas.

Wang et al.[167] prepared Cu−Co supported on alumina catalysts with different ratios of Cu/Co and investigated them for HAS from syngas. $CuCo_2O_4$ mixed spinels were detected in the calcined catalysts, which indicated a strong interaction between copper and cobalt species. The addition of Cu was shown to significantly decrease the reducibility of the cobalt species. It was speculated that this step is critical to the synthesis of $C_{2+}OH$. A study has investigated Co@Cu core−shell catalyst mixed Cu−Co catalyst for HAS from syngas. The results showed that the latter catalyst with strong interaction between Cu and Co exhibited a better catalytic performance toward $C_{2+}OH$, while the former catalyst with core−shell structure showed high selectivity of alkanes.[168]

Cu−Co catalysts supported on alumina, silica, and CNTs have been investigated by Wang et al.[169] Both $CoAl_2O_4$ and $CuAl_2O_4$ were detected in the Cu/Co supported on Al_2O_3 catalysts.[149] However, the obvious separation of CuO and Co_2O_3 occurred when SiO_2 and CNTs supports were used; this was attributed to a weaker interaction between Cu−Co species and the supports. In addition, Lee et al. prepared three different catalysts of Cu/Co supported on ZnO, MgO, and Al_2O_3 supports and investigated them for HAS from syngas.[170] The ZnO support was considered to be better for $C_{2+}OH$ production than the other supports.

As indicated above, the strong interaction between Co and Cu species played a crucial role in the formation of $C_{2+}OH$. In order to solve the problem of poor solubility of Co and Cu species, researchers have designed Co−Cu encapsulated in KIT-6 catalysts with different Co/Cu ratios.[171] It was shown that Co_3Cu_1/KIT-6 exhibited the best catalytic performance for HAS from syngas; this was attributed to the confinement of KIT-6 keeping bimetallic CoCu highly dispersed.

Other new supports have been used for catalyst design to enhance the $C_{2+}OH$ formation. For example, CoGa particles that were homogeneously dispersed on layered double oxides (LDOs) were prepared by reduction of CoZnGaAl-LDHs/γ-Al_2O_3 catalyst precursors, with Co and Ga doped into the lattice frameworks of the LDHs.[172] A similar method was used to prepare the desired Cu/Co/Mo catalysts by Prieto et al.[163] The results showed that when the atomic ratio of Cu/(Cu +Co) was 0.3, the catalyst exhibited the highest space time yield of $C_{2+}OH$ (Figure 14). The satisfied catalytic performance was attributed to the slightly enriched Co sites on the CuCo alloy surface.

5. MO/MOS_2-BASED CATALYSTS

Since Murchison et al. used Mo-based catalysts for HAS from syngas in the 1980s, the catalysts have been widely studied.[173] It was found that MoO_x catalysts showed low yield of $C_{2+}OH$.[174,175] The $C_{2+}OH$ and hydrocarbon distribution of Mo-based catalysts followed the ASF distribution.[176,177] Recent developments on MoO_2, Mo_2C, Mo_2N, MoP, and

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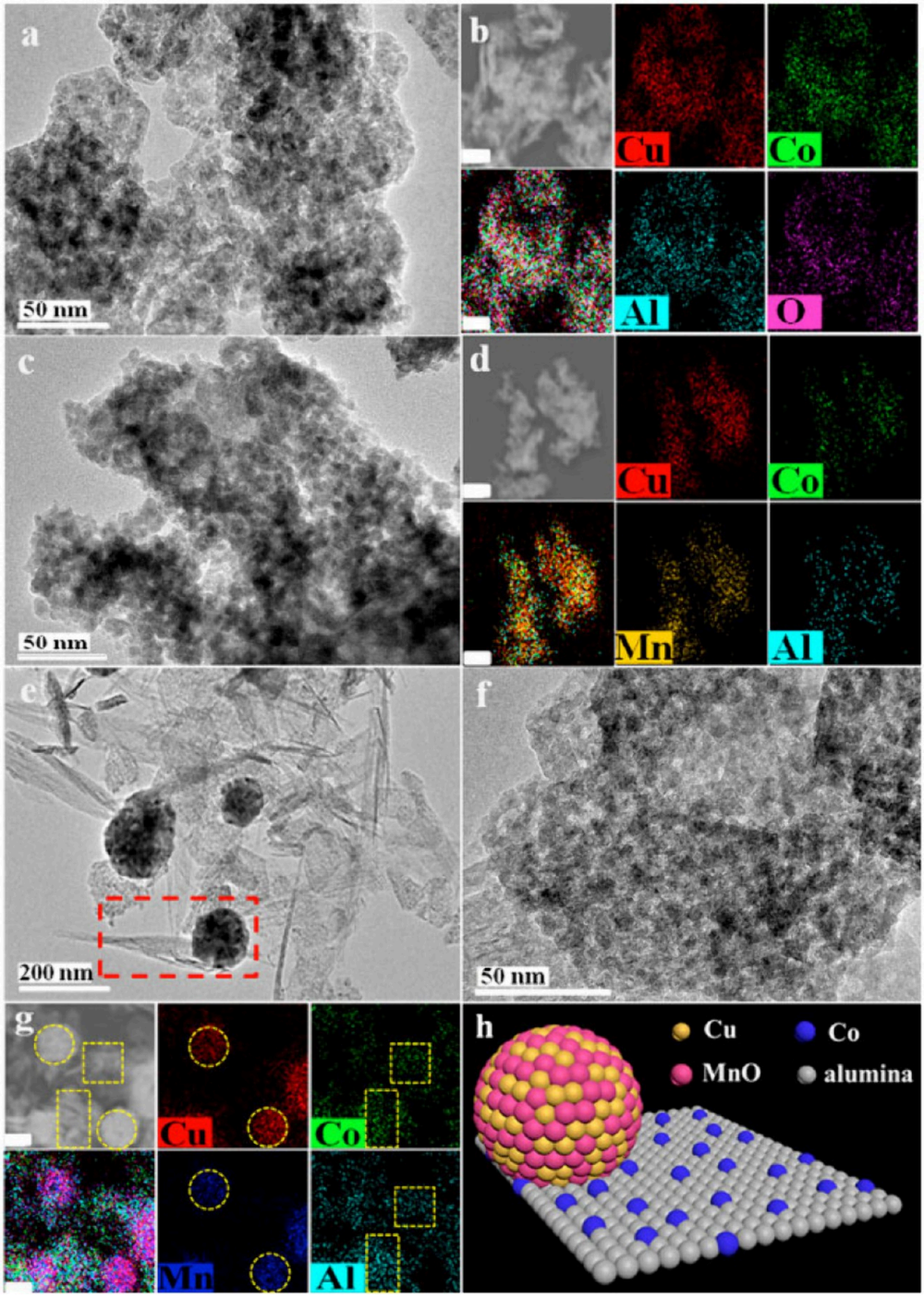


Figure 13. TEM/HHADF-STEM images and EDX elemental mapping of the reduced (a and b) CuCo, (c and d) Mn/CuCo, and (e and g) CuCoMn catalysts. (f) TEM image of nanosheets over reduced CuCoMn catalysts. (h) The corresponding architectural model of the reduced CuCoMn catalyst on the basis of the selected region in image (e). Reproduced from ref 165 with permission from Elsevier, copyright 2019. Note: the white scale bars represent 100 nm in panels b, d, and g.

MoS_2 catalysts, which have shown substantial improvement in the HAS reaction, are discussed in this section.

Molybdenum catalysts are typically supported on SiO_2, Al_2O_3, and carbon, and various promoters have been used for Mo-based catalysts.[175,178] Ma and co-workers prepared Ni/Mo/K supported on MCNTs catalysts for HAS from syngas.[30] The results showed that the catalyst exhibited high selectivity of 59% toward C_1~C_3 alcohols, with STY recorded as being 205 mg/(g_{cat}·h). It was assumed that Mo^{4+} and $Ni^{\delta+}$ species in the catalyst played an important role in alcohol synthesis. The authors emphasized that MCNTs, rather than alkali, caused a significant increase of the active sites.[179]

Mo_2C catalysts are interesting due to their ability to improve $C_{2+}OH$ formation.[180,181] Xiang et al. concluded that the C_{2+} alcohols were improved by promoters after completing a systematic study of Fe, Co, and Ni promoters.[181] Co_3Mo_3C compounds were detected when Co was added to the Mo_2C catalyst, which was attributed to the active sites of the Co

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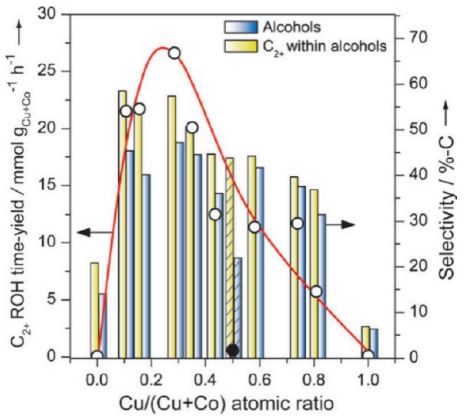


Figure 14. Catalytic performance over K/Cu/Co/MoO_x catalysts for HAS from syngas. Reproduced from ref 163 with permission of Wiley-VCH Verlag GmbH & Co. KGaA, copyright 2014.

promoted catalyst. Xiang et al.[182] also found Co and Ni promoted K/β-Mo_2C exhibited high selectivity of $C_{2+}OH$.

The mechanism of Cu/β-Mo_2C catalyst in HAS from syngas was investigated by Zhang et al.[183] It was found that the Cu/β-Mo_2C catalyst exhibited a higher yield of $C_{2+}OH$, compared with individual Cu(111) and β-Mo_2C(001) catalysts. Analysis of the electronic and structural properties of the catalyst indicated that the interface between β-Mo_2C and Cu promoted the charge transfer, resulting in more CH_x species formation, which were beneficial for the C−C coupling reaction to form $C_{2+}OH$ (Figure 15).

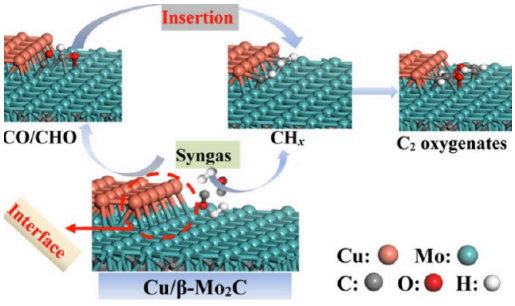


Figure 15. Mechanism of Cu/β-Mo_2C catalyst used for HAS from syngas. Reproduced from ref 183 with permission from the American Chemical Society, copyright 2019.

Mo_2N and MoP catalysts for HAS from syngas were also investigated.[184,185] For example, Zaman et al. prepared K-MoP supported on a SiO_2 catalyst for higher alcohol synthesis. They found that 5K-15MoP/SiO_2 catalyst exhibited high $C_{2+}OH$ STY of 147.2 mg/(g_{cat}·h) and 5K-10MoP/SiO_2 catalyst showed the highest $C_{2+}OH$ selectivity of 72.6%.[186]

Promoted MoS_2 catalysts have been more extensively studied than other Mo-based catalysts due to their preferable sulfur-resistance properties, higher yields of C_{2+} alcohols, and effective suppression of carbon deposition.[174,176,187] Similar to unmodified MoO_x-based catalysts, MoS_2 alone primarily provided undesired hydrocarbon products, especially methane.[188] Alkali metal promoters were used to neutralize the acidic sites of MoS_2 and stabilized the $Mo^{\delta+}$ species, which led to a decrease in hydrocarbon production and the enhancement of $C_{2+}OH$ formation.[174] Recently, it was reported that the K promoted catalysts could enhance the reaction of aldol condensation.[176] However, others have claimed that no aldol condensation reaction occurred when using K/Co/MoS_2 catalysts.[189]

Various alkali metals were used as promoters to improve the formation of $C_{2+}OH$, the catalytic performance followed the order Cs > Rb > K.[190] The physicochemical properties of the catalysts (such as the surface area or the dosage of alkali) also influenced the order of the promotional effect.[138] Consequently, the promotional effect reported by some studies followed a different order, i.e., Cs < Rb < K.[188,191]

Transition metals[191,192] as well as noble metals[193] were also used as promoters in MoS_2 catalysts to enhance $C_{2+}OH$ formation. It was found that CH_x species were formed on transition metals (Fe, Co, Ni) sites; then the activated CO was inserted into CH_x species to form C−C bonds, resulting in high yield of $C_{2+}OH$.[194] Recently, K/Co/MoS_2/Al_2O_3 catalysts were examined in a study reported by Toyoda et al.[189] The highest selectivity toward higher alcohols was approximately 40%, and this was obtained using $K_{0.6}/Co_{0.5}/MoS_2/Al_2O_3$ catalysts (Table 3). It was indicated that the dissociation of CO occurred on the Co_xS_y sites instead of the MoS_2 sites.

CNTs-supported K/MoS_2 catalysts promoted with Ni were reported by Wang et al.[195] The authors showed that when the ratio of Ni/Mo was 0.5:1, the catalyst exhibited a high $C_{2+}OH$ yield of 113 mg/(g_{cat}·h), with 64% $C_{2+}OH$. Rh promoted MoS_2 catalysts also have been investigated for HAS from syngas. The catalyst exhibited a high yield of alcohols, which was attributed to the Rh species promoted Mo (VI) reduced to Mo (IV).[193]

Chen et al.[196] studied the reaction mechanism of $C_{2+}OH$ formation over Cu_4 modified MoS_2 catalysts by DFT method. It was found that CO was first hydrogenated to CHO, and then the formed CHO is dissociated to form CH_x. The C−C coupling reaction between nondissociative CO/CHO and CH_x species formed a C−C bond. It was indicated that the activated CO/CHO species were formed on Cu_4 cluster sites, while the Cu_4 cluster and MoS_2 interface provides active sites for CH_2 formation and promotes the formation of the C−C bond.

The mechanism involved in $C_{2+}OH$ synthesis over transition metal (Fe, Co, and Ni) modified MoS_2 catalysts is similar to that of Rh-based catalysts and Cu modified FTS catalysts.

Table 3. Catalytic Performance of K/Co/MoS_2/Al_2O_3 Catalysts[a]

		Selectivity (C %)							
T (°C)	CO Conversion(%)	CO_2	MeOH	EtOH	PrOH	BuOH	Alkanes	α[b]	STY of $C_{2+}OH$ mol/(kg_{cat}·h)
260	4.4	33.2	8.9	31.6	4.1	1.1	21.1	0.19	1.8
300	6.3	32.2	6.7	29.3	4.0	0.6	27.1	0.21	2.4
320	7.1	34.5	5.4	21.3	3.8	1.1	33.9	0.28	2.0

[a]Reaction conditions: GHSV = 5000 h^{-1}, H_2/CO = 1, P = 7 MPa. Reproduced from ref 189 with permission from the American Chemical Society, copyright 2013. [b]Chain growth probability.

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Briefly, it is presumed that the nondissociative CO/CHO is inserted into CH_x to form a C−C bond and then forms $C_{2+}OH$ by subsequent hydrogenation. For Cu-modified methanol synthesis catalysts, the rate-determining step for $C_{2+}OH$ synthesis is also the C−C coupling reaction. However, the C1 intermediates can be obtained from both CH_3OH or nondissociative CO.

6. NEW MULTIFUNCTIONAL CATALYST TYPES

In the past decade, many investigators have worked on the direct conversion to HAS from syngas using a single catalyst. Higher alcohol synthesis involved several steps, including H_2 dissociation, the activation of nondissociative CO, CO dissociation, the insertion of nondissociative CO into CH_x to form C−C bond, and the eventual formation and removal of products form the catalyst surface. The intermediates can lead to complicated reactions, with methane, methanol, C_{2+} hydrocarbons, and C_{2+} oxygenates also being formed. However, it is known that the regulation of $C_{2+}OH$ selectivity requires controlling the C−C coupling reaction between nondissociative CO and CH_x species. However, it is very difficult to regulate a single reaction channel using a traditional catalyst. Tandem catalysis can offer a strategy to perform multistep sequential reactions in a single reactor. In this section, we discuss several multifunctional catalysts for improving HAS from syngas.

6.1. Oxide-Zeolite Catalysts. It is well-known that the bifunctional catalysts can promote C_2-C_4 olefins or aromatics synthesis from syngas, compared with traditional FT catalysts. The bifunctional catalysts are typically composed of oxides and zeolites. It is assumed that oxides were the active sites for CH_3OH/DME or ketene intermediate formation, while the reaction of C−C coupling occurs on the acidic sites of zeolites. The different types and carbon number distribution of products can be regulated by the use of zeolites. Using this concept, oxide-zeolite catalysts were also investigated for HAS from syngas.

For the C_{2+} oxygenate synthesis over oxide-zeolite catalysts, many studies have been aimed at reaction channel-controlled C−C coupling rather than shape selectivity. The syngas can enable the performance of both hydrogenation and carbonylation to produce the C_2 oxygenate. Zhou et al.[197] synthesized $ZnAl_2O_4$|H-MOR|$ZnAl_2O_4$ in combination with a sandwich configuration and reported optimal $C_{2+}OH$ selectivity of about 52% at 6% CO conversion (Figure 16 and Table 4). It was assumed that DME was a key intermediate for C_{2+} oxygenates synthesis. When placed downstream of $ZnAl_2O_4$H-MOR, $ZnAl_2O_4$ functions as a hydrogenation catalyst for the conversion of MA and AA into C_2H_5OH. Similarly, a recent study reported on a feasible route for synthesizing ethanol from syngas using a sandwich catalyst of $CuZnO_x$|Cu−H-MOR|$CuZnO_x$.[198] It was found that the catalyst showed higher ethanol selectivity of 15.62%, compared with the unpromoted catalyst of $CuZnO_x$|H-MOR|$CuZnO_x$.

Kang et al.[199] designed a trifunctional tandem catalyst of K-ZnO-ZrO_2|H-MOR|Pt-Sn/SiC for HAS from syngas, which could accomplish the conversion of syngas to $C_{2+}OH$ (>90%). They demonstrated that K^+-ZnO-ZrO_2 and mordenite with an eight-membered ring channel catalyzed syngas conversion to acetic acid, which then formed $C_{2+}OH$ on the catalyst of Pt−Sn/SiC (Figure 17).

6.2. Co/Co_2C-CuZnAlZr Oxide Coupling Catalysts. Co_2C and modified Co_2C catalysts were also investigated for HAS from syngas. Pei et al.[200] synthesized Co−Co_2C catalysts for higher alcohol synthesis. It was found that the catalyst exhibited high selectivity of $C_{2+}OH$, which was attributed to the formation of an interface between cobalt carbide and metallic Co (see Figure 18).

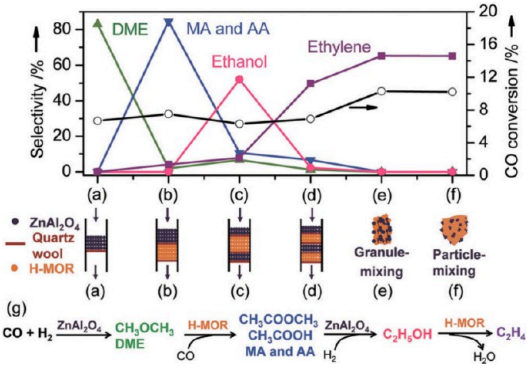


Figure 16. Effect of the arrangement of $ZnAl_2O_4$ and H-MOR on the catalytic conversion of syngas. (a) $ZnAl_2O_4$. (b) $ZnAl_2O_4$|H-MOR. (c) $ZnAl_2O_4$|H-MOR|$ZnAl_2O_4$. (d) $ZnAl_2O_4$|H-MOR|$ZnAl_2O_4$| H-MOR. (e) Mixture of $ZnAl_2O_4$ and H-MOR granules (250−600 mm). (f) Mixture of $ZnAl_2O_4$ particles (4−9 nm) and H-MOR particles (0.3−1 mm). Reproduced from ref 197 with permission of Wiley-VCH Verlag GmbH & Co. KGaA, copyright 2018.

K promoted CoMn catalysts for high alcohol synthesis were investigated by Xiang et al.[201] They synthesized the catalysts using the coprecipitation method and used it for HAS from syngas. The results showed that K promoted CoMn catalyst exhibited high oxygenates selectivity of 50 wt %, which was attributed to the K promoters promoting the formation of Mn_5O_8−Co_2C interface, enhancing the reaction of C−C coupling.

It was reported that a CoMn catalyst that contained Co_2C nanoprisms with facets (101) and (020) enabled HAS in the syngas conversion reaction. This catalyst exhibited high $C_{2-4}^{=}$ selectivity (about 60.8%) with very low methane selectivity.[202] Based on this, Yang et al.[203] prepared Na promoted CoMn catalysts and measured the catalytic performance of HAS from syngas. It was found that the Na promoted CoMn catalyst showed an oxygenated selectivity of 20 C%. The authors assumed that the nondissociative CO were activated on Co_2C, and then C−C bonds were formed by the insertion of nondissociative CO into CH_x on Co species. Liao et al.[204] also found that the highest STY and selectivity of alcohols were obtained when the ratio of Co/Mn was 2.

Lin et al.[205] introduced a CoMn-CuZnAlZr oxide multifunctional catalyst for HAS synthesis from syngas. As shown in Figure 19, the two different oxides were placed in the reactor with different configurations. The results showed that molar mixing oxides exhibited the highest alcohols selectivity of 58.1 wt %, and about 92.0 wt % of alcohols were higher alcohols. It was assumed that a suitable proximity between the two components was a benefit for higher alcohol formation. The method provided a novel strategy for higher alcohol synthesis from syngas.

7. THEORETICAL STUDIES BASED ON DENSITY FUNCTIONAL THEORY

Theoretical studies based on density functional theory (DFT) can serve as a powerful supplement for experimental mechanistic studies in the $C_{2+}OH$ synthesis. In the past

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Table 4. Catalytic Performances of Cu−Zn−Al/Zeolite Catalysts for Oxygenate Synthesis from Syngas[a]

Catalyst	T (K)	CO Conv.	CO_2 Select.	Selectivity (%)				
				CH_3OH	DME	MA	AA	HC
Cu−Zn−Al/H-ZSM-5|SAPO-34	473	3.3	29	3.1	88	3.2	0	5.9
Cu−Zn−Al/H-ZSM-5|H-ZSM-5	473	3.2	28	5.1	68	14	1.6	11
Cu−Zn−Al/H-ZSM-5|H-β	473	3.5	28	7.5	43	21	1.4	27
Cu−Zn−Al/H-ZSM-5|H-ZSM-35	473	3.7	28	4.0	56	33	0.6	6.1
Cu−Zn−Al/H-ZSM-5|H-MOR	473	4.5	22	0.3	0.8	84	13	2.1
Cu−Zn−Al/H-ZSM-5|H-MOR	483	7.5	21	0.1	2.5	83	14	0.9
Cu−Zn−Al/H-ZSM-5|H-MOR	493	10	21	0.1	0.6	85	12	2.3
Cu−Zn−Al/H-ZSM-5/H-MOR	473	4.1	47	1.3	7.2	0	0	92

[a]Reaction conditions: $H_2/CO = 1$; $P = 3$ MPa; $F = 25$ mL/min; time on stream, 5 h. Reproduced from ref 197 with permission from the Wiley-VCH Verlag GmbH & Co. KGaA, copyright 2018.

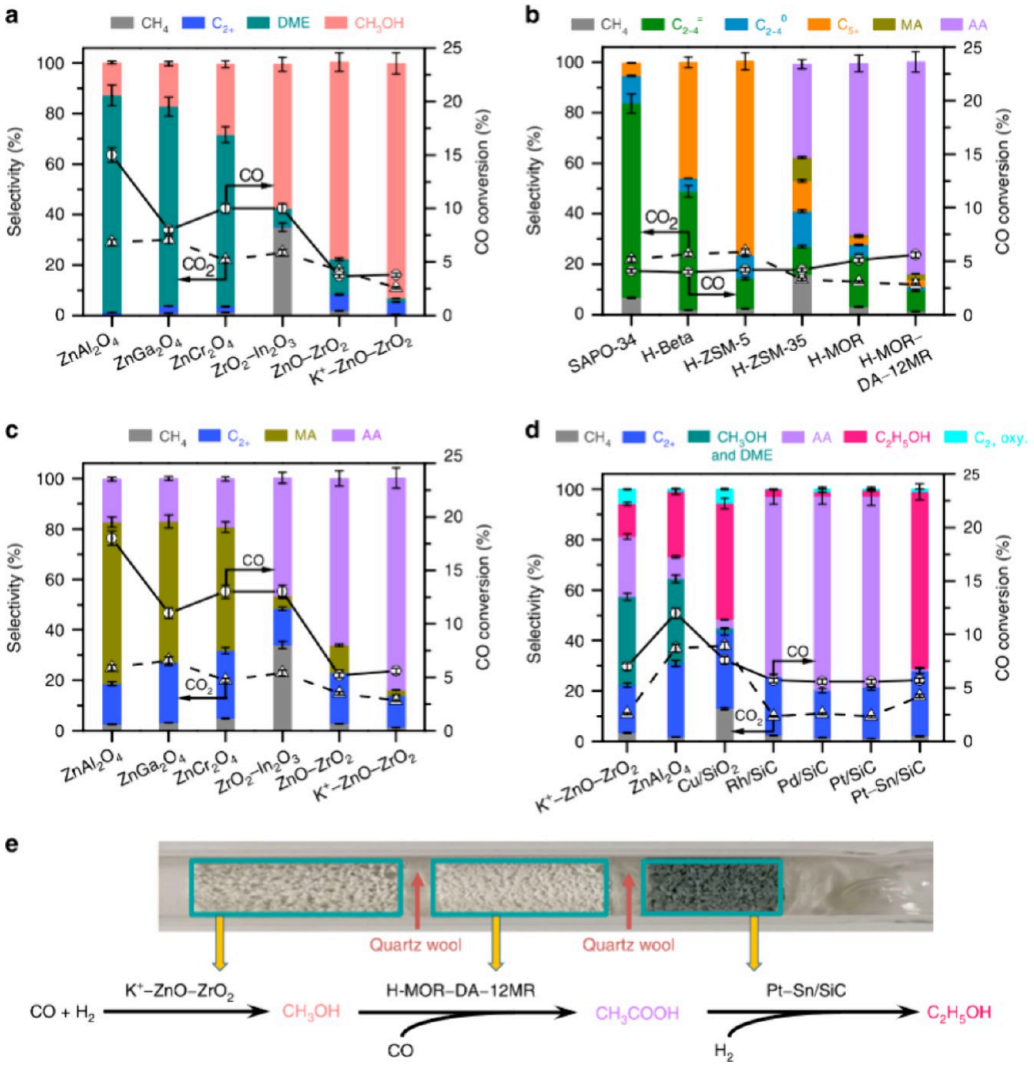


Figure 17. Catalytic behavior and schematic illustration of catalyst system. (a) Different oxides catalysts. (b) Combination of K promoted ZnO-ZrO_2 and different zeolites. (c) Combination of different oxides and modified-H-MOR. (d) Combination of K promoted ZnO-ZrO_2, modified-H-MOR, and hydrogenation catalysts. (e) Schematic illustration of the catalyst system. Reproduced from ref 199 with the permission of Springer-Nature, copyright 2020.

decade, theoretical studies have been explored to identify plausible mechanisms for ethanol synthesis, focusing on the activation of CO, the formation of some intermediates and C−C coupling reaction.[206−208] The mechanism for the formation of methane, methanol, and higher alcohols are usually included for the purpose of comparison.

The stepped surfaces of Rh(211) and the defect-free Rh(111) surfaces have been used as a catalyst model to simplify practical catalysts. Choi et al. investigated the mechanism of $C_{2+}OH$ using Rh(111) as the model catalyst.[206] The detailed reaction routes are listed in Figure 20. In the first step, the formation of HCO by hydrogenation of CO was

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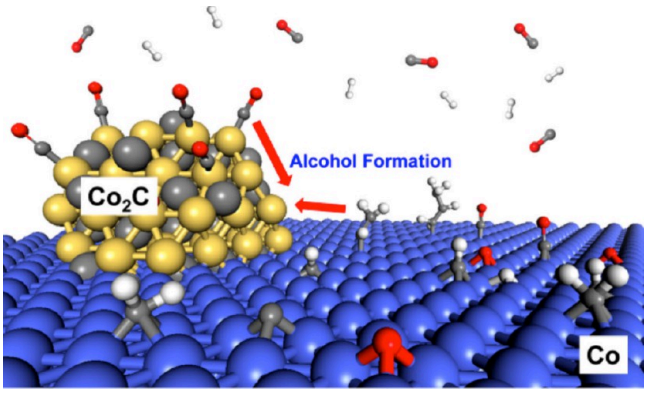


Figure 18. Mechanism for alcohol formation when using the Co/Co_2C catalyst. Reproduced from ref 200 with permission from the American Chemical Society, copyright 2015.

preferred, with the activation barrier being 1.35 eV. This is much lower than that of the direct dissociation of CO (3.72 eV) and of COH formation (1.67 eV). This is in agreement with the results found in a previous study.[209] The HCO intermediates were more easily hydrogenated to CH_2O relative to dissociation to CH and O. CH_2O was also shown to preferentially undergo hydrogenation toward CH_3O rather than CO dissociation. There were two possibilities for the next step in the conversion of CH_3O into products: one was further hydrogenation of CH_3O to generate methanol while the other was the dissociation reaction of CH_3O into CH_3 and O. In view of the activation barriers and the heats of reaction, the authors argued that both routes were favorable. The initial C−C bonds were attributed to the insertion of CO into the CH_3 fragments. As methane formation was preferred through CH_3 hydrogenation, the Rh centers required the assistance of promoters to suppress methane generation and enhance the initial C−C bond formation to ensure the synthesis of ethanol.

Microkinetic studies based on CO + CH have recently been reported in the literature.[210,211] Filot et al. showed that ethanol was formed over the stepped Rh(211) surface.[211] Ethanol formation was preferred at intermediate temperatures over

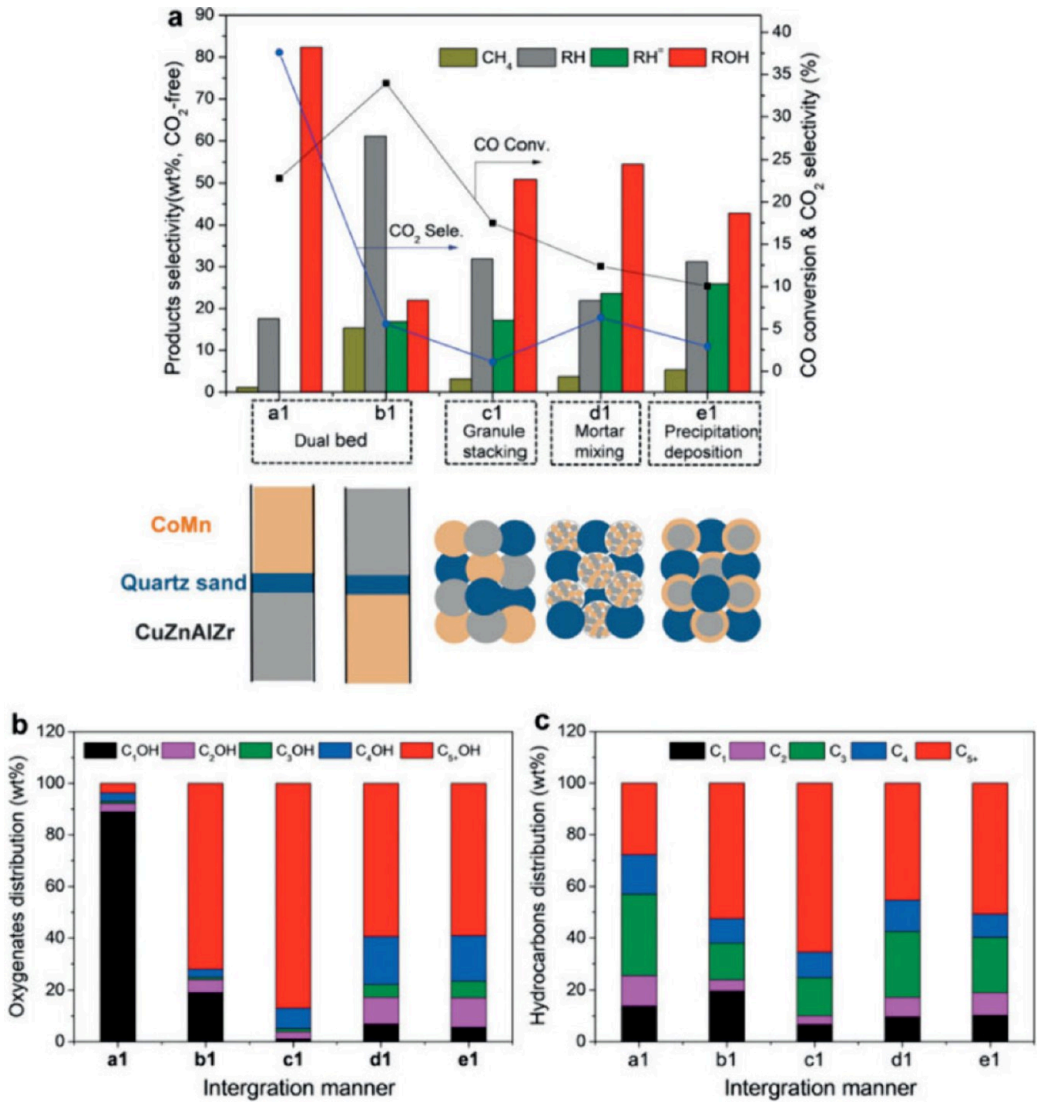


Figure 19. (a) Catalytic performance of multifunctional catalysts with different proximity. (b) Alcohol distribution of different catalysts. (c) Hydrocarbon distribution of different catalysts. Reproduced from ref 205 with permission of Wiley-VCH Verlag GmbH & Co. KGaA, copyright 2019.

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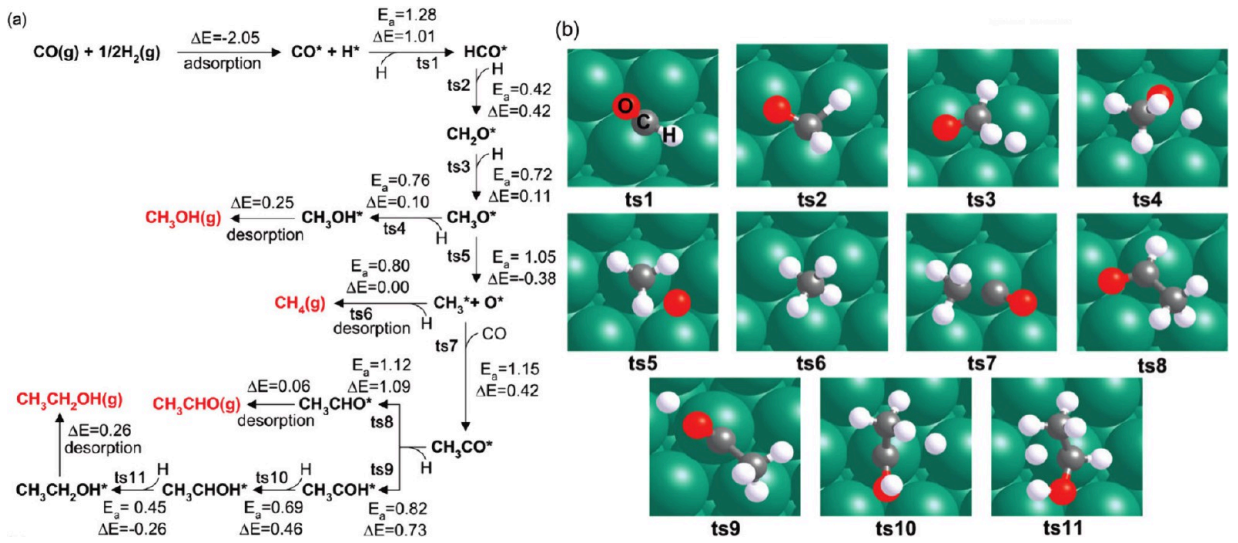


Figure 20. (a) Reaction pathways for higher alcohol synthesis over the Rh(111) catalyst. (b) Preferential adsorption morphologies of transition states (top view). (Green, Rh; red, O; gray, C; white, H). Reproduced from ref 206 with permission from the American Chemical Society, copyright 2009.

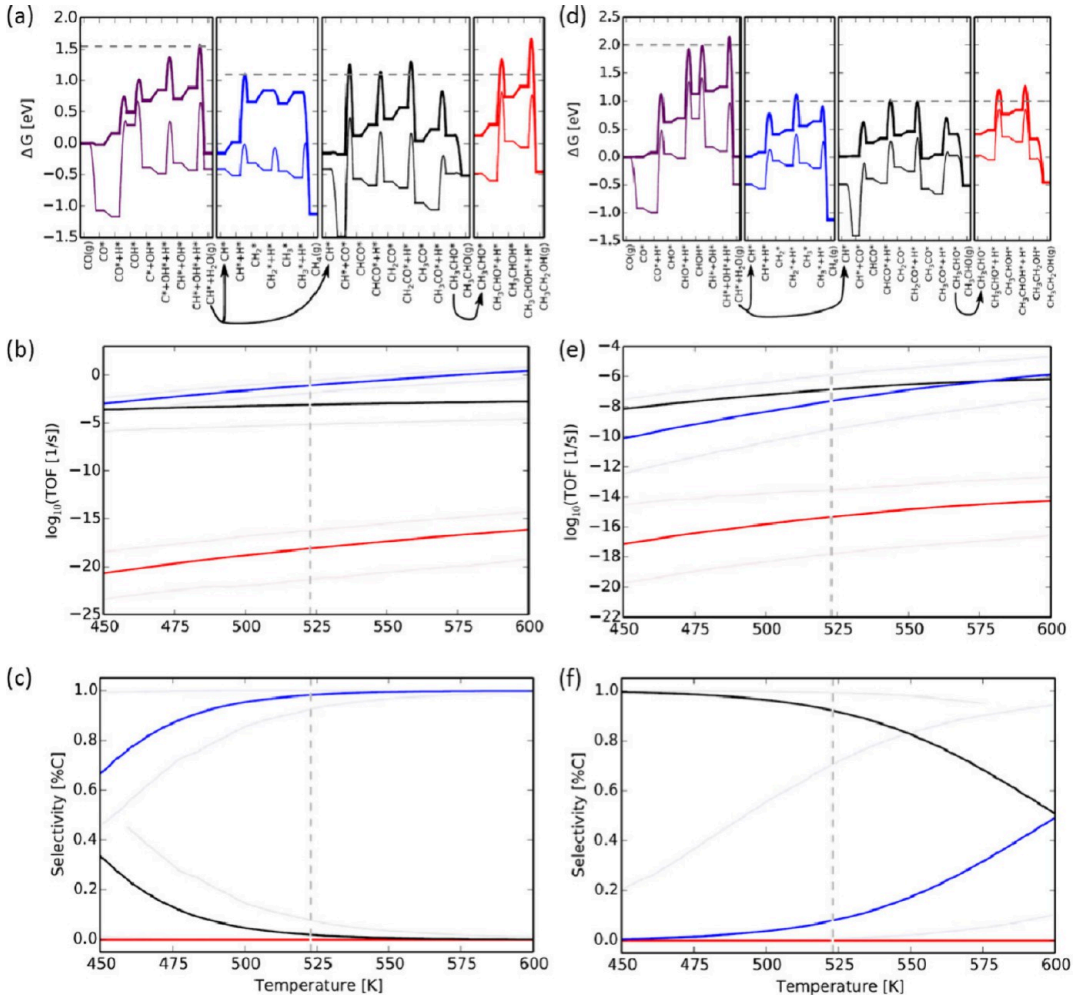


Figure 21. Rh(211): calculated free energy diagram (a) (bold line, with lateral adsorbate interactions; light line, without lateral adsorbate interactions), turnover frequencies (b) and carbon selectivity (c) for CH_4 (blue), acetaldehyde (black), and ethanol (red). Rh(111): free energy diagram at 250 °C (d), turnover frequency (e), and carbon selectivity (f) for methane (blue), acetaldehyde (black), and ethanol (red). Reproduced from ref 210 with permission from the American Chemical Society, copyright 2016.

https://doi.org/10.1021/acs.energyfuels.4c01419
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long-chain hydrocarbon formation at intermediate temperatures because the activation barrier of CO + CH was lower compared to the coupling reaction between CH_x species. Removing O from the surfaces was the rate-determining step because empty sites were required to catalyze the dehydrogenation steps for ethanol formation. The selectivity of ethanol was limited by the rate of the CH and/or CH_3 hydrogenation reaction along with CH_3CH dehydrogenation. In the study done by Yong et al., microkinetic analysis was conducted over the surface of Rh(211) and Rh(111) to examine the intrinsic selectivity of methane, acetaldehyde, and ethanol.[210] The formation of the C−C bond was attributed to insertion of CO into CH_x, which is consistent with previous literature.[63,206] The calculated free energies of the three products over Rh(211) and Rh(111) are shown in Figure 21a,d, respectively. With Rh(211), the rate of methane formation was dominant, with a TOF of 10^{-1} s^{-1}, which is orders of magnitude higher than that of ethanol (10^{-18} s^{-1}) and acetaldehyde (10^{-3} s^{-1}) formation. However, the rate of methane formation over Rh(111) was much lower, with a TOF of only 10^{-8} s^{-1}, which is compatible to that of acetaldehyde formation (10^{-7} s^{-1}), but it is still much higher than that of ethanol formation (10^{-15} s^{-1}). These results indicated that the formation of C_{2+} oxygenates was more likely over close-packed Rh(111) surfaces than over stepped Rh(211) surfaces. Nevertheless, Rh(211) was more active than Rh(111). It was also suggested that selectivity toward C_{2+} oxygenates was strongly sensitive to structure, when using Rh metal, and that Rh catalysts were intrinsically selective to acetaldehyde and not to ethanol.

In contrast to CO insertion into CH_x (x = 1−3) for the initial C−C bond formation mentioned above, HCO insertion into CH_x (x = 1−3) was suggested in the study done by Zhao et al., using Rh(111) as the model catalyst.[212] They compared HCO insertion into CH_x to that of CO insertion and found that the energy for CO insertion into CH_x was higher than that of the HCO insertion reaction. Moreover, the insertion of HCO into CH_x was more thermodynamically favorable, given the reaction energy data (Figure 22d). The researchers concluded that the insertion of HCO into CH_2 (CH_3) was the most favorable step. They suggested that the HOMO level and LUMO level of HCO shifted upward and downward, respectively, and both were closer to the d-band center of the Rh metal than that of CO. Additionally, the HOMO−LUMO gap of HCO was lower than that of CO, which facilitated charge transfer and hybridization between HCO and the active Rh metal. The reported transition states of insertion of CO and HCO into CH_2 are shown in Figure 22a,b. HCO coverage and the stability of CH_2 versus CH_3 over Rh(111) were not discussed in detail, and the overall reaction pathways were not given in that study.

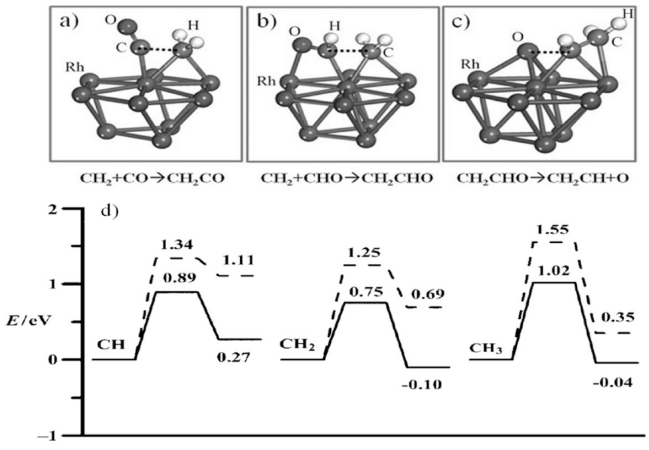


Figure 22. Structure of transition state for (a) CO, (b) HCO insertion into CH_2, and (c) C═O bond scission on the catalyst. (d) Calculated barriers and reaction energy for the formation of C−C bond. Reproduced from ref 212 with permission of Wiley-VCH Verlag GmbH & Co. KGaA, copyright 2011.

As indicated in the experimental part of this Review, previous studies have suggested that the production of C_{2+} oxygenates is negligible over promoter-free Rh-based catalysts, and hydrocarbons are the main products.[38] This suggests that the promoters on the surface should be of importance and that they may be essential parts of the active site. The difficulty in developing a monometallic catalyst that exhibits outstanding catalytic performance in $C_{2+}OH$ synthesis was discussed in the work reported by Medford et al.[213] When using various monometallic catalysts, the rate of ethanol formation was very low and produced a small region for higher selectivity of ethanol, where no pure metal was located. The authors proposed two strategies for improving ethanol selectivity, including (a) improvement of the CO bond splitting capability of Cu and (b) passivating the activity of the promoters (e.g., Fe, Co, and Ni).

The effect of the Mn promoter was discussed by Mei et al.[63] Two vital steps (i.e., methanation (CH_3 + H) for methane formation and the insertion of CO into CH_x for higher alcohol formation) were investigated using Rh_{50}, $Rh_{49}Mn$, and $Rh_{47}Mn_3$ clusters as catalyst models. The authors reported that the CO + CH_3 step was kinetically preferred to CO + CH and CO + CH_2 on pure Rh due to its lower reaction barrier. Doping Mn into Rh dramatically decreased the reaction barriers for insertion of CO into CH over $Rh_{49}Mn$ (0.69 eV) and over $Rh_{47}Mn_3$ (0.58 eV). The influence of Mn on CO + CH_2 was negligible since the activation barrier was only slightly decreased, and the insertion step was found to be highly endothermic over the Mn-modified Rh catalysts. CO insertion into CH is the preferential step for higher alcohol synthesis because of the lower activation barrier compared to CO insertion into CH_3. Mei et al. concluded that doping Mn into Rh had no real impact on the activation barrier in methane formation, which suggested that methane production is inevitable when using the Mn promoter.[65]

The mechanism involved in $C_{2+}OH$ synthesis over both modified FT catalysts and Mo-based catalysts is similar to that of the Rh-based catalysts.[7] The C−C coupling reaction between undissociated CO and CH_x species requires bifunctional sites, the latter being the result of the dissociation of CO with the assistance of H_2.[214] With the modified FT catalysts such as Cu−Co and Cu−Fe catalysts, the bifunctional sites consist of Cu and Co/Fe sites. Cu sites contribute to the adsorption of undissociated CO, while the Co/Fe sites contribute to the formation of CH_x. With the Co/Fe sites, hydrogenation of CO results in CH_xO, and cleavage of the C−O bonds in the CH_xO species then leads to CH_x formation. However, it is still debatable whether the undissociated species from CO participates in the coupling reaction with CH_x through activated CO* or the HCO intermediate. In the work done by Wang et al., the initial C−C bond formation over Co(111) and Ni(111) was considered to be from a CO + CH_x reaction.[215] The authors added that unlike the case over Co(111), the coupling reaction of CO + CH_x could not

https://doi.org/10.1021/acs.energyfuels.4c01419
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compete with the hydrogenation of CH_x over Ni(111), where methane was the main product. Xu et al. suggested that the insertion of HCO into CH_x was more facile thermodynamically and kinetically over Cu_6Co_3 because of the relatively smaller HOMO−LUMO gap of HCO than CO,[216] which is consistent with a previous study using Rh-based catalysts.[212] The addition of Cu partially blocked the Co sites for cleavage of the C−O bond and facilitated the HCO insertion reaction to generate the initial C−C bond.[216]

Using Mo-based catalysts such as the Mo_2C catalysts, molecular CO preferentially adsorbed on the Mo sites rather than the C-terminated surfaces, and the adsorption of CO on Mo_2C surfaces was facilitated by a potassium promoter.[217] Dissociation of CO also preferentially occurred on Mo-terminated surfaces; however, this can be inhibited by the presence of a potassium promoter. Tominaga et al. suggested that adding Co to Mo_2C altered the route for CH_x generation.[218] They proposed that over a β-$Mo_2C(100)$ surface, CH_x was formed by hydrogenation of CHO, CH_2O, and CH_2OH, with CH_2 and H_2O being the products. When β-$Mo_2C(100)$ surfaces were doped with Co, CH_x formed by hydrogenation of CHO, CH_2O, with CH_3 and O being the products. As shown in Figure 23, the activation energy barriers

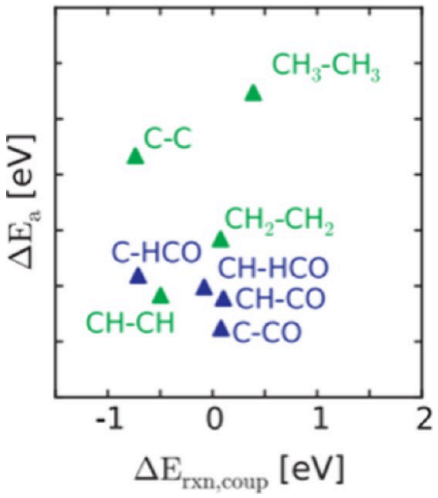


Figure 23. Reaction and activation energy for CH_x-CH_x/CH_x-H_yCO (green/blue). Reproduced from ref 219 with permission from Elsevier, copyright 2012.

of several coupling reactions, accounting for the initial C−C formation over Mo-terminated $Mo_2C(001)$, were investigated.[219] The insertion reactions of CH_x with either CO or HCO were kinetically favorable.

The primary elementary reactions that were critical for the selectivity of different products were determined in a microkinetic study done by Li et al.[220] Ethanol was suggested to mainly derive from the coupling reaction of CO with CH_2/CH_3. Hydrogenation of CO predominately benefited the selectivity of ethanol, and it suppressed the formation of CO_2 and methane. Methane was generated mainly from the hydrogenation of CH_3, which competed with the formation of ethanol and ethane.

The $C_{2+}OH$ synthesis mechanism based on DFT calculations over Cu-based catalysts is controversial. It has been suggested that the $C_{2+}OH$ mechanism over Cu(211), Cu(100), Mn-doped Cu(211), and the Cu cluster model catalyst is similar to that over Rh-based catalysts, where the initial C−C formation was generated from the insertion of CO/HCO into CH_x species.[221−224] It was reported that the optimal route for ethanol formation on Cu(211) surfaces was from the insertion reaction of CO with CH_3, with CH_3 being preferentially obtained from the process of CO + 3H → CHO + 2H → CH_2O + H → CH_3O + H → CH_3 + OH.[221]

However, with Cu(100) and Mn-doped Cu(211), the formation of HCO was more favorable, and the authors suggested that on this occasion the precursor to ethanol was predominately derived from the insertion of HCO into CH_3.[222,223] However, it was noted that with Cu/ZnO-based catalysts, the selectivity of alkanes was much lower compared to that of methanol and $C_{2+}OH$, especially when the catalysts were modified with alkali promoters.[25] This indicated that generating the precursors of alkanes (such as CH, CH_2, and CH_3 intermediates) is not favorable when using Cu/ZnO-based catalysts in the presence of alkali promoters. In the work done by Sun et al., it has been suggested that the coupling reactions of HCO + HCO/H_2CO are the main contributors to the initial C−C formation.[111] The authors suggested that the primary effects of the cesium promoter were to stabilize the key intermediates such as HCO and H_2CO and a decrease in the activation energy barriers of the HCO+HCO coupling reaction.

8. EVALUATION OF THE STABILITY OF DIFFERENT TYPES OF CATALYSTS

As shown in eqs 3−6, higher alcohol synthesis from syngas includes several reactions.[25,26] Thus, in the future, the stability of different catalysts is of critical importance when considering their use in industrial applications. As mentioned in the Review, it is unlikely that homogeneous catalysts will be used in industry; the stability of heterogeneous catalysts is rarely described.

With Cu/Co catalysts used for HAS from syngas, it was found that phase separation could lead to an increase in the production of alkanes.[142] Carenco et al. also investigated the nanoscale evolution of Cu/Co core−shell catalysts.[225] They found that Co was extracted from the bimetallic nanoparticles suppressed $C_{2+}OH$ formation. Sun and co-workers[226] synthesized a series of Cu−Fe catalysts with different Cu/Fe ratios. It was found that the CO conversion decreased in the early stage of the reaction and then changed slightly. However, the $C_{2+}OH$ selectivity decreased monotonically. STEM and EDS-mapping images indicated that the Cu and Fe components were homogeneously dispersed at the early stage of the HAS reaction, leading to high $C_{2+}OH$ selectivity. However, the Cu and Fe components gradually separated as the reaction continued, and the Cu−Fe synergism was weakened, leading to a decrease of total $C_{2+}OH$ selectivity. These results showed that it is important to increase the concentration of Cu-M sites to maintain good stability of modified FT catalysts for HAS from syngas. On the other hand, Mo-based catalysts exhibited good stability for HAS from syngas.

Compared to the high-temperature methanol synthesis catalysts (ZnO/Cr_2O_3), research has paid more attention to the stability of low-temperature catalysts (alkali promoted Cu-based). Fortunately, it was showed that alkali metals promoted catalysts exhibited optimal stability.[227] For example, the activity of Cs_2O-promoted $Cu/ZnO/Al_2O_3$ catalysts declined by only 7% after 80 h.[12]

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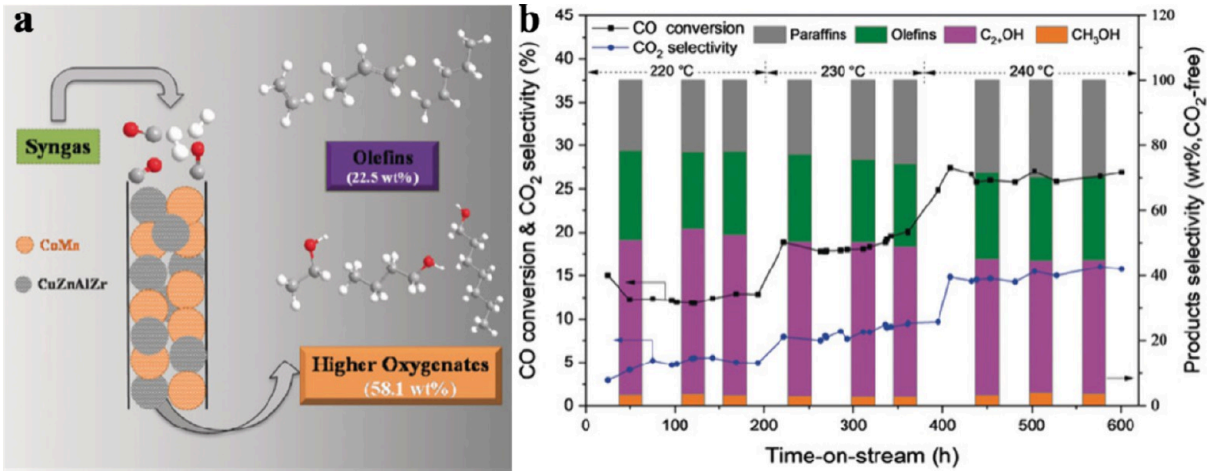


Figure 24. (a) Schematic illustration of the CoMn|CuZnAlZr multifunctional catalyst for syngas hydrogenation to $C_{2+}OH$. (b) Stability test of CoMn|CuZnAlZr catalyst. Reproduced from ref 205 with permission of Wiley-VCH Verlag GmbH & Co. KGaA, copyright 2019.

Table 5. Catalytic Performances of Different Types of Catalysts for the Direct Conversion of Syngas

					Selectivity (C %)			
Catalyst	P (MPa)	T (K)	H_2/CO	CO Conv.	CO_2	CH	CH_3OH	$C_{2+}OH$
Rh−La/V/SiO_2[38]	1.4	543	2	7.9	3.1	21.1	5.0	70.9
RhMn@S-1[70]	3	593	2	42.4	4.8	54.6	1.6	38.7
CuZnAl[123]	4	523	2	7.9	24.5	38.5	11.5	25.3
CuZnAl@S-1[124]	4	553	2	15	21.4	51.3	13.4	13.87
CuCo[154]	3	523	2	50.8	2	57.3	3.3	37.2
CoCuAl[164]	5	523	2	13.1	18.2	39.2	6.9	35.7
CuCoMn[165]	2.5	543	2	29.7	0.4	51.9	13.7	32.5
$KCoMoS_2/Al_2O_3$[21]	7	533	1	4.4	33.2	21.1	8.9	36.8
NiMoK-CNT[195]	5	593	1	13.4		32.7	9.8	57.5
$ZnAl_2O_4$|H-MOR|$ZnAl_2O_4$[197]	3	603	1	6		32.2	12	55.8[a]
K^+-ZnO-ZrO_2|H-MOR|Pt−Sn/SiC[199]	5	523	1	3.8	3.2	20	1.6	78.4[a]
CoMn|CuZnAl[205]	6	523	1	29	21.6	41.9	4.6	53.5[a]

[a]CO_2 free.

Tandem catalysts also showed good stability during the reaction. Lin and co-workers[205] investigated the stability of the CoMn|CuZnAlZr catalyst, and it was found that the CO conversion and $C_{2+}OH$ selectivity were almost unchanged at the temperature stages of 220, 230, and 240 °C (Figure 24).

$$2CO + 4H_2 = C_2H_5OH + H_2O$$
$$\Delta H_r^\circ = -253.6\ \text{kJ/mol} \quad (3)$$

$$CO + 2H_2 = CH_3OH$$
$$\Delta H_r^\circ = -90.4\ \text{kJ/mol} \quad (4)$$

$$CO + 3H_2 = CH_4 + H_2O$$
$$\Delta H_r^\circ = -205.9\ \text{kJ/mol} \quad (5)$$

$$CO + H_2O = CO_2 + H_2$$
$$\Delta H_r^\circ = -41.1\ \text{kJ/mol} \quad (6)$$

9. CHALLENGES AND PERSPECTIVES

Traditional heterogeneous catalysts such as Cu, Co, Mo, Rh, and Fe, enhance the dissociation of CO to form the $*CH_x$ intermediate, which subsequently reacts with the undissociated CO (CH_xO* and/or CO*) to generate $C_{2+}OH$. Two factors are reported to play the crucial role in ensuring the reaction proceeds with selectively to $C_{2+}OH$. The understanding on how to balance the production between $*CH_x$ and CH_xO*/CO* species is important for the coupling reaction to produce $C_{2+}OH$ rather than CO_2 and the deep hydrogenation reaction to form methane. In this Review, we have summarized the studies of five types of catalysts that exhibit considerable catalytic performances in HAS (Table 5). It can be seen from the Review that improvements in catalyst design must be made to further enhance the performance of syngas to the $C_{2+}OH$ reaction.

First, although Rh-based catalysts exhibit high ethanol selectivity, their industrial applications are limited due to the low yield of ethanol and expensive price of Rh. Nowadays, atomically dispersed metal catalysts have been synthesized for syngas conversion with improved performance. For example, Rh single atoms aggregate to form nanoclusters during syngas conversion and the combination of Rh single atoms and nanoclusters is beneficial to the ethanol selectivity and reaction rate (Figure 25).[228] However, it is still a challenge to ascertain whether stable Rh single-atom catalysts have better catalytic performance than Rh clusters. Therefore, it would be helpful to reduce the cost of a noble metal catalyst by designing stable metal single-atom catalysts for HAS.

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Energy Fuels 2024, 38, 14769−14796

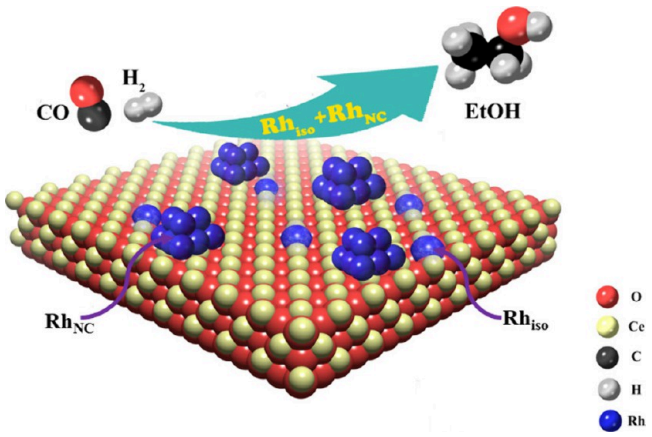


Figure 25. Schematic illustration showing Rh single atoms and nanoclusters on a surface. Reproduced from ref 228 with permission from the American Chemical Society, copyright 2022.

Second, for the modified methanol synthesis catalysts, two kinds of catalysts, low-temperature Cu-based and high-temperature ZnO/Cr_2O_3, have been studied extensively. However, both catalysts still have lower $C_{2+}OH$ selectivity due to the primary formation of methanol and CO_2. Recently, numerous promoted Cu-based catalysts were investigated by researchers to enhance the production of $C_{2+}OH$, in which both Cu^+ and Cu^0 were indispensable for $C_{2+}OH$ formation. To further improve the catalytic performance, it will be necessary to determine the best Cu^+/Cu^0 ratio to achieve high $C_{2+}OH$ selectivity and to understand how to facilitate the stabilization of Cu^+ during the reaction process.

Third, according to literature results, alkanes are the primary byproducts when using Cu modified FT catalysts and Mo-based catalysts. This is different from the byproducts obtained when using Cu-based catalysts. The active sites of the Cu modified FT catalyst are still unclear. For example, with the Cu-M (M = Fe, Co, etc.) catalysts, some researchers believe that a CuM alloy is the active site, while others indicated that both metallic Cu and M are active sites. Therefore, the design of Cu-M catalysts with different distances between metallic Cu and M may help us to understand deeply the nature of the active sites.

Finally, a new type of multifunctional catalyst has been designed to ensure high selectivity to $C_{2+}OH$. A trifunctional tandem system composed of a potassium-modified $ZnO\text{-}ZrO_2$, modified zeolite mordenite, and Pt-n/SiC catalyst has generated a high ethanol selectivity (90%) by controlling the multisteps in the tandem catalyst in one reactor. However, with the Co/Co_2C-CuZnAlZr catalyst, the Co/Co_2C component served to make the higher oxygenates. The CuZnAlZr oxides, in contrast, were able to effectively and selectively tailor the reaction network via boosting the insertion reactions by hydrogenating aldehydes to the corresponding alcohols. They also provided supplementary CH_xO^* as an adsorption species for the insertion reaction. Although trifunctional tandem catalysts exhibit high ethanol selectivity, it is still a challenge to increase the selectivity to the higher alcohols ($C_nH_{2n}OH$, $n > 2$). These Co/Co_2C-CuZnAlZr catalysts produce ~50% olefins and paraffin products, and further optimization of promoters to improve $C_{2+}OH$ selectivity by modifying the Co/Co_2C catalyst appears to be promising.

10. CONCLUSIONS

In this Review, we summarize the recent advances in catalyst design for converting syngas to higher alcohols, mainly focusing on obtained in the past decade. The challenges are provided, and we also give our perspective in this field. The syngas reaction over a catalyst requires that both CO and H_2 interact with the catalyst surface. The catalytic performance is dependent on the absorption of both the dissociated and nondissociated CO over catalysts used in the $C_{2+}OH$ synthesis. The mechanism involved in $C_{2+}OH$ synthesis over Mo-based catalysts is similar to those of Rh-based catalysts and Cu modified FTS catalysts. Briefly, the insertion of nondissociative CO/CHO into CH_x forms C−C bond and then forms $C_{2+}OH$ by subsequent hydrogenation. With modified Cu/ZnO catalysts, bound formyl species are key intermediates in the presence of syngas. The subsequent coupling reactions of HCO and HCO/H_2CO leads to the formation of the C−C bonds of $C_{2+}OH$, and this is considered as the rate-determining step. Tandem catalysts can also be used to improve HAS efficiency, especially the oxide−zeolite and Co/Co_2C−CuZnAlZr coupling catalysts, which can drive CO hydrogenation to high selectivity for $C_{2+}OH$.

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https://doi.org/10.1021/acs.energyfuels.4c01419
Energy Fuels 2024, 38, 14769−14796

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■ ACKNOWLEDGMENTS

This work received financial support from the National High-Level Talent Fund and the National Natural Science Foundation of China (Grant Nos. 22372138 and 22072118). We are also thankful for the financial support from the State Key Laboratory of Physical Chemistry of Solid Surfaces of Xiamen University. Part of the funding was supported by the Science and Technology Projects of Innovation Laboratory for Sciences and Technologies of Energy Materials of Fujian Province (IKKEM) and the Fundamental Research Funds for the Central Universities (20720220008). We thank the NSFC Center for Single-Atom Catalysis (22388102, H.X.).

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https://doi.org/10.1021/acs.energyfuels.4c01419
Energy Fuels 2024, 38, 14769−14796