

CHAPTER 5: CO OXIDATION OVER Au/Me-MCM-41 (Me = Si, Fe, Co) MATERIALS

5.1 Introduction

Carbon monoxide is an odourless, tasteless, highly toxic gas formed in large quantities during incomplete combustion of fuel-rich mixtures. CO is fatal at concentrations above 1000 ppm. Due to the ability of CO to attach to blood hemoglobin 240 times easier than oxygen [1], it can intoxicate a person at much lower levels causing nausea, dizziness, and headaches. It achieves this by depriving the body of oxygen [1 - 4].

Together with the oxides of nitrogen (NO_x) and non-methane hydrocarbons (HCs), carbon monoxide (CO) is one of the major pollutants emitted by internal combustion engines in automotive transportation. Three-way catalysts (TWCs) have been widely used to simultaneously reduce emissions of hydrocarbons (HC), carbon monoxide (CO), and nitrogen oxides (NO_x) from gasoline engine-powered vehicles [5]. Classical components of these systems usually include Rh, Pt, and/or Pd as active metals and ceria as promoter [5, 6]. However, the present TWCs are only effective when their temperature is above 250-300 °C. This temperature is known as the light-off temperature. Tests have shown that 50-80 % of the total unburned hydrocarbons from automobiles are emitted during cold start, i.e. the period before the converter reaches its active temperature. Therefore, a catalyst is needed which will convert these emissions to environmentally-benign gases such as N_2 , CO_2 and H_2O at relatively low temperatures (cold-start phase).

Although it was demonstrated as early as 1906 that gold is a catalyst for the hydrogen plus oxygen reaction to give water, gold has generally been regarded as a poor catalyst [7]. This long-held notion of the inertness of gold has in recent years been brushed aside as a result of the groundbreaking work by Hutchings, Haruta and

others. Hutchings [8] showed that gold supported on carbon was the catalyst of choice for the hydrochlorination of acetylene, and Haruta [9, 10] demonstrated that nanoparticulate gold on oxide supports could be used for the oxidation of carbon monoxide at ambient and subambient temperatures. This radical change in perception has been summarized in literature review on the subject of gold catalysis by Bond and Thompson [7]. Another review of the mechanism of carbon monoxide oxidation over gold was subsequently undertaken [11]. The conclusions were that notwithstanding the seemingly confused state of the literature, there is a large measure of agreement as to the principal factors responsible for the activity (inactivity) of gold catalysts evaluated for carbon monoxide oxidation:

(i) high activities are shown by oxide-supported small gold particles less than 5 nm in size.

(ii) Choice of support is very important: success depends on using an oxide of the first row of transition elements in Groups 4-12, e.g., titania (TiO_2) and iron oxide (Fe_2O_3), supports that have not previously found much use for Platinum Group Metals.

(iii) The method of preparation is critical: Three methods in particular have been widely used: coprecipitation, deposition-precipitation, and Iwasawa's method in which a gold-phosphine complex (e.g., $[\text{Au}(\text{PPh}_3)]\text{NO}_3$) is made to react with a freshly precipitated support precursor. Other procedures such as the use of colloids, grafting and vapour deposition meet with varying degrees of success.

(iv) The mode of pretreatment before use is also important: calcination is frequently used with good results, while reductive procedures are usually not helpful.

The relationship between gold particle size and catalytic activity in CO oxidation has been clearly demonstrated by Valden et al [12] (see also Figure 4.1 in chapter 4).

These authors observed that the specific reaction rate increases with particle size to a maximum at ~3.2 nm, followed by a decline in activity with a further increase in size. This observation is identical to the behaviour observed for high surface area Au/TiO₂ catalysts [13, 14].

To expatiate on the support effect, it has been demonstrated that gold crystallites dispersed on *n*-type semiconductors (e.g., Co₃O₄, Fe₂O₃, TiO₂) generally display a higher activity in the low-temperature CO oxidation reaction than those dispersed on insulators (e.g., Al₂O₃ and SiO₂) [15]. Supported gold catalysts are also active toward catalyzing many partial and deep oxidation reactions. Good catalytic activity was generally found when gold was dispersed on cobalt oxides [16]. Cobalt oxides themselves also exhibited a good activity towards CO oxidation at moderate temperatures. The observed catalytic activity of cobalt oxides, however, increased with the oxidation state of cobalt [17, 18]. Other studies [19, 20] have also found that catalysts Co₃O₄ and Au/Co₃O₄ displayed a high catalytic activity towards oxidation of CO in air, showing a 100 % conversion at a temperature of 200 °C or less. The spinel (Co_{1.66}Al_{1.34}O₄) has also shown significant catalytic activity for CO oxidation at low temperatures [21]. To further illustrate the importance of cobalt oxide supports, Mellor et al [22] have used Au catalysts supported on cobalt oxide as a model catalyst for a three-way catalytic converter in gasoline and diesel applications. They noticed that the T₅₀'s (T₅₀ represent the light-off temperature for a particular catalyst, i.e., the temperature at which a catalyst achieves 50 % conversion of the starting material) for CO, HC and NO_x conversion on this catalyst system were 85 °C, 240 °C and 310 °C respectively in TWCs. For diesel engines, the T₅₀'s were 170 and 60 °C for HC and CO conversions. Previous results [23] showed that for catalysts containing 1.2 % gold supported on Co₃O₄, the activation energy (E_{act}) for CO oxidation was significantly lower (16.3 kJ.mol⁻¹) than that measured for 0.66 % gold on α-Fe₂O₃ (E_{act} = 35.1 kJ.mol⁻¹) or 1.0 % gold on TiO₂ (E_{act} = 29 kJ.mol⁻¹). Catalysts containing Co₃O₄ as a promoter also display the lowest T₅₀'s for the conversion of methane, propene, trimethylamine and propane [24].

Reactions catalyzed by gold include [25, 26]: (i) the oxidation of carbon monoxide and hydrocarbons under mild conditions, (ii) selective oxidation, (iii) selective hydrogenation, (iv) hydrogenation of carbon monoxide and carbon dioxide, (v) the water gas shift (WGS), (vi) reduction of nitrogen oxides with propene, carbon monoxide or hydrogen, (vii) destruction of halogenated compounds such as dioxins, and (viii) the hydrogen plus oxygen reaction to give water or hydrogen peroxide. The most likely first use of gold catalysts in association with fuel cells will be for the selective removal of carbon monoxide impurities from hydrogen feed streams. The absence of carbon monoxide would enable fuel cells to run more efficiently and at lower temperatures. Effectiveness in this application has already been demonstrated [27 - 29]. With regard to pollution control, the most attractive potential application is air cleaning to remove malodorous and poisonous gases, and indeed gold-containing systems have already been used in toilets in Japan for this purpose [30].

The field of catalysis by gold is so advanced and diversified that reference gold catalysts for use as standards are now available and distributed by the World Gold Council (WGC) [28]. The compositions, preparation methods and pretreatments of these reference catalysts are given in Table 5.1 below:

Table 5.1. WGC Reference Gold Catalysts [28]

Catalyst type	Preparation method	Calcination (K)
3 wt% Au/TiO ₂ (P25)	Deposition-Precipitation	573
0.3 wt% Au/Fe ₂ O ₃ on Al ₂ O ₃ beads	Deposition-Precipitation	573
5 wt% Au/Fe ₂ O ₃	Coprecipitation	573
10 % Au/C (CabotXC72)	Gold sol	-

5.1.1 Gold Catalysts Supported on Mesoporous Silica-derivatives

Since the efficiency of supported metal catalysts often depends on the dispersion and metal-support interaction, the excellent mesoporous properties of MCM-41 can provide a remarkable dispersion medium for catalytically-active metal components in order to prepare highly active catalyst systems. The discovery in the last decade of the unusually high catalytic activity of supported gold catalysts make MCM-41 a good candidate for evaluation as a support for Au nanoparticles. However, Au catalysts supported on silica have not been studied much due to the difficulty in stabilizing small Au particles on this support. The problem in preparing silica-based supported Au catalysts is the inapplicability of solution-based methods in the deposition of Au on SiO₂ due to (i) the high acidity of SiO₂ [31], the low melting point of Au [32] and the low isoelectric point (IEP = 2) of SiO₂ [26, 33]. Therefore, it is necessary to modify the chemistry of siliceous MCM-41 if established methods are to be used to synthesize supported Au catalysts on this material.

Studies on the vapour phase epoxidation of propylene over Au/Ti-MCM-41 catalysts prepared by DP [34 - 37], have revealed that the presence of well-dispersed tetrahedrally coordinated Ti sites and the Au nanoparticles on the support surface are necessary for epoxidation activity. Au/MCM-41 has also shown high efficiency in the selective oxidation of cyclohexane to cyclohexanol and cyclohexanone using oxygen as oxidant under moderate reaction conditions [38].

The oxidation reactions catalyzed by Au-containing mesoporous materials have also been extended to CO oxidation. Au/MCM-41 prepared by CVD yielded Au particles in the 2.2-3.1 nm size range [32], showing exceptionally high activity for the CO oxidation reaction (with T₅₀ values of -15 to -10 °C). Also, using gas-phase grafting methods, Okumura et al [39] have prepared Au/MCM-41 catalysts with high activity towards low-temperature CO oxidation, with T₅₀ in the range 259-264 K and activation energies in the range 23-27 kJ/mol. Very recently, Liu et al [40] have prepared a

highly active catalyst for CO oxidation, based on Au nanoparticles in aluminosilicate MCM-41, by a one-pot synthetic method. Up to 70 % CO conversion could be obtained over a catalyst with a gold loading of $\text{Au/SiO}_2 = 24 \text{ wt}\%$. Direct dispersion of pre-formed Au nanoparticles inside the mesoporous MCM-41 matrix gave rise to materials with a low catalytic activity for the CO oxidation reaction. Functionalization of SBA-15 with positively charged groups, followed by incorporation of $[\text{AuCl}_4]^-$ and subsequent reduction with NaBH_4 resulted in a composite material showing a rate of $2.7 \times 10^{-4} \text{ mmol g}_{\text{cat}}^{-1} \text{ s}^{-1}$ in the CO oxidation reaction [41].

In the field of micelle-templated mesoporous materials, Overbury et al [42] have published an extended study that compares the catalytic activity of Au supported on mesoporous silica (MCM-41 and wormhole structured silica) with that supported on mesoporous titania. For the Au particle sizes in the range 2-3 nm, the mesoporous TiO_2 -based materials exhibited a much higher CO oxidation activity than the SiO_2 -based materials. These results demonstrated that the presence of 2-3 nm particle sizes is not sufficient to achieve high activity in CO oxidation, but that the chemical nature of the support may also influence the activity. The results of the CO oxidation activity study obtained by these authors are shown in Figure 5.1 (*next page*). It can be seen from this figure that the mesoporous silica-based catalysts only starts showing activity at 100 °C, whereas the mesoporous TiO_2 -based ones are already active at negative temperatures (regardless of the similarity in Au particle sizes). Also, the mesoporous TiO_2 catalysts shows 100 % CO conversion at ~50 °C, while the mesoporous SiO_2 catalysts attain 100 % CO conversion at ~300 °C.

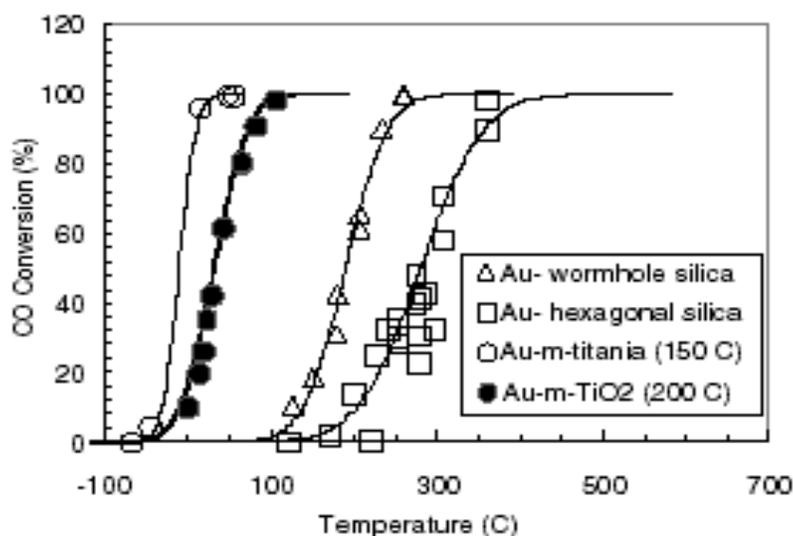


Figure 5.1. CO conversion as a function of temperature for different supported Au catalysts: Au on wormhole mesoporous silica, Au on hexagonally ordered mesoporous silica, Au on mesoporous titania calcined at 150 °C, and Au on mesoporous titania calcined at 200 °C [42].

The aim of the present chapter is to extend the idea of framework premodification, particularly the ones causing a silicate framework charge imbalance like trivalent cations, to other transition metals. We have investigated a series of Au/Me-MCM-41 materials (Me = Si, Co and Fe) obtained by different preparation methods, and containing different amounts of Au and Me, for catalytic activity in the CO oxidation reaction. The preparation methods have been described in the previous chapter (chapter 4), but will also be given in *section 5.2* for ease of reference.

5.2 Experimental

5.2.1 Starting Materials

Materials used in this study have included synthetic supports such as Si-MCM-41, Fe-MCM-41, and Co-MCM-41. $\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$ (Aldrich, 99.999 %) was used as a Au(III) precursor, with either a 1 M ethylenediamine solution or a 2 M Na_2CO_3 solution used to generate the $\text{Au}(\text{OH})_3$ required by either the coprecipitation (CP) or

deposition precipitation (DP) synthetic approaches. The base metal precursors used to modify the charges on the silica framework were $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Aldrich, 98 %) and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Fisher Scientific, 100.2 %). Deionized water was mostly used as a solvent medium, although a few samples were prepared with distilled water.

5.2.2 Catalyst Preparations

All Au-containing materials used/reported in this chapter were synthesized following the methods reported in chapter 4. For some materials, the catalytic behaviour will be correlated with or rationalized in terms of the data in chapter 4, particularly the Au crystallite sizes and BET surface areas.

Method A

A few Au-containing materials were prepared by direct hydrothermal synthesis, involving the in situ generation of the mesoporous support in the presence of gold precursors. After recovery by Buchner filtration, the product was washed several times with deionized water to a negative halide (Br^- and Cl^-) test, dried at ambient temperature and then calcined at 500 °C for 12 h. It was noted in chapter 4 that such high temperature treatments are accompanied by the formation of large Au particles, which are not expected to show near-ambient temperature catalytic activity.

Method B

A measured volume of an aqueous solution of $\text{H}[\text{AuCl}_4]$ with a Au(III) molarity of 0.0295 M was added drop-wise into a magnetically stirred slurry of Me/MCM-41 (Me = Si, Fe, Co). The mixture was stirred magnetically at room temperature for 1 h, following which a 1 M ethylenediamine (en) solution was added to bring the pH of the resultant slurry to *ca.* 8-9. Stirring was continued at room temperature for 13 h, after which the solid product was recovered by filtration, washed several times with

deionized water until a negative Cl^- test was observed, dried overnight at room temperature and then calcined at $400\text{ }^\circ\text{C}$ for 4 h, unless stated otherwise.

Method C

This method has been devised to be intermediate between the well-known deposition-precipitation and co-precipitation synthetic strategies using various bases as precipitants.

In a combined co-precipitation and deposition-precipitation approach, calcined pure silica MCM-41 prepared hydrothermally at $120\text{ }^\circ\text{C}$ for 3 days was added into a magnetically-stirred aqueous solution containing Fe(III)/Au(III) or Co(II)/Au(III) ions in order to prepare supported bimetallic composite materials. After equilibrating the mixture for 15 minutes at room temperature, an aqueous solution of Na_2CO_3 was added to bring the pH to 9. Stirring was continued at room temperature for 20 h, followed by filtration, washing the solid free of Cl^- ions, and then drying both samples at room temperature and at $150\text{ }^\circ\text{C}$ with no high temperature calcination.

The metal contents reported in this study were calculated based on the composition of the starting materials, and not from elemental analysis (i.e., the exact metal content was not determined).

5.2.3 Activity Testing Procedure

Figure 5.2 below illustrates the schematic representation of the CO oxidation reactor used in this study:

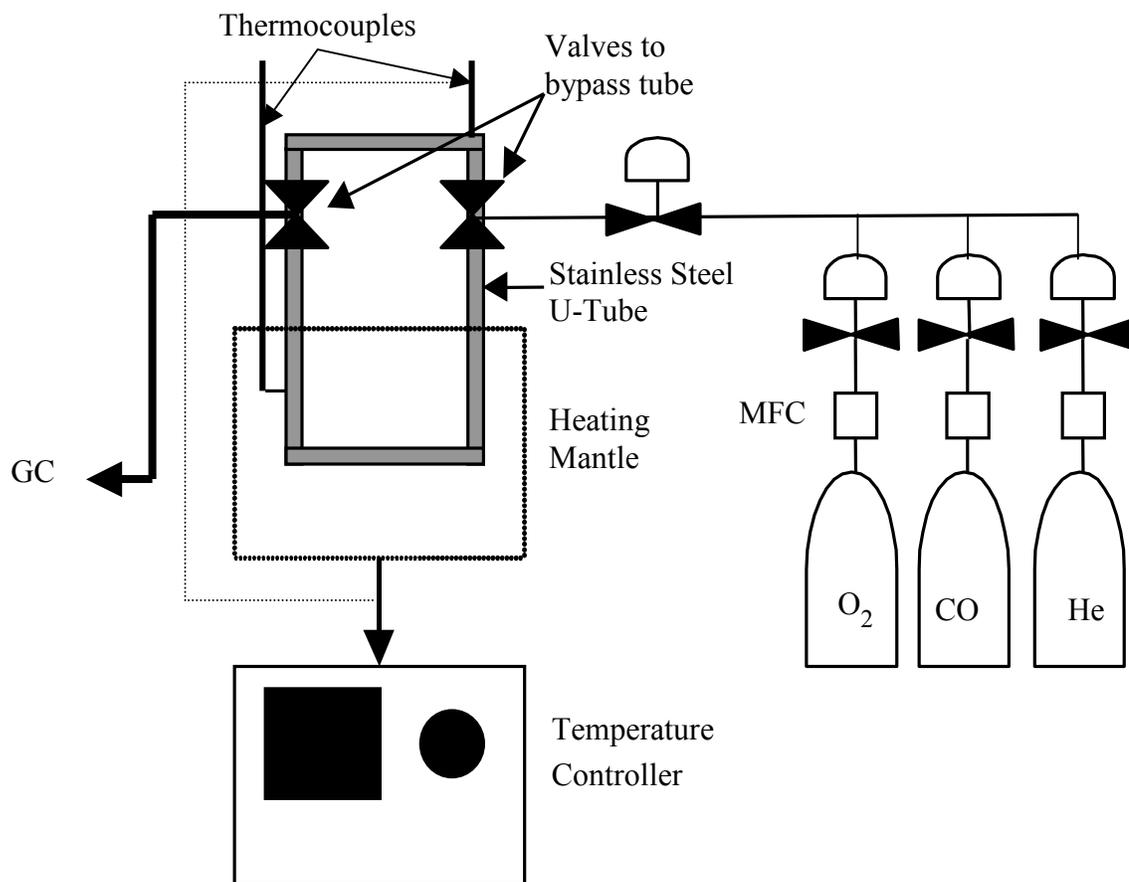


Figure 5.2. The catalyst testing set-up for the CO oxidation reaction

The reactor system comprised a U-shaped stainless steel reactor, a GC equipped with a TCD and a computer for data collection. The reactor could be heated to a desired temperature by using a heating mantle. Prior to the reaction, the lines were flushed with flowing helium gas until no traces of CO, O₂ or CO₂ could be detected. Mass-flow controllers were used to regulate the incoming gas flows. Then the reactant gases, CO and O₂, were mixed in the by-pass mode of the reactor system until a stoichiometric ratio of 2 : 1 (CO : O₂) was obtained. At this point the reactant gas mixture was then allowed to pass through the reactor (space velocity of $\sim 48\,000\text{ ml}\cdot\text{h}^{-1}\cdot\text{g}_{\text{cat}}^{-1}$), during a single run at a particular temperature, starting from room tempera-

ture. A catalyst sample (50 mg) was loaded into the reactor and kept in position by quartz wool plugs, i.e., a fixed bed laboratory microreactor type of system. Product gases were analyzed by gas chromatography to determine the catalyst conversion and selectivity. The appearance of a third peak, due to the CO₂ product, at higher retention times (~15 minutes) and the reduction in peak intensities and areas of the reactant gases signalled that a reaction was taking place at a particular temperature.

5.3 Results and Discussion

Various Au-containing MCM-41-type materials have been synthesized and tested for catalytic activity in the CO oxidation reaction using a stoichiometric CO : O₂ reactant mixture. Their activity was monitored in terms of % CO conversion as a function of reaction temperature. All the data reported in this chapter represent the initial activities of the catalysts, i.e., non-steady state activities. The results are presented as light-off curves, which are plots of the % CO conversion as a function of reaction temperature. In some cases, reference will be made to the light-off temperature (T₅₀), defined as the temperature at which a catalyst attains 50 % conversion of CO.

5.3.1 Gold Catalysts on Pure Silica MCM-41 Supports

Mesoporous silica-based gold catalysts were prepared via both direct hydrothermal synthesis and post-synthesis approaches. The catalytic activity of the resulting materials used in the CO oxidation reaction is shown in Figures 5.3-5.5 below. The physical characterization data for each catalyst are included in the footnote of each figure.

A gold on silica sample, with nominal composition 1.285 wt% Au/MCM-41, was prepared by aging the synthesis gel at room temperature for 20 h, and then heating at 96 °C for 3 h. After calcination of the processed material at 500 °C for 12 h, it showed the CO oxidation activity trend shown in the Figure 5.3 below:

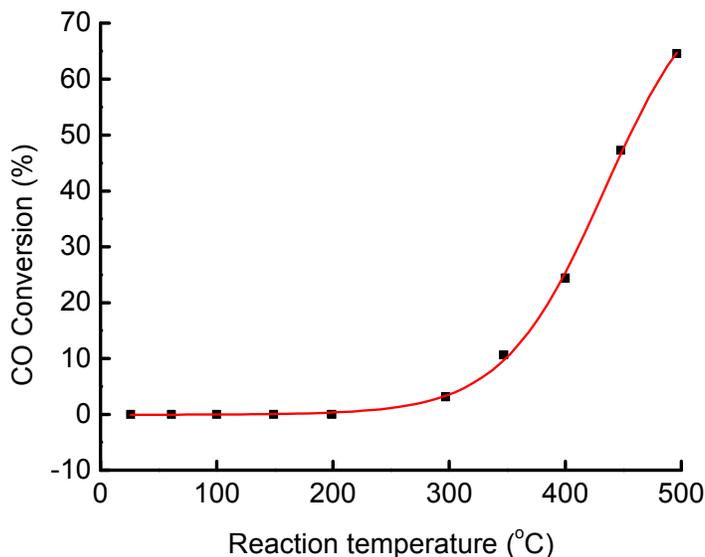


Figure 5.3. Light-off curve for 1.285 wt% Au/Si-MCM-41 prepared by prior aging the synthesis gel at room temperature for 20 h, followed by treatment at 96 °C for 3 h and 500 °C calcination for 12 h.

Although this material has a reasonably high BET surface area (1064 m²/g), the figure above shows that this nanocomposite material does not show any catalytic activity up to reaction temperatures above 200 °C. This inactivity at mild temperatures can be associated with the exceedingly large (18 nm) Au nanoparticles observed in this material (see chapter 4 for the HRTEM micrograph). This material never reached 100 % conversion. Reaction temperatures above 500 °C were not recorded as structural changes would take place in the catalyst system.

A post-synthesis preparation of Au/Si-MCM-41 requiring the high calcination temperatures usually invoked in directly-synthesized materials has also been evaluated. This method was based on the electrostatic interaction between AuCl₄⁻ and the occluded CTA⁺ cation in the as-synthesized Si-MCM-41. This was followed by precipitation of the Au(III) species with an (en) solution to deposit and keep the Au inside the mesoporous channels of the host CTAB-Si-MCM-41 (TEM showed no Au until

after calcination). Figure 5.4 below shows the light-off curve for this material after calcination at 500 °C for 12 h.

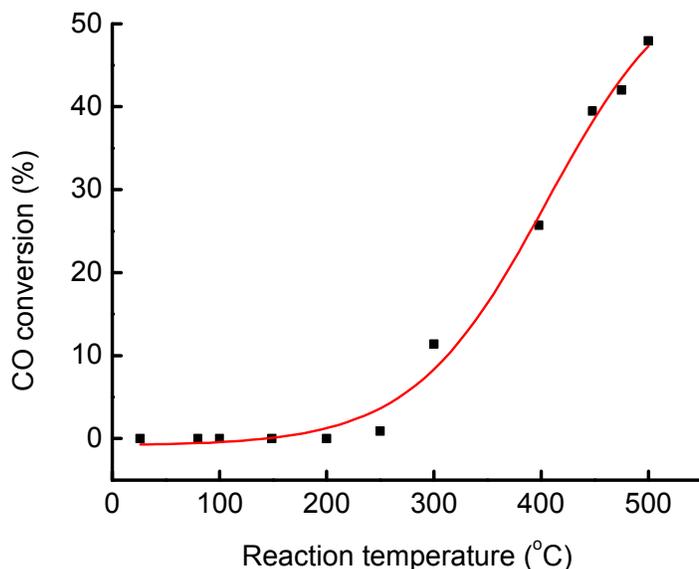


Figure 5.4. Light-off curve for 2.28 wt% Au/Si-MCM-41 prepared from AuCl_4^- and as-synthesized Si-MCM-41 via the (en) route. Material calcined at 500 °C for 12 h.

Like the one-pot-synthesized material, this material commences to show some activity at $T > 250$ °C. Also, this material comes nowhere closer to 100 % CO conversion even at 500 °C, corresponding to the calcination temperature. This behaviour is also attributed to the large size of the gold nanoparticles (12 nm) relative to the recommended 2-5 nm required for low temperature catalytic activity. Again reaction temperatures above 500 °C would not give any useful information.

Another post-synthesized Au/Si-MCM-41 catalyst was prepared via the ethylenediamine deposition route using precalcined Si-MCM-41 as support, thus offering the possibility of using calcination temperatures < 500 °C. Upon calcination at 400 °C for 4 h, this material (with a nominal composition 5 wt% Au/Si-MCM-41), showed the catalytic activity illustrated in the figure below:

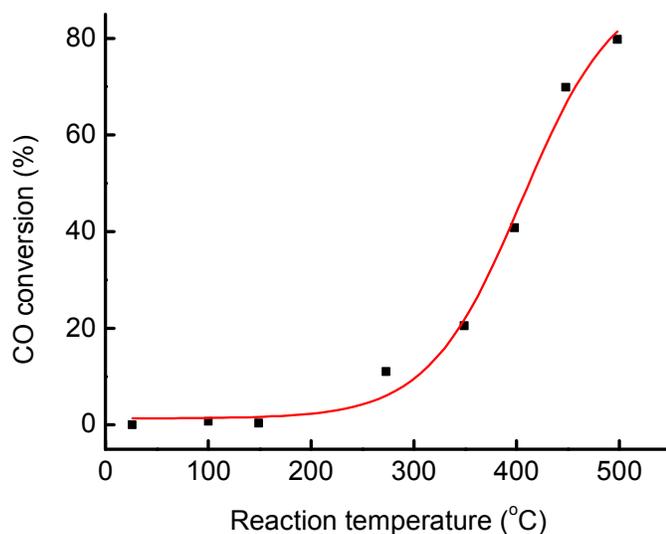


Figure 5.5. Light-off curve for 5 wt% Au/Si-MCM-41 prepared by (en) deposition-precipitation of AuCl_4^- onto precalcined Si-MCM-41. The catalyst system was then calcined at 400 °C for 4 h. $S_{\text{BET}} = 790 \text{ m}^2/\text{g}$ and Au average particle diameter = 10 nm (std. dev. = 3).

Although no direct comparison can be made between this catalyst system and the preceding two samples (on account of the fundamental differences in synthesis methods, Au contents and calcination processes), it is important to note that the 5 wt% Au/Si-MCM-41 system shows significant activity between 200 and 300 °C. Also this material attains a conversion of ~80 % around 500 °C. This seemingly improved catalytic behaviour compared to the preceding two materials can be attributed to the decreased average particle diameter of the Au nanoparticles (10 nm) through the latter synthesis approach.

Table 5.2 summarizes the method of preparation, average particle size and catalytic activity data for the catalysts discussed above.

Table 5.2. Correlation of preparation method, Au particle size and catalytic activity for Au/Si-MCM-41 catalysts

Catalyst	Preparation method	Au particle size /nm	T ₅₀ /°C
1.285 % Au	One-pot	18	~450
2.28 % Au	(en), CTA/MCM-41	12	~500
5 % Au	(en), Si-MCM-41	10	~400

The average Au particle size on these systems is relatively large, partially accounting for the observed lack of catalytic activity.

5.3.2 Gold Catalysts on Cobalt-functionalized Mesoporous Supports

These catalyst systems were prepared post-synthetically using precalcined 5 wt% Co-MCM-41 via the ethylenediamine (en) route followed by calcination. Figure 5.6 (*next page*) shows the effect of the Au content on the catalytic activity of the catalyst system calcined at 400 °C for 4 h. It can be seen from this figure that the gold/cobalt-containing samples show CO oxidation activity at lower temperatures than those on siliceous supports (Figure 5.5). Also worth noting is the fact that increasing the Au content from 1 wt% to 5 wt% lowers the light-off temperature significantly with the 5 wt% Au sample achieving 100 % CO conversion at temperatures between 150 and 200 °C. Since the average Au particle sizes for the two materials is the same (4.5 ± 0.5 nm), the observed difference in activity cannot be attributed to the particle size effect, but may rather be associated with the difference in the number of active sites.

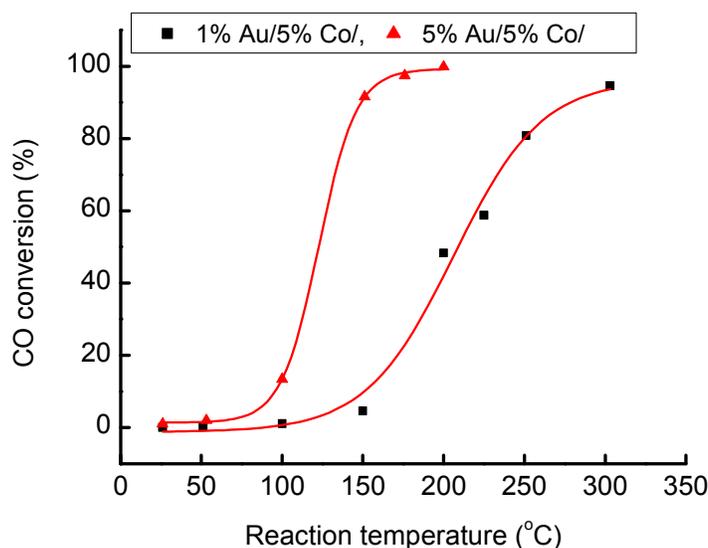


Figure 5.6. The light-off curves of Au/5 wt% Co-MCM-41 prepared by DP with (en) solution and calcination at 400 °C for 4 h: The effect of varying the Au content. The average Au particle diameters are 4 nm and 5 nm respectively for the 1 wt% Au/ and the 5 wt% Au/5 wt% Co-MCM-41 materials.

Figure 5.7 below illustrates the light-off curves for materials obtained by different calcination procedures of two portions of the same Au/5 wt% Co-MCM-41 material prepared via the (en) route. This figure illustrates the importance of low-temperature calcination in the catalytic performance of Au/Co catalysts for the CO oxidation process. It can be seen that the material calcined at 325 °C for 6 h lights off at a lower temperature ($T_{50} \sim 170$ °C) than the corresponding material calcined at 325 °C for 6 h in one cycle, and then at 400 °C for 4 h ($T_{50} \sim 240$ °C), making the former material a more active catalyst. The former catalyst reaches 100 % CO conversion at relatively lower reaction temperatures (*see appendix A.6*). This observation seems to support literature reports [43 - 45] that some degree of moisture or hydroxyl groups is a component of the active site in supported gold catalysts, i.e., excessive calcination dehydrates the catalyst and renders it inactive. Therefore, it can be concluded that optimization of the calcination temperature for this catalyst system may result in a good catalyst for CO oxidation.

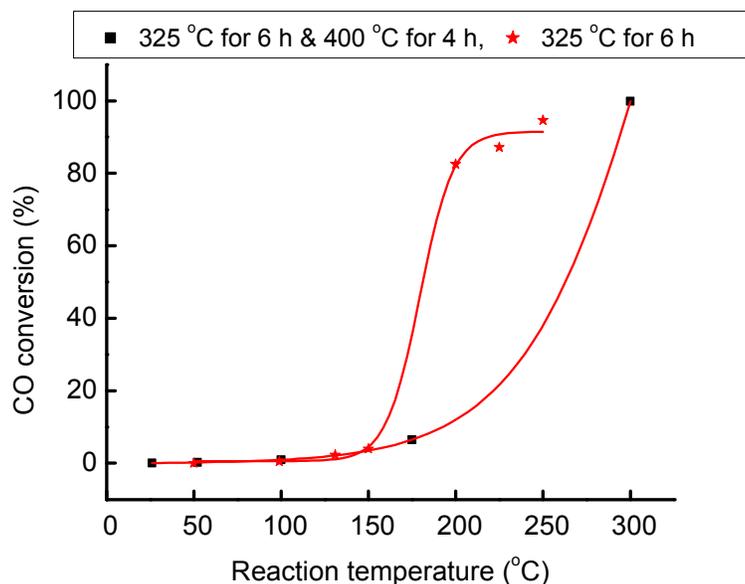


Figure 5.7. The light-off curves of 1.48 wt% Au/5 wt% Co-MCM-41 prepared via the (en) deposition route and subjected to two different calcination processes. Neither HRTEM nor BET analysis was done on these samples and therefore, no average Au particle diameter has been determined.

Table 5.3 summarizes the activity data together with other physicochemical characteristics for the catalysts supported on 5 wt% Co-MCM-41.

Table 5.3. Activity and other properties of Au on 5 wt% Co-MCM-41 catalysts

Catalyst	Calcination	Au particle size/nm	T ₅₀ /°C
1 % Au	400 °C, 4 h	4	~200
5 % Au	400 °C, 4 h	5	~120
1.48 % Au	325 °C, 6 h	-	~160
1.48 % Au	325 °C, 6 h & 400 °C, 4 h	-	~240

The T₅₀'s are significantly lower than those obtained with pure silica supports, disregarding the method of preparation and the Au content. This shows the importance of the presence of Co in the support.

5.3.3 Gold Catalysts on Fe-functionalized Mesoporous Supports

On the basis of the high-temperature calcination requirement, and the consequent Au crystallite growth at high temperature, only a few Au samples on Fe-derivatized MCM-41 have been prepared by the one-pot route and explored for CO oxidation activity in this study. These materials were prepared by treating the synthesis gel containing both metal precursors at 80 ± 2 °C for 6 h, followed by calcination of the processed materials at 500 °C for 12 h. The light-off curves of the resulting materials, showing the effect of varying the Au content of the synthesis gel are shown in Figure 5.8.

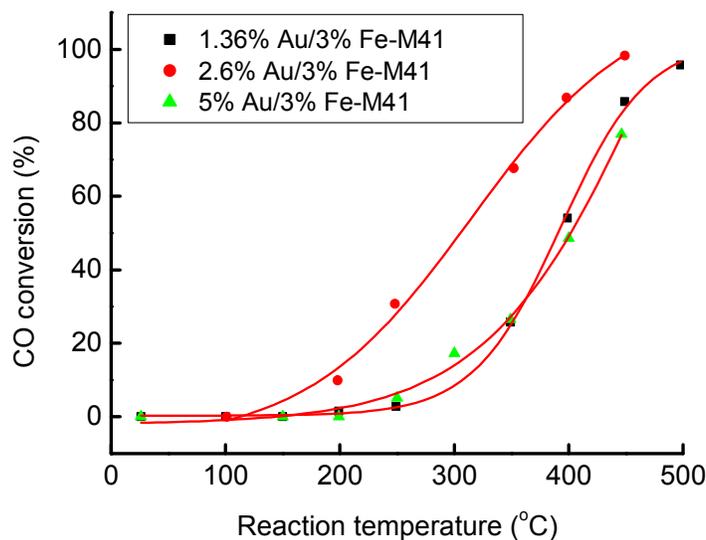


Figure 5.8. The light-off curves for Au/3 wt% Fe-MCM-41 prepared by direct hydrothermal synthesis at 80 ± 2 °C for 6 h, followed by calcination at 500 °C for 12 h: The effect of Au content. For 1.36 wt% Au, $S_{\text{BET}} = 1047$ m²/g; for 2.6 wt% Au, $S_{\text{BET}} = 1126$ m²/g and average Au particle size = 23 nm. The 5 wt% Au/3 wt% Fe-MCM-41 material was not characterized.

Figure 5.8 suggests that the catalytic performance of 1.36 wt% Au/3 wt% Fe-MCM-41 is similar to that of 5 wt% Au/3 wt% Fe-MCM-41 (~2 % error bar). Both show inferior activity ($T_{50} \approx 400$ °C) compared to 2.6 wt% Au/3 wt% Fe-MCM-41 prepared similarly, which exhibits a light-off temperature of ~290 °C. No correlation

between catalytic activity and the average particle size of these systems could be inferred because Au particles sizes were not measured for 1.36 wt% Au/ and the 5 wt% Au/3 wt% Fe-MCM-41 materials.

The 5 wt% material showed negligible room temperature activity, and Figure 5.9 below illustrates the variation of the CO conversion with the time on stream (TOS) at 22 °C.

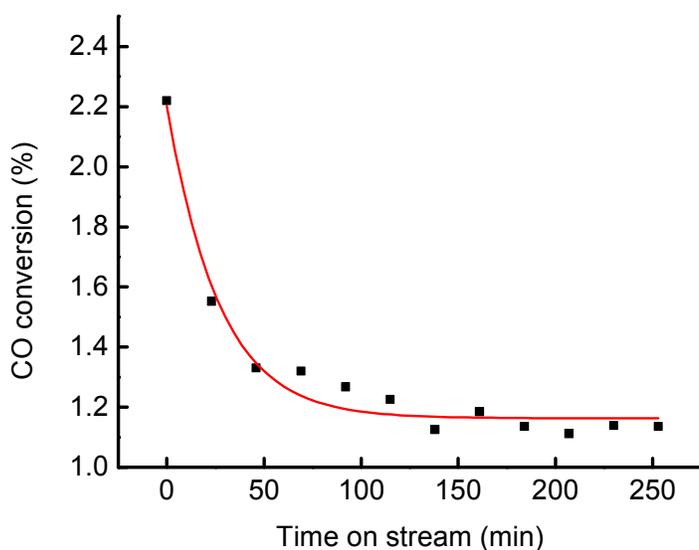


Figure 5.9. TOS curve for CO oxidation using 5 wt% Au/3 wt% Fe-MCM-41 prepared by hydrothermal synthesis at 80 ± 2 °C for 6 h, followed by calcination at 500 °C for 12 h. Activity measurements were performed at 22 °C.

Although the CO conversion never drops to zero in this time, the figure shows that the catalyst deactivates in the first 50 minutes and then attains a steady state for the remainder of the time. This deactivation can stem from the formation of a surface carbon species, as no sintering of the gold particles can be expected at room temperature. This observation of slight activity at room temperature may suggest that a refinement in the synthesis or even pretreatment of this material could lead to highly active catalysts.

5.3.4 Gold Catalysts on Fe-functionalized MCM-41: Ethylenediamine Synthesis route

Other Au-containing Fe-derivatized materials have been prepared by a variety of post-synthesis methods, with the majority involving the ethylenediamine deposition route followed by calcination. The CO oxidation activity of such post-synthetically prepared catalysts are discussed below.

Figure 5.10 below compares the catalytic activity of catalysts prepared by the deposition of the Au(III) species onto preformed 3 wt% Fe-MCM-41 in the presence of aqueous ethylenediamine as a precipitant. All the materials were calcined at 400 °C for 4 h.

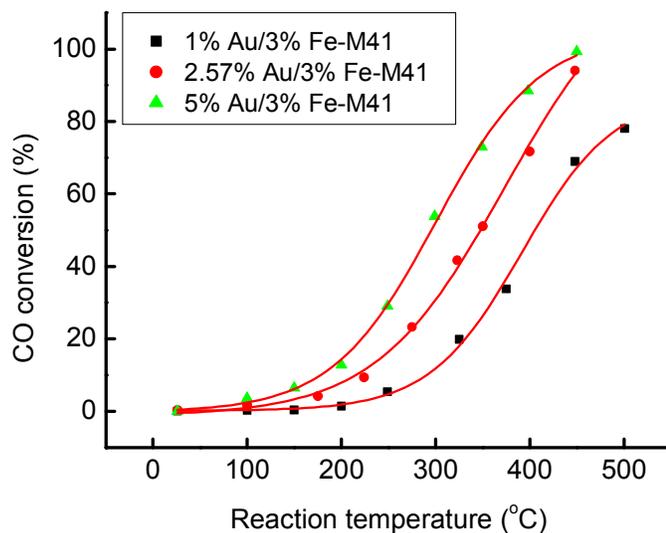


Figure 5.10. The light-off curves for Au/3 wt% Fe-MCM-41 prepared by (en) deposition of Au(III) onto 3 wt% Fe-MCM-41, showing the effect of the Au content. All samples calcined at 400 °C for 4 h.

It can be seen from the above figure that all the catalysts based on 3 wt% F-MCM-41 are inactive at room temperature. The 1 wt% Au-containing catalyst never shows

activity until a reaction temperature of 200 °C. However, the catalytic activity improves with an increase in Au content from 1 to 5 wt% Au. The materials with Au loadings in excess of 1 wt% shows some activity at reaction temperatures of ~100 °C (compare with Figures 5.8 and 5.9). The results in the figure above also show that the catalytic activity of supported Au catalysts is not determined solely by the average particle size for each sample. A correlation of the activity of these systems with their physical properties is shown in the table below.

Table 5.4. Activity and physical properties of 1-5 wt% Au/3 wt% Fe-MCM-41

Catalyst	Au particle size/nm	S _{BET} /m ² · g ⁻¹	T ₅₀ /°C
1 wt% Au	6	862	~400
2.57 wt% Au	5.6	-	~350
5 wt% Au	9	829	~290

It is interesting to see that the catalyst with the largest average Au particle size is the most active, suggesting that the particle size is not the only property of Au that determines activity.

At a fixed Au loading, the amount of Fe in the support also affects the catalytic activity of the systems (see Figure 5.11).

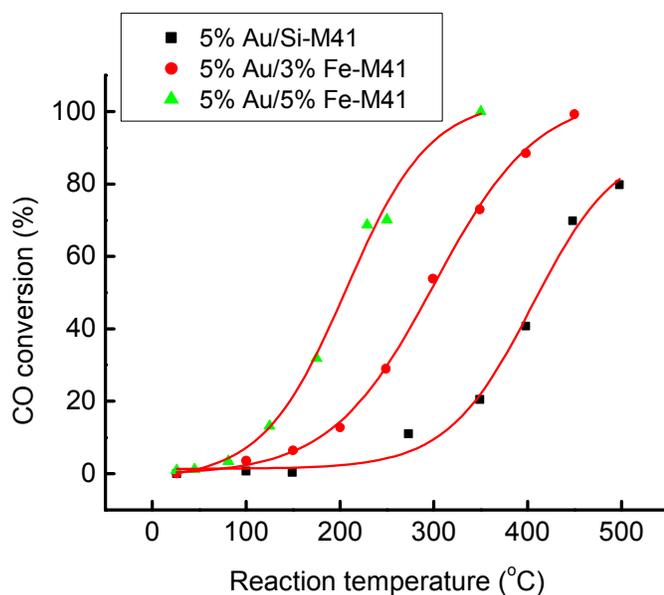


Figure 5.11. Light-off curves of 5 wt% Au-containing materials prepared by the (en) route, showing the effect of the amount of Fe in the support. All materials were calcined at 400 °C for 4 h. *M41 stands for MCM-41*

All the catalysts are inactive at room temperature. The presence of a base metal modifier in the support material has a strong and positive influence on the catalyst activity at temperatures between 100 and 200 °C, where the Au on Si-MCM-41 still fails to show any appreciable activity (see Figure 5.11). The catalytic activity of these materials improves as the amount of Fe in the support increases, as shown by the shift of the light-off temperature to lower temperatures (~400 °C, 285 °C and 196 °C for the 0, 3 and 5 wt% Fe-MCM-41 based materials respectively) and the temperature required for 100 % CO conversion. It is interesting to note that the increasing order of activity correspond to a decreasing order of the average Au particle size. The Fe species on the support serve as nucleation sites for Au nanoparticles, leading to improved dispersion and particle size and hence enhanced catalytic activity of Au catalysts as the Fe content increases. The table below correlates activity and physical properties for these catalysts.

Table 5.5. Activity and physical property data for 5 wt% Au on 0-5 wt% Fe-MCM-41

Fe content/wt%	Au particle size/nm	S _{BET} /m ² . g ⁻¹	T ₅₀ /°C
0 or Si-MCM-41	10	790	~420
3	9	829	~280
5	7	825	~180

The presence of Fe improves the catalytic activity of these systems significantly, showing also a correlation between catalytic activity and average Au particle size, i.e. as the average Au particle size decreases, the light-off temperature decreases likewise.

Two materials of composition 5 wt% Au/5 wt% Fe-MCM-41 were prepared via the ethylenediamine deposition route in the presence of preformed 5 wt% Fe-MCM-41, but one of the materials was impregnated with a reducing alkaline solution of NaBH₄ before calcination. The catalytic behaviour of these materials in the CO oxidation reaction is shown in Figure 5.12 (*see below*). The two materials had different catalytic activity. The material with no NaBH₄ treatment reached 100 % CO conversion at reaction temperatures of ~ 350 °C. The NaBH₄-treated material did not reach 100 % conversion even at reaction temperatures equivalent to the calcination temperature (400 °C). Since NaBH₄ is a reducing agent, this treatment may increase the amount of metallic Au [45 - 47] (presumed to be inactive) and hence the poorer activity.

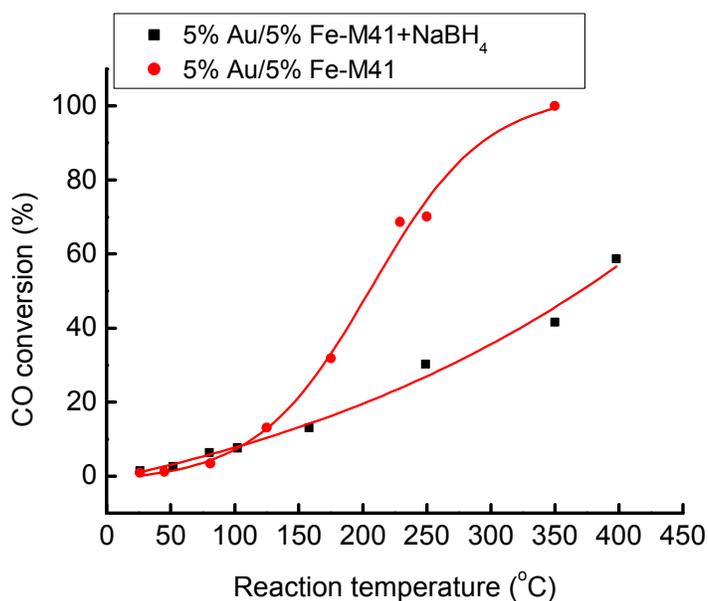


Figure 5.12. Light-off curves for differently treated 5 wt% Au/5 wt% Fe-MCM-41 materials prepared via the (en) route: Effect of NaBH₄ treatment prior calcination at 400 °C for 4 h. The physical properties of these materials are: (i) no NaBH₄ treatment, $S_{\text{BET}} = 825 \text{ m}^2/\text{g}$ and average particle size = 7 nm; (ii) NaBH₄ treated, $S_{\text{BET}} = 221 \text{ m}^2/\text{g}$ and average particle size = 5 nm.

Figure 5.13 below shows the variation of the CO conversion at 27 °C with the time on stream for the catalytic system 5 wt% Au/5 wt% Fe-MCM-41 prepared by the (en) route, but pretreated with an alkaline NaBH₄ solution prior to calcination at 400 °C for 4 h.

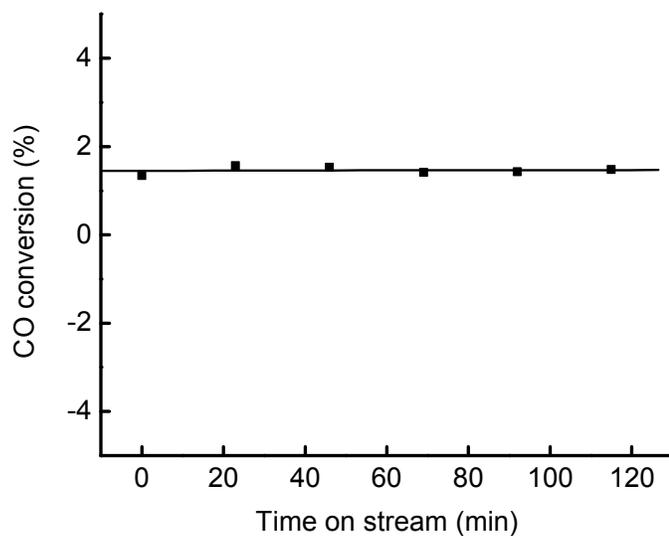


Figure 5.13. CO conversion versus time on stream for 5 wt% Au/5 wt% Fe-MCM-41 prepared by ethylenediamine deposition of Au(III) onto preformed 5 wt% Fe-MCM-41, treated with NaBH_4 and then calcined at 400 °C for 4 h.

This material shows modest activity at room temperature, i.e., (1.4 ± 0.2) % CO conversion, which is maintained over the next 120 minutes on stream.

Increasing the Au content to 10 wt% in the ethylenediamine deposition route, and lowering the calcination temperature to 325 °C for 6 h, gave rise to a catalyst system whose activity is shown in Figure 5.14.

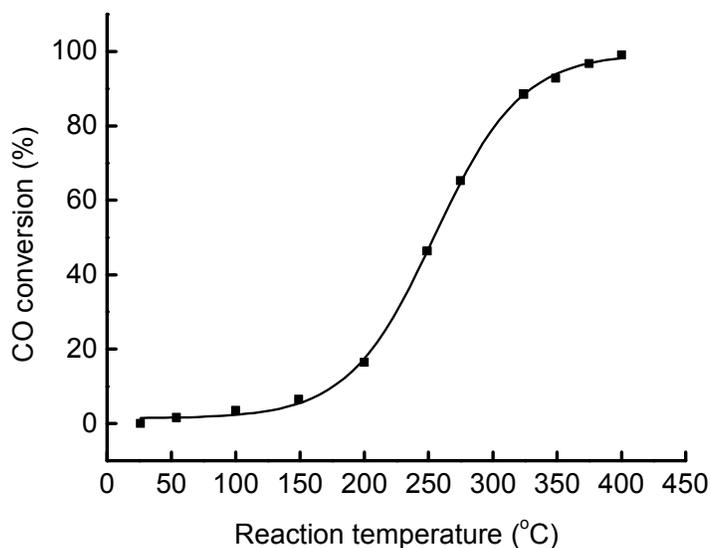


Figure 5.14. The light-off curve for 10 wt% Au/5 wt% Fe-MCM-41 prepared by ethylenediamine deposition onto preformed 5 wt% Fe-MCM-41, calcined at 325 °C for 6 h.

As seen from the figure above, this material is not catalytically active at room temperature. However, it starts to show activity immediately above room temperature and has a light-off temperature at 275 °C. Coincidentally, this material reaches 100 % CO conversion at a reaction temperature the same as that used in the calcination procedure (400 °C). The inactivity at room temperature may suggest that the resulting gold particles are relatively large as a result of this high loading, and presumably contains fewer Fe anchoring sites on the support. This may lead to agglomeration and ease of sintering.

Increasing the amount of Fe in the support to a 14 wt%, and synthesizing the Au catalyst via the ethylenediamine deposition route (5 wt% Au/14 wt% Fe-MCM-41), resulted in the catalytic behaviour depicted in Figure 5.15.

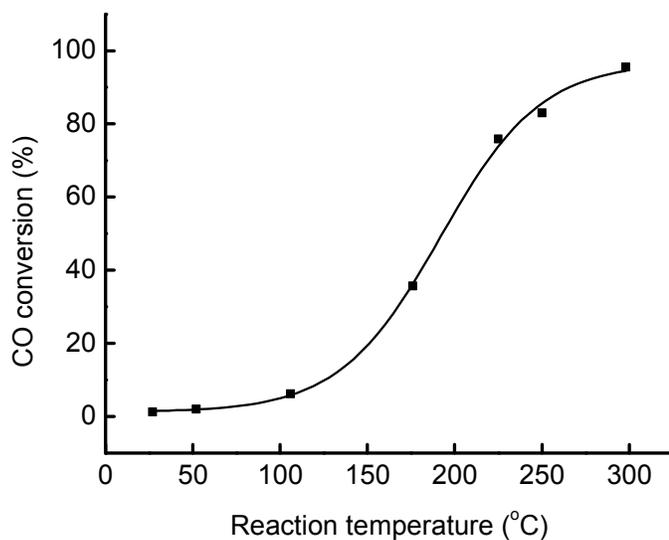


Figure 5.15. The light-off curve for 5 wt% Au/14 wt% Fe-MCM-41 prepared via ethylenediamine deposition of Au(III) onto preformed 14 wt% Fe-MCM-41, calcined at 350 °C for 6 h. Average gold particle diameter = 4 nm.

The material shows some room temperature activity. However, the catalyst is more active at $T > 100$ °C, with a light-off temperature of 225 °C. This catalyst system is likely to achieve a 100 % CO conversion at about the same temperature at which it was calcined.

Figure 5.16 compares the effect of the identity of the base metal modifier used in the support material. In all samples, Au was introduced post-synthetically following the ethylenediamine deposition route onto preformed supports, and all materials were calcined at 400 °C for 4 h.

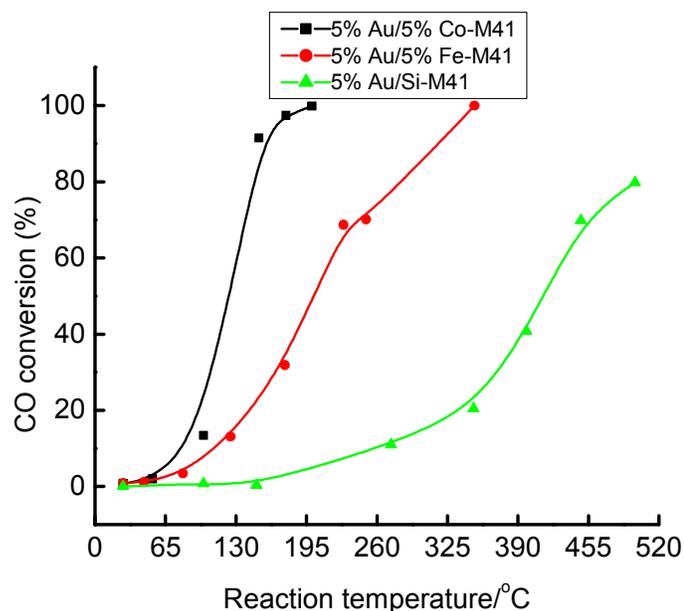


Figure 5.16. Effect of metal identity on the light-off temperatures of 5 wt% Au catalysts prepared by ethylenediamine deposition of Au(III) on various supports. All materials calcined at 400 °C for 4 h. -M41 designates MCM-41.

Again the figure shows that the presence of the base metal in the support improves the catalytic performance of these systems significantly. The order of increasing catalytic activity is 5 wt% Au/Si-MCM-41 < 5 wt% Au/5 wt% Fe-MCM-41 < 5 wt% Au/5 wt% Co-MCM-41. Justification for this activity order is provided by the table below.

Table 5.6. Correlation of activity with physical properties of 5 wt% Au on different supports (Fe- and Co-modified MCM-41)

Support	Au particle size/nm	$S_{\text{BET}}/\text{m}^2 \cdot \text{g}^{-1}$	$T_{50}/^{\circ}\text{C}$
Si-MCM-41	10	790	~420
5 wt% Fe-MCM-41	7	825	~200
5 wt% Co-MCM-41	5	838	~120

The presence of the base-metal in the support leads to smaller Au nanoparticles in the resulting catalyst systems, with the Co-based support producing the smallest Au particles. This decrease in Au particle size when supports are varied from Si- through Fe- to Co-MCM-41 agrees well with the observed improvement in the catalytic activity. Notably, the activity order of these systems is also the order of increasing BET surface area. In order to further elucidate the origin of the observed difference in catalytic activity of these systems, Arrhenius plots ($\ln k$ versus $1/T$) were constructed in order to estimate the activation energies of this process for each catalyst system. Figure 5.17 below shows the Arrhenius plots for these catalyst systems, and the corresponding apparent activation energies are given in Table 5.7.

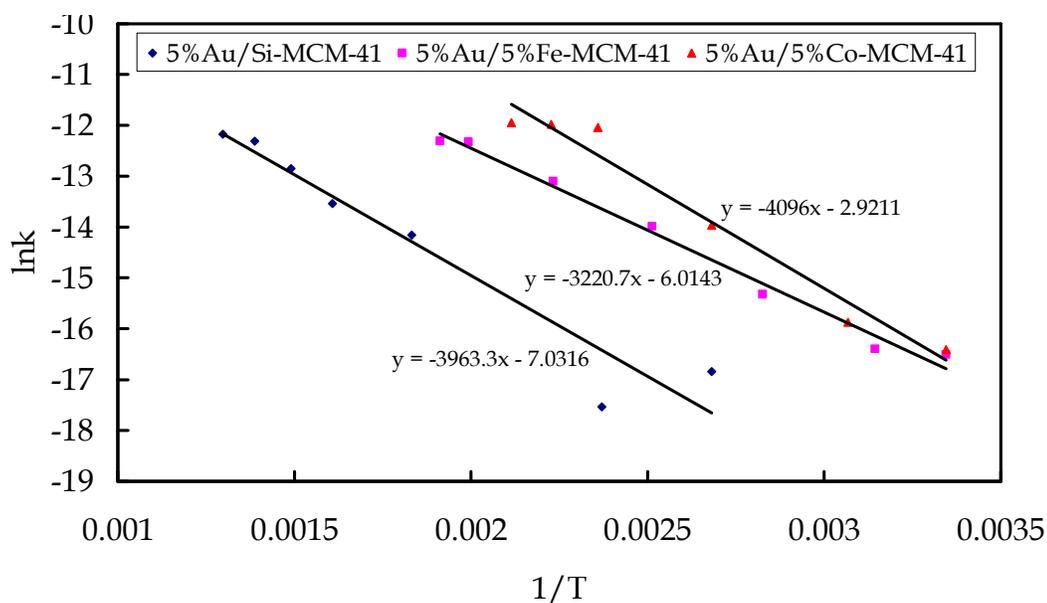


Figure 5.17. The Arrhenius plots for the CO oxidation reaction using 5 wt% Au catalysts supported on Si-MCM-41, 5 wt% Fe-MCM-41 and 5 wt% Co-MCM-41. The materials were prepared via the ethylenediamine deposition route and calcined at 400 °C for 4 h.

The calculated apparent activation energies are given in the table below:

Table 5.7. Activation energy (E_a) for Au/Me-MCM-41 (Me = Si, Fe and Co)

Au content/ wt%	Support	E_a /kJ/mol
5	Si-MCM-41	33.0 ± 2.3
5	5 wt% Fe-MCM-41	26.8 ± 2.3
5	5 wt% Co-MCM-41	34.1 ± 2.3

It is worth noting that these apparent activation energy values agree with those reported in the literature for this process: Okumura et al [39] reported E_a values in the range 23 – 27 kJ/mol for Au/MCM-41, while Haruta et al [23] reported values of 16.3, 35.1 and 29 kJ/mol for Au/Co₃O₄, Au/ α -Fe₂O₃ and Au/TiO₂ respectively. The influence of the chemical nature of the support has also been highlighted by Overbury et al [42], who demonstrated that Au on mesoporous Si-MCM-41 is inferior to Au on mesoporous TiO₂ for the CO oxidation reaction.

5.3.5 Gold Catalysts on Fe-functionalized MCM-41: Other Post-synthesis methods

Other post-synthesis procedures to prepare supported Au catalysts included (i) deposition-precipitation of [AuCl₄]⁻ by heating with urea at ~90 °C in the presence of preformed 3 wt% Fe-MCM-41, (ii) coprecipitation of Au(III) and Fe(III) with NaOH in the presence of preformed Si-MCM-41 (made with tetradecyltrimethylammonium bromide), and (iii) sodium citrate reduction of Au(III) in the presence of 3 wt% Fe-MCM-41. The results of the CO oxidation study are shown and discussed below:

Figure 5.18 below shows the effect of Au content in the Au/3 wt% Fe-MCM-41 materials prepared by DP using urea as a precipitant (i.e. homogeneous generation of basicity):

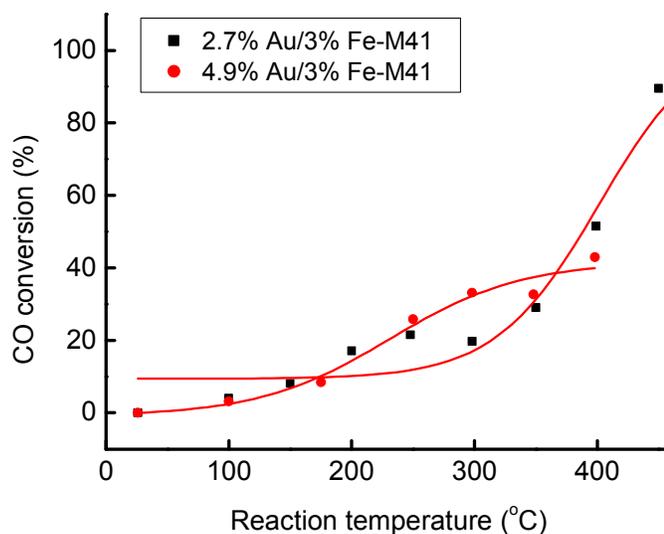


Figure 5.18. Light-off curves for the Au-containing materials prepared by urea deposition-precipitation of Au(III) onto preformed 3 wt% Fe-MCM-41, calcined at 400 °C for 4 h.

These materials are completely inactive at room temperature, and show increasing activity in the temperature range 100 - 400 °C. There is a significantly small error bar (~2 %) linking the catalytic performance of these materials in the temperature range up to 400 °C, suggesting similar catalytic activity.

Figure 5.19 shows the CO oxidation activity data for materials prepared by co-precipitating Au(III) and Fe(III) in the presence of Si-MCM-41 at 90 °C.

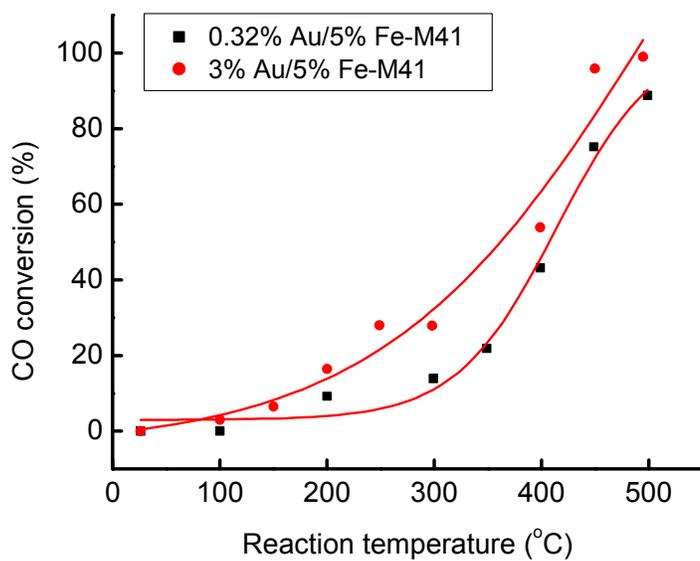


Figure 5.19. Light-off curves for Au/5 wt% Fe-MCM-41 materials prepared by CP of Au(III) and Fe(III) with NaOH at 90 °C, calcined at 400 °C for 4 h.

The figure shows that the materials are not appreciably active for this process. The light-off temperatures for both materials are > 300 °C (339 °C for 3 wt% Au/5 wt% Fe-MCM-41 and 449 °C for 0.32 wt% Au/5 wt% Fe-MCM-41), and the lower Au-content material never reaches 100 % conversion up to a reaction temperature of 500 °C.

A material was also prepared by a sodium citrate reduction route using 3 wt% Fe-MCM-41 as a support material, followed by calcination at 325 °C for 6 h. The catalytic activity of this material is shown in Figure 5.20 below:

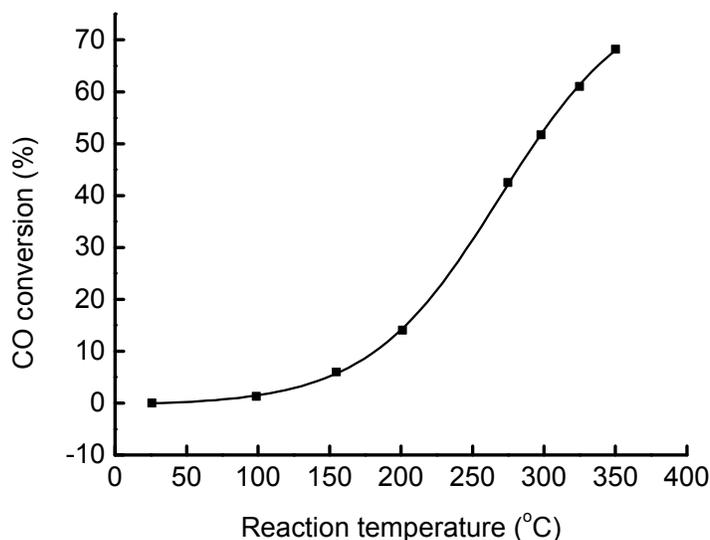


Figure 5.20. Light-off curve for 1.07 wt% Au/3 wt% Fe-MCM-41 prepared by sodium citrate reduction at 80 °C, calcined at 325 °C for 6 h. Average gold particle diameter = 2 nm.

The material is not only inactive at room temperature, but also does not attain 100 % CO conversion for $T > 300$ °C, regardless of the average particle diameter (2 nm) of the Au nanoparticles in this system. This confirms once again that the particle size is not the sole determinant for activity in catalysis by Au [42]. The inability of these relatively small Au nanoparticles to effect catalysis can be attributed to the reductive preparation employed, which makes the Au nanoparticles predominantly metallic [48, 49].

The CO oxidation reaction was also carried out on Au-containing materials of the form Au/Me/MCM-41 (with Me = Fe or Co), prepared by coprecipitating Au(III) and Fe(III) or Co(II) in the presence of calcined Si-MCM-41 that was synthesized hydrothermally at 120 °C for 3 days. These materials were either air-dried or oven-dried briefly (~15 min) and were not calcined at higher temperatures.

Figure 5.21 shows the effect of Au loading on the catalytic activity of the materials prepared by coprecipitation of Au(III) and Fe(III) in the presence of preformed siliceous MCM-41.

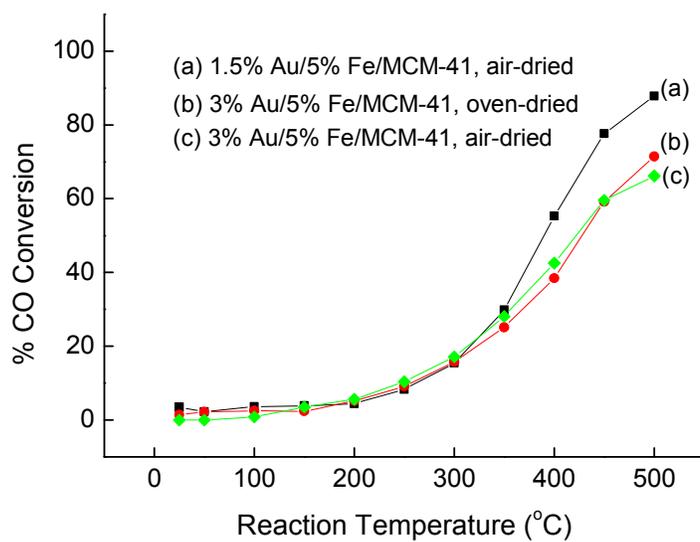


Figure 5.21. Light-off curves for uncalcined Au-containing materials prepared by coprecipitation in the presence of Si-MCM-41, showing the effect of Au loading.

These materials are inactive at low temperatures (up to 200 °C). The low Au-containing sample shows better activity at higher temperatures compared to the high Au-content materials. None of the materials attains 100 % conversion. An important observation is that regardless of the drying procedure, the 3 % Au/5 % Fe/MCM-41 materials show identical catalytic activity, which is slightly inferior to that of the material containing half the Au loading.

The figure below shows the variation of the catalytic activity as influenced by changes in the Fe content for the materials prepared by coprecipitation in the presence of Si-MCM-41.

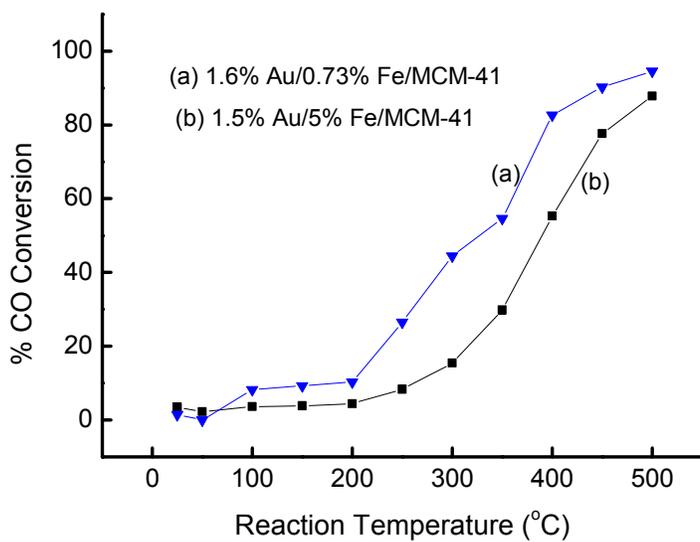


Figure 5.22. Light-off curves for uncalcined Au-containing materials prepared by coprecipitation of the Au(III) and Fe(III) in the presence of preformed Si-MCM-41, showing the effect of Fe content.

The materials show minimal activity at low temperatures, and only become active at higher temperatures (>200 °C). Notably, the material with a low Fe content (0.73 wt%) shows better activity than the corresponding material containing 5 wt% Fe. The materials were used without calcination.

A comparison of the catalytic activity dependence on the identity of the base metal component of the materials prepared by the above procedure is shown in Figure 5.23.

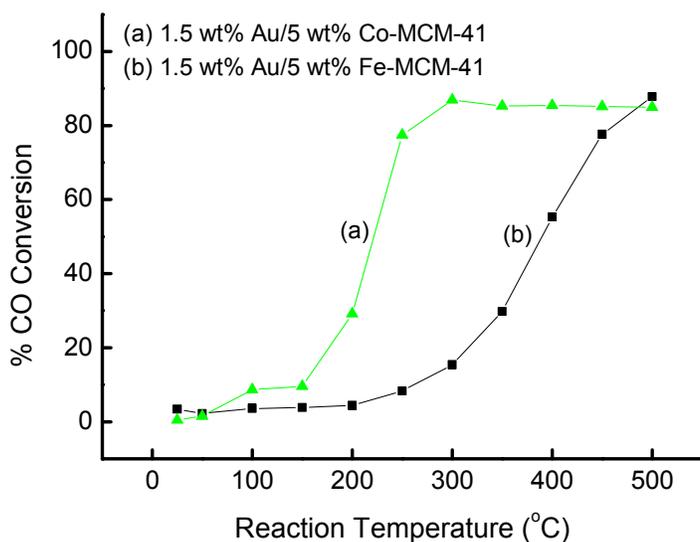


Figure 5.23. Light-off curves for uncalcined 1.5 wt % Au/Me-MCM-41 materials (Me = Fe or Co) prepared by coprecipitation in the presence of Si-MCM-41, showing the effect of metal identity on the activity of the catalyst

Although the materials are not appreciably active at low temperatures, they gain catalytic activity as the reaction temperature is increased. It is worth noting that the cobalt-based material has a much lower light-off temperature compared to its Fe-based counterpart (see also Figure 5.16). In addition, the CO conversion for this material increased until a reaction temperature of 300 °C, and was almost constant (~80 % CO conversion) between 300 and 500 °C. This may suggest that a stable form of the catalyst has been formed after reaction at 300 °C, and that prior calcination of this system at 300 °C could give a highly active catalyst.

5.4 Conclusions

Au/Me-MCM-41 catalysts (with Me = Si, Fe, and Co) have been prepared using numerous different synthetic strategies, ranging from 1-pot synthesis to various post-synthesis preparations. Different pre-treatment procedures have also been executed on the resulting materials. The resulting samples were evaluated for catalytic activity in the CO oxidation reaction using stoichiometric amounts of feed gas ($O_2/CO = 1/2$) in a fixed-bed flow reactor. The importance of Fe or Co premodification of the support material has been clearly demonstrated: it improves the particle size distribution of Au nanoparticles, decreased the average particle sizes of the Au nanoparticles, improves catalytic efficiency, and induces reducibility in the otherwise nonreducible Si-MCM-41 (see Chapter 3). The improvement in the Au particle size distribution is presumed to occur at the base metal sites, which serve as anchoring or nucleation sites for Au nanoparticles, and reduce their surface mobility during the calcination step.

•*Si-MCM-41 Supported Au Catalysts*

All SiO_2 -based Au catalysts, regardless of their Au content, were inactive for the CO oxidation reaction. Catalysts calcined at 500 °C only showed some activity at $T > 200$ °C, whereas the catalyst calcined at 400 °C showed some activity at lower temperatures. None of these materials attained 100 % CO conversion, even at reaction temperatures of 500 °C. This inactivity of Au/Si-MCM-41 catalysts can be attributed to the large Au particles formed because the metal-support interactions are weak in these systems. The average Au particle sizes ranged from 10 nm in the material calcined at 400 °C to 18 nm in the material calcined at 500 °C. Thus, calcination above the Tammann temperature of Au (395.5 °C) is accompanied by formation of very large Au particles which renders these catalyst systems inactive. Therefore, Si-MCM-41 is not a good support for the preparation of Au catalysts. This has also been

demonstrated [42] by the comparison of the catalytic performance of Au/Si-MCM-41 and Au/mesoporous TiO₂ catalysts.

•*Co-MCM-41-Based Au Catalysts: Ethylenediamine (en) Deposition Route*

The materials containing Co and with Au contents of 1 and 5 wt% Au, prepared by an ethylenediamine (en) deposition route and calcined at 400 °C, showed improved catalytic performance as compared to the Au-containing catalysts based on Si-MCM-41. In addition, the 5 wt% Co-MCM-41 showed remarkably higher catalytic activity ($T_{50} \approx 120$ °C) when compared to the material containing a lower Au loading (i.e., 1 wt% Au). Both materials exhibited similar average Au particle sizes that agree well within a reasonable error bar (4.5 ± 0.5 nm).

The calcination pretreatment of the 1.48 wt% Au/5 wt% Co-MCM-41 has been found to influence the catalytic activity of the resulting material. The material calcined at 325 °C for 6 h showed better catalytic activity than the corresponding material calcined at 325 °C for 6 h and then calcined at 400 °C for 4 h. This observation suggests the importance of moisture or hydroxyl groups as a component of the catalytic active site of supported Au catalysts [43-45], as the high temperature calcination is expected to dehydroxylate the support or even drive off all the moisture associated with the support.

•*Fe-MCM-41 Supported Au Catalysts: One-Pot Synthesis*

The catalytic activities of the Au/3 wt% Fe-MCM-41 materials prepared by direct hydrothermal synthesis suggest the existence of an optimum Au loading. The low activities observed in these materials may partially be attributed to the high calcination temperature (500 °C) required to decompose the surfactant template, which is considerably higher than the Tammann temperature of Au.

•*Fe-MCM-41 Supported Au Catalysts: Ethylenediamine (en) Deposition*

The materials prepared by depositing 1 wt%, 2.57 wt% and 5 wt% Au on 3 wt% Fe-MCM-41 via the (en) route showed minimal room temperature CO oxidation activity after calcination at 400 °C for 4 h. However, the catalytic performance of these materials is superior to that showed by 5 wt% Au/Si-MCM-41 catalysts prepared analogously. Notably, the catalytic activity of these materials improves with an increase in Au content.

At a fixed Au content (5 wt%), increasing the Fe content of the support significantly improved the activity of these systems for the CO oxidation reaction. This behaviour may possibly be due to the increased numbers of Au nucleation sites in the support, generated by Fe centres, which help stabilize and disperse the Au nanoparticles. The decreased average particle size of the Au nanoparticles with increasing Fe content also supports the proposal of improved catalytic activity of these materials.

Increasing the Au content to 10 wt% on 5 wt% Fe-MCM-41 (prepared via the en route) and calcining the material at 325 °C did not improve the catalytic activity to any significant extent. Neither did increasing the Fe content to 14 wt% in 5 wt% Au/14 wt% Fe-MCM-41 followed by calcination at 350 °C for 6 h produce a significantly active catalyst. These observations may suggest the existence of optimum amounts of Au and Fe needed for high activity of these systems.

•*Effect of Base Metal Identity: 5 wt% Au/5 wt% Me-MCM-41 (Me = Fe, Co)*

Both these materials, obtained via the ethylenediamine deposition route, showed measurable activity (~1.3 % CO conversion) at room temperature, while an analogously prepared 5 wt% Au/Si-MCM-41 was completely inactive. This can be attributed to the formation of large Au crystallites formed during calcination [50]. The observed activity order 5 wt% Au/Si-MCM-41 < 5 wt% Au/5 wt% Fe-MCM-41

< 5 wt% Au/5 wt% Co-MCM-41, corresponds to the order of decreasing Au particle size for these materials (10 nm > 7 nm > 5 nm, respectively). It is worth noting that the superiority of the Co-based system over its Fe-based counterpart is remarkable.

One of the possible causes of the enhanced activity of the Co-based Au catalysts is the ability of Co_3O_4 to catalyze CO oxidation in the absence of Au [17, 18, 21]. Another factor can be based on the TPR data given in Chapter 3, where it was shown that the Co-MCM-41 materials were more easily reduced as compared to their Fe-MCM-41 counterparts. Reducibility of the support is among the factors influencing the activity of supported Au catalysts in the oxidation processes [10]. Since the apparent activation energies (E_a) are similar for these three catalyst systems, we propose that the activity difference is associated with different active sites in these systems.

•Other Methods for obtaining Au/Fe-MCM-41 and Au/Co-MCM-41

Synthesis of Au/Fe-MCM-41 materials by methods based on urea precipitation of Au(III) in the presence of 3 wt% Fe-MCM-41, high temperature (90 °C) coprecipitation in the presence of 5 wt% Fe-MCM-41, sodium citrate reduction in the presence of 3 wt% Fe-MCM-41, and coprecipitation at room temperature in the presence of Si-MCM-41 showed poor catalytic activity for CO oxidation.

To summarize:

-The new materials are not appreciably active at room temperature

-Base metal pre-modification improved the catalytic performance of the systems. This reveals the influence of the support in determining the CO oxidation activity, as opposed to the particle size factor.

-Au catalysts supported on cobalt-derivatized MCM-41 supports are more active than their iron-derivatized counterparts.

5.5 References

1. K. R. Hardy and S. R. Thom, *J. Clin. Toxicol.* **32**(6), 613 (1994)
2. P. S. Heckerling, J. B. Leiken and A. Maturen, *Am. J. Med.* **84**(2), 251 (1988)
3. J. C. Raphael, D. Elkharrat, M. C. Jars-Guinestre, et al, *Lancet* **2**(8660), 414 (1989)
4. E. P. Sloan, D. G. Murphy, R. Hart, et al, *Ann. Emerg. Med.* **18**(6), 629 (1989)
5. E. S. J. Lox and B. H. Engler, in “*Environmental Catalysis*”, (G. Ertl, H. Knozinger and J. Weitkamp, Eds.), p.1. Wiley-VCH, Weinheim, (1999)
6. A. Trovarelli, *Catal. Rev.-Sci. Eng.* **38**, 97 (1996)
7. G. C. Bond and D. T. Thompson, *Catal. Rev.-Sci. Eng.* **41**, 319 (1999)
8. G. J. Hutchings, *J. Catal.* **96**, 292 (1985)
9. M. Haruta, T. Kobayashi, H. Sano and N. Yamada, *Chem. Lett.* **4**, 405 (1987)
10. M. Haruta, N. Yamada, T. Kobayashi and S. Iijima, *J. Catal.* **115**, 301 (1989)
11. G. C. Bond and D. T. Thompson, *Gold Bull.* **33**, 41 (2000)
12. M. Valden, S. Pak, X. Lai and D. W. Goodman, *Catal. Lett.* **56**, 7 (1998)
13. G. R. Bamwenda, S. Tsubota, T. Nakamura and M. Haruta, *Catal. Lett.* **44**, 83 (1997)
14. M. Valden, X. Lai and D. W. Goodman, *Science* **281**, 1647 (1998)
15. J. D. Grunwald, C. Kiner, C. Wogerbauer and A. Baiker, *J. Catal.* **181**, 223 (1999)
16. R. D. Waters, J. J. Weimer and J. E. Smith, *Catal. Lett.* **30**, 181 (1995)
17. G. A. Elshobaky, T. Elnabarawy and I. F. Hewaidy, *Surf. Tech.* **10**, 311 (1980)

18. Y.-J. Chen, D.-e. Wu and C.-t. Yeh, *Rev. Adv. Mater. Sci.* **5**, 41 (2003)
19. W. S. Epling, G. B. Holund, J. F. Weaver, S. Tsubota and M. Haruta, *Appl. Catal. B: Environ.* **6**, 117 (1995)
20. Y. J. Chen and C.-T. Yeh, *J. Catal.* **200**, 59 (2001)
21. P. Thormahlen, E. Fridell, N. Cruise, M. Skoglundh and A. Palmqvist, *Appl. Catal. B: Environ.* **31**, 1 (2001)
22. J. R. Mellor, A. N. Palazov, B. S. Grigorova, J. F. Greyling, K. Reddy, M. P. Letsoalo and J. H. Marsh, *Catal. Today* **72**, 145 (2002)
23. M. Haruta, S. Tsubota, T. Kobayashi, H. Kageyama, M. Genet and B. Delmon, *J. Catal.* **144**, 175 (1993)
24. M. Haruta, *Now Future* **7**, 13 (1992)
25. D. T. Thompson, *Chem. Brit.* **37**, 43 (2001)
26. M. Haruta, *CATTECH* **6**(3), 102 (2002)
27. R. Grisel, K.-J. Westrate, A. Gluhoi and B. E. Nieuwenhuys, *Gold Bulletin* **35**(2), 39 (2002)
28. D. T. Thompson, C. W. Corti and R. J. Holliday, *ATT Congress*, Paris, July 2002, Paper 2002-01-2148
29. D. Cameron, R. Holliday and D. Thompson, *J. Power Sources* **118**, 298 (2003)
30. *World Gold Council*, http://www.gold.org/discover/sci_indu/gold_catalysts/
31. M. Haruta, *Catal. Today* **36**, 153 (1997)
32. M. Okumura, S. Tsubota, M. Iwamoto and M. Haruta, *Chem. Lett.* 315 (1998)
33. H. G. Zhu, B. Lee, S. Dai and S.-H. Overbury, *Langmuir* **19**, 3974 (2003)

34. A. K. Sinha, S. Seelan, T. Akita, S. Tsubota and M. Haruta, *Appl. Catal. A: General* **240**, 243 (2003)
35. M. Haruta, B. S. Uphade, S. Tsubota and A. Miyamoto, *Res. Chem. Intermed.* **24**, 329 (1998)
36. M. Okumura, S. Tsubota and M. Haruta, *Appl. Catal. A: General* **190**, 43 (2000)
37. B. S. Uphade, Y. Yamada, T. Akita, T. Nakamura and M. Haruta, *Appl. Catal. A: General* **215**, 137 (2001)
38. G. Lü, R. Zhao, G. Qiang, Y. Qi, X. Wang and J. Suo, *Chem. Mater.* **97**(3-4), 115 (2004)
39. M. Okumura, S. Tsubota and M. Haruta, *J. Mol. Catal. A: Chem.* **199**, 73 (2003)
40. J.-H. Liu, Y.-S. Chi, H.-P. Lin, C.-Y. Mou and B.-Z. Wan, *Catal. Today* **93-95**, 141 (2004)
41. C.-M. Yang, M. Kalwei, F. Schüth and K.-J. Chao, *Appl. Catal. A: Gen.* **254**, 289 (2003)
42. S. H. Overbury, L. Ortiz-Soto, H. Zhu, B. Lee, M. D. Amiridis and S. Dai, *Catal. Lett.* **95**(3-4), 99 (2004)
43. S. K. Tanielyan and R. Augustine, *Appl. Catal. A: Gen.* **85**, 73 (1992)
44. A. P. Kozlova et al, *J. Catal.* **176**, 426 (1998)
45. C. K. Costello, M. C. Kung, H.-S. Oh, Y. Wang and H. H. Kung, *Appl. Catal. A: Gen.* **232**, 159 (2002)
46. M. Brust, M. Walker, D. Bethell, D. J. Smith and R. Whyman, *J. Chem. Soc., Chem. Commun.* 801 (1994)
47. S. Chen and K. Kimura, *Langmuir* **15**, 1075 (1999)}

48. J. Turkevich, P. C. Stevenson and J. Hillier, *Discuss. Faraday Soc.* (11), 55 (1951)
49. G. Frens, *Nature Phys. Sci.* **241**, 20 (1973)
50. M. Okumura, S. Nakamura, S. Tsubota, T. Nakamura, M. Azuma and M. Haruta, *Catal. Lett.* **51**, 53 (1998)