DECLARATION

I declare that this thesis is my own, unaided work. It is being submitted for the Degree of Doctor of Philosophy in the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University.

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(Signature of candidate)

…….. day of ……..…….. 2007

Abstract

The study of the aromatisation of methane was conducted at 750^{o}C over metal-impregnated H-ZSM-5 catalysts with a feed flow rate of 13 ml/min and the composition of the feed was 90% methane balance argon. Typical products that were detected from the outlet stream were ethene, ethane, benzene and toluene. The amount of coke produced was determined by using 10% argon as an internal standard. The effects of different parameters such as the type of the support material, the molybdenum content, the %XRD crystallinity and SiO_2/Al_2O_3 ratio of H-ZSM-5, the reaction temperature, the feed flow rate, the type of the molybdenum precursor, the catalysts preparation method, the addition of dopants, silanation and the regenerability of the catalysts were investigated.

The results obtained showed that H-ZSM-5 was a better support for the preparation of catalysts used for the aromatisation of methane. Mo/H-ZSM-5 catalysts were more active when the molybdenum loading was between 2 and 4 wt% and loadings higher than 4% led to lower activities. The lower activities observed at higher molybdenum loadings was related to the poor dispersion and decrease in the pore volumes and surface areas observed due to the formation of MoO_3 crystallites. Furthermore, the zeolite structure collapsed under the reaction conditions when the molybdenum loading was more than 4 wt%. The study showed that the conversion of methane increased linearly with increasing reaction temperature and the apparent activation energy of the reaction was found to be 64.5 kJ/mol.

The results of the effect of the %XRD crystallinity of H-ZSM-5 on the performance of H-ZSM-5 catalysts showed that 2%Mo/H-ZSM-5 catalysts were more active when the crystallinity of the zeolite was between 50 and 70%. The conversion of methane decreased with an increase in the SiO_2/Al_2O_3 ratio of H-ZSM-5. Higher aromatisation activities were observed when the SiO_2/Al_2O_3 ratio of H-ZSM-5 was

60. The type of the molybdenum precursor used in the preparation of 2%Mo/H-ZSM-5 catalysts did not have a significant influence on the conversion of the catalysts, but higher selectivities for aromatics were observed when ammonium heptamolybdate was used as a source of molybdenum. The catalysts prepared by physical mixing of MoO_3 and H-ZSM-5 catalysts were more active than those prepared by impregnation with solutions of ammonium heptamolybdate.

The presence of dopants such as boron, silver and alkali metal ions (Li^+, Na^+ and K^+) in 2%Mo/H-ZSM-5 catalysts was also investigated. Boron (0.05-0.2 wt%) did not affect the conversion level of the catalysts but changed their selectivity properties. The selectivity for C_2 hydrocarbons increased with boron content, while the selectivity for aromatics decreased. The addition of silver ions (0.5 wt%) significantly improved the conversion of the catalysts. This was attributed to the enhancement of the acvidity of the catalysts upon addition of silver ions which was observed by temperature programmed desorption of ammonia and pyridine adsorption studies of the infrared spectra of the catalysts. The addition of alkali metal ions in the Mo:Metal ratio of 0.5 led to decreased catalytic activities, due to the lowered acidities of the catalysts.

The silanation of H-ZSM-5 improved the conversion of methane but lowered the selectivity for aromatics. A comparative study of the W-based and Mo-based catalyst at equivalent molar contents showed that molybdenum-based catalysts were more active than tungsten based catalysts. The study also showed that the catalytic performance of 2%Mo/H-ZSM-5 catalysts could be regenerated to appreciable levels by treatment of the catalysts in air at 600^{o}C.

The possibility of using Mo/H-ZSM-5 catalysts for the aromatisation of propane was also evaluated at 530^{o}C, with consideration of three variables, namely, the molybdenum loading, the reaction temperature and %XRD crystallinity. The results indicated that impregnation H-ZSM-5 catalysts with molybdenum led to lower

propane aromatisation activities. This lower activity was attributed to the lower Brønsted acid sites in the Mo/H-ZSM-5. The activities of the catalysts could be improved by operation at higher temperatures, but the rate of deactivation was also improved at higher temperatures. In line with the observations from the conversion of methane, higher activities were observed when the %XRD crystallinity of the catalyst was 61%.

This thesis is dedicated to the memory of my grandfather

Ngwako William Marutha

(1935-1999)

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Methane conversion to chemicals, carbon and hydrogen (MCCH) over modified molybdenum-NAS catalysts, The 8th Natural Gas Conversion Symposium, Natal, Brazil, 2007.

Oral presentations

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List of Abbreviations and Symbols

Ag	Silver
AHM	Ammonium heptamolybdate
AM	Ammonium molybdate
B	Boron
BE	Binding energy
BET	Brunauer-Emmet-Teller
BJH	Barret, Joyner, Halender
BTX	Benzene, toluene and xylene
CNG	Compressed natural gas
CO	Carbon monoxide
CO_2	Carbon dioxide
CO_x	Carbon oxides
DDMP	Dodecylmolybdophosphoric acid
DRIFTS	Diffuse reflectance spectroscopy
DRS	Diffuse reflectance spectroscopy
DSC	Differential scanning calorimetry
DTA	Differential thermal analysis
ERS	Electron spin resonance
FCC	Fluid catalytic cracking
FID	Flame ionisation detector
FT-IR	Fourier Transform infrared spectroscopy
h	hour
IEP	Isoelectric points
LPG	Liquefied petroleum gas
min	minute
Mo	Molybdenum

nm	nanometre
N_A	Avogadro's number
NMR	Nuclear magnetic resonance
OCM	Oxidative coupling of methane
OPEC	Organization of the Petroleum Exporting Countries
S_g	Specific surface area
SEM	Scanning electron microscopy
STEM	Scanning transmission electron microscopy
TCD	Thermal conductivity detector
TEM	Transmission electron microscopy
TG	Thermogravimetry
TOS	Time on stream
TPD	Temperature programmed desorption
TPO	Temperature programmed oxidation
TPR	Temperature programmed reduction
TPSR	Temperature programmed surface reaction
UV-Vis	Ultraviolet-visible
V_m	Monolayer volume
W	Tungsten
XAS	X-ray absorption spectroscopy
XPS	X-ray photoelectron spectroscopy
XRD	X-ray powder diffraction
ZSM-5	Zeolite Saucony Mobil number 5
λ	Wavelength
θ	Bragg angle
β	Full line-width at half-maximum intensity
σ	Area covered by one molecule of adsorbate
γ	Surface tension