Methanol oxidation over copper supported catalysts.

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Abstract

Oxidation of methanol has been studied over a range of temperature and contact times with a synthesised, 1wt % copper catalysts supported over Al₂O₃ and SiO₂. Characterisation of these catalysts was performed by nitrogen adsorption and porosity measurements (BET), X-Ray Diffraction (XRD), and IR spectroscopy of adsorbed CO. BET measurement revealed surface areas reducing from 105 to 104 m²g⁻¹ for pure alumina to copper supported catalyst while the silica ones reduced from 247 to 240 m²g⁻¹ for pure silica to the copper supported respectively. Pore sizes also reduced from 32 – 23 nm and 23 – 20.3 nm for the alumina and silica catalysts respectively. No crystalline phases from the diffraction patterns of the loaded metals were found to be present on the XRD. CO adsorption studies showed the presence of small cluster metal atoms adsorbed on the surface of the catalysts with Temperature Programmed Reduction (TPR) experiments revealing the presence of partially oxidised and well dispersed Cu atoms. The alumina supported catalyst were more active than the silica ones while for selectivity and yield for formaldehyde, the reverse was the case. The alumina supported significantly showed high yields of Dimethyl ether (DME) while the silica showed high yield for methyl formate (MF) with CO_x and CH₄ detected in very small quantities.

Keywords: methanol, oxidation, supported, oxidation, copper, catalyst

Introduction

Efficient catalysts have been synthesised over the years for possible good selectivity for the oxidation of alcohols to the corresponding carbonyl compounds [1]. Consequently, various catalysts have been synthesised to this effect [2] and investigations to understand their reaction pathways have also been made [3]. Methanol oxidation is mainly performed catalytically and precedes either through the partial or total oxidation paths. The partial path produces a variety of compounds while the total oxidation path leads to the production of CO_x with formaldehyde being the most prominent [3]. These products are a consequence of various conditions including the type of site, the intermediate formed on the catalyst site and the reaction condition (e.g. temperature and partial pressure of the reactants, contact time/gas hourly space velocity). In this process, methanol molecules are proposed to either adsorb wholly or dissociatively on the catalyst [4-6]. The two main processes that take place during the course of this oxidation reaction either in parallel or simultaneously are oxidation and dehydrogenation [5]. During the oxidation of methanol, there are various processes that can possibly take place. These can take place simultaneously or consecutively. These processes include; selective/partial oxidation, dehydrogenation and total oxidation/combustion [5].

Figure 1: A schematic diagram showing the adsorption of the formate and methoxy species onto a catalyst surface

Total oxidation/ combustion

Selective/partial oxidation;

Dehydrogenation

From the above, the combustion pathway with the formation of total oxidation products (CO₂) and (H₂O) are thermodynamically favoured compared to formaldehyde formation pathway.

The popular production process for formaldehyde is air oxidation of methanol. This has been reported to be an exothermic reaction at atmospheric pressure and in the temperature range 300– 400 °C [8]. All industrial production of formaldehyde use air to oxidise methanol. Air is preferred as an oxidant for this reaction, for economic reasons, and since the use of organic oxidants poses environmental problems of which there are strict environmental laws [3]. When a catalyst is employed in this process, there are a variety of processes that are possible, within the thermodynamic and kinetic boundaries for the formation of different products. Other conditions of reaction also have marked influence on the process. For instance, in the silver-catalysed process, a higher methanol/air ratio favours the production of formaldehyde, while for the other metal oxide catalysts; the reverse is true in order to obtain similar results. In this research, some 1wt% Cu supported on both silica and alumina supports (Silica as a support for heterogeneous catalysts was employed to provide good thermal stability, fairly chemical inertness and surface areas, while alumina was used offers similar properties but with slightly higher acidity) were synthesised, these catalysts were used to investigate the methanol oxidation reaction to study the product distributions under the different reaction conditions.

Experimental

Preparation of catalysts

While considering a method of supported catalyst preparation, the fine dispersion of the metal particles in the pores of the support is of paramount importance [9]. The conventional impregnation method where the support is impregnated with a solution of the salt of the target metal oxide [10, 11] was used. The preparation of similar catalysts at low metal loading gave the desired properties after characterisation.

These supports were impregnated with the metal salts under investigation. The active metals were loaded onto the various supports as described below.

The 1 wt % Cu/Al₂O₃, Cu/SiO₂, catalysts were prepared simply by the wet impregnation of the various supports with their respective salts to obtain the desired catalyst in the right quantity as described below.

For a target weight of 10 g of catalyst (1 wt. % Cu/Al₂O₃), 0.380 g of Cu (NO₃)₂·3H₂O (BDH) was weighed and added to distilled water containing 9.900 g γ-Al₂O₃ (Degussa) in a beaker. This was stirred on a heating/stirring mantle at < 80 °C until a thick slurry was formed. The beaker content was then further dried more gradually at lower temperatures overnight. This was then ground into finer powder and further dried in at temperatures <60 °C. Then grinding was performed in a 30 – 60 min interval until a fine dried powder was formed. Calcination of the produced catalyst was carried out using parameters used by Kaichev *et al.* [12] where the catalyst was calcined at 400 °C for 4 h. Calcination was carried out by placing the catalyst samples prepared as stated above in a porous tubular quartz glass, which was placed in a calcination unit containing a furnace. Air was flowed through the tube containing the catalysts at a 50 ml.min⁻¹ flow rate with the furnace temperature ramped 10 °Cmin⁻¹.

Characterisation of catalysts

Nitrogen adsorption studies.

These experiments were conducted on a Micromeritics Tristar 3000 V4.02 surface area and pore volume analyser instrument where 0.15 – 0.20 g sample catalysts were and pre-treated by outgassing at 200 °C for 3 h. The surface analyses of the samples were measured and calculated using the BET and BJH methods at liquid nitrogen temperature and normalized per gram of each sample. The BET method employed for the measurement of surface area uses N₂ as the adsorptive at its liquefying temperature (-195°C) assuming the BET monolayer is closely packed, giving average area of N₂ to be 0.162 nm² [10].

CO adsorption

The catalysts were pressed into ~16 mm discs and suspended in a CaF₂ IR cell attached to a vacuum line set-up. The discs were pre-treated by in-situ calcination or reduction, cooled and contacted with different pressures of CO as stated in each case presented in the results. The carbonyl region of the IR bands was distinguished from the gas phase CO contribution in case of overlaps by gaseous CO evacuation by the vacuum pump. The CO adsorption was carried out using the reaction procedure of the FTIR set-up mentioned above. This gave spectra of CO adsorbed on the metals which were measured over a range of 2000 - 2500 cm⁻¹ with a resolution of 4 cm⁻¹ after 150 scans, after scanning the background and the software automatically ratioing the background and sample signals.

Temperature-programmed reduction (T P R)

TPR experiments were conducted using a TPDRO 1100 Thermo-Quest CE Instruments. About 0.250 g of the copper catalyst was weighed into a quartz reactor sample holder held between quartz wool plugs and loaded unto the instrument. A reducing gas mixture, 5 % H diluted in He was flown over the sample under programmed conditions of temperature and flow rate of the reducing mixture gas. A thermal conductivity detector (TCD) recorded changes in the thermal conductivity of the gas stream. The TCD signal was then converted to concentration of active gas using a calibration factor and presented as a spectrum where the peak maxima indicate the temperature that corresponds to the maximum rate of reduction. The instrument was programmed to carry out a reduction on the catalysts from 40 – 800 °C with a flow rate of the reducing gas at 20 ml/min at a heating rate of 10 °C/min. A Thermo Finnigan version 2.0 release 0.1 software which presents the result as TCD signal (mV or mV/g), oven and sample temperatures *versus* time was used to process the data accordingly.

X-Ray Diffraction (X R D)

Phase identification and crystallinity studies were carried out, with the aid of Bruker-AXS model X-ray diffractometer with Cu α monochromatic radiation (0.15418 nm wavelength). Measurements were performed at 22 °C with steps of 0.02 ° of 2 θ range of 5 - 70° and 2.5 s/step. Phase identifications from the diffraction patterns obtained from the results received were performed with the aid of a program developed in the Bruker-D8 software stored in a PC connected to the spectrometer.

Catalytic activity studies

Catalyst testing

The catalytic experiments were carried out in a fixed-bed tubular quartz reactor and a fitted analyser HP 5860 series Gas Chromatograph coupled with a HP FFAB (cross-linked FFAB) capillary column (30.0mm x 0.32mm x 25 μ m) with a maximum temperature 250°C, coupled with an FID and an attached mass spectrometer, EcoSys-P Field Portable Mass Spectrometer.

Methanol oxidation was carried out at; 250, 290, 350 and 400 °C. A given amount of catalyst was diluted with 0.2 – 0.25 g inert phase SiC. The molar flow ratio (methanol / air) was varied in some reactions to probe it's effect. The residence times was between 0.195 – 2.166 s respectively by varying the diluent gas flow rate or the amount of catalysts. Products from this reaction were analysed online on the GC using the parameters stated on **Table 1**

Table 1: GC conditions for analysing products from the oxidation of methanol

PARAMETER	VALUE
Injector temperature	60 °C
Oven temperature	30 °C isothermal
Column	HP-FFAP (crosslinked FFAP) 30m x 0.32mm x 25 μ m.
Carrier gas flow rate	N ₂ , 0.2 mL/min
Detector temperature	240 °C
Detector gas	H ₂ and air

Results

Nitrogen adsorption/desorption studies

The textural properties of the catalysts used such as surface area, pore volume and pore size distribution were obtained from the N₂ adsorption–desorption isotherms. The specific surface areas calculated using the Brunauer–Emmett–Teller (BET) method and the pore size and volume information were calculated from the desorption branch of the isotherms using Barrett–Joyner–Halenda method (BJH)) are as presented in Figure 2 and Figure 3 with Table 2 showing a summary of the other parameters extrapolated

Alumina Supported catalyst

For the alumina supported materials, Figure 2, the nitrogen adsorption/ desorption isotherms corresponds to the type IV of the IUPAC classification [13] and exhibits hysteresis loop H1 and H3 also according to the IUPAC classification, extrapolated from the desorption route employing the BJH method calculated from the Kelvin equation. A slight decrease in the surface area of the catalyst was also observed on loading the active metal from 105 m²g⁻¹ for the pure alumina to 104, for the supported catalyst. The pore sizes reduced from 32 nm for the pure silica to 23 nm for the copper supported catalyst.

Figure 2: N_2 adsorption isotherms with inserted BJH pore volume distributions of (a) pure Al_2O_3 (b) 1wt% Cu/ Al_2O_3

Figure 3: N_2 adsorption isotherms with inserted BJH pore volume distributions of (a) pure SiO_2 (b) 1wt% Cu/ SiO_2

Silica supported catalysts

The silica supported samples exhibited similar trends in the surface area with metal loading similar to that observed on the alumina supported materials. The nitrogen adsorption/desorption isotherms also correspond to the type IV of the IUPAC classification [13] and exhibit similar hysteresis loops as those observed for the alumina based materials. The surface area of the pure silica was measured to be $247 \text{ m}^2 \text{ g}^{-1}$ and decreased to 240, for the silica supported catalyst. The pore sizes reduced from 23 nm for the pure silica to 20 nm

Surface densities of the various metals on the catalyst surfaces were also calculated. The copper loaded samples appear to exhibit a higher surface density as compared to the silver ones. The silica supported catalysts show a lower metal density as compared to those based on alumina

Table 2: Results of the N_2 studies characterisation of the catalysts

Catalyst	Surface area/ $\text{m}^2 \text{ g}^{-1}$	BJH Pore Vol. / $\text{cm}^3 \text{ g}^{-1}$	Pore Diameter/nm	Metal Surface Density / atom nm^{-2}
1wt % Cu/ Al_2O_3	104	0.9	23	0.771
1wt % Cu/ SiO_2	240	1.7	20.3	0.315
Pure γ - Al_2O_3	105	1.5	32	-
Pure SiO_2	247	2.1	23	-

Surface densities of the various metals on the catalyst surfaces were calculated using formulae from references [14, 15].

Power X-Ray Diffraction

The XRD patterns of the catalysts used in this study together with their supports are presented in Figure 4 and Figure 5 for the alumina and the silica based catalysts respectively.

The alumina mono-metal supported catalysts show patterns that correspond to the patterns of γ - alumina only [16] while the silica based catalysts were amorphous to XRD analysis; showing no crystalline phases, where there was clearly the absence of diffraction patterns that are characteristic of the loaded metals or their oxides nor the support.

Figure 4: XRD patterns of the (a) pure Al_2O_3 (b) 1wt%Cu/ Al_2O_3 catalysts

For the silica supported samples, no reflexions were observed on the XRD patterns presented in Figure 5 (a) and (b).

Figure 5: XRD patterns of the (a) pure SiO_2 (b) 1wt% Cu/ SiO_2 catalyst

An accepted explanation for such an observation in the literature has it that the loaded metals may likely be too amorphous or well dispersed on the surface of the support in the form of small clusters which are likely not detectable by the XRD technique [17-19] or due to the formation of finely dispersed species of the metals loaded which are also suggested not to be detectable by the technique [20]. These assumptions can as well be supported by characterisation with other techniques like TPR (presented and discussed further on)

Temperature programmed reduction experiments

Figure 6 shows the reduction profiles of 1wt% Cu/ Al_2O_3 and Cu/ SiO_2 , samples. Two unresolved signals were observed for the 1wt% Cu/ Al_2O_3 , one centred around 267 °C and a shoulder at 297 °C. The signal centred around 267 °C is attributed to highly dispersed Cu species [21] which is reported to weakly interact with the support on the surface of the alumina [22] whilst the 297 °C shoulder is attributed to the reduction of Cu species contained within slightly larger three-dimensional clusters. In addition, a very broad and weak/ non-intense signal centred on 717 °C was observed and is characteristic of larger clusters of CuO [21] or possibly due to the reduction of aluminium oxides from the support of these samples.

Figure 6: TPR profile of 1wt% Cu/ Al_2O_3 and 1wt% Cu/ SiO_2 respectively

The Cu/SiO₂ displays similar characteristics with the addition of a signal centred on 542 °C. The two lower reduced signals centred at around 321 and 383°C, are due to the reduction of highly dispersed Cu and small CuO clusters, respectively. The additional signal is typical of larger cluster Cu species which are characteristic at higher reduction temperature as compared to smaller and well dispersed clustered species. From the intensities of these signals, it can be confirmed that the main copper species present at the surface are the highly dispersed and small cluster Cu species. This is similar with trends of a copper sample result reported by Wang *et al*, [9]. From the intensities of the signals identified, it can be seen that in the case of the Cu/Al₂O₃, there are better dispersed Cu (II) small clusters at the surface than within the bulk, while for the Cu/SiO₂, the reverse is observed, although this difference is not so significant. The redox properties of a metal- support system is known to be normally influenced by the support. The smaller copper clusters have also been reported to reduce more easily than the larger ones [20].

CO adsorption

Characterisation of the surface coverage of metal atoms or molecules with the use of infra-red spectroscopy of probe molecules such as CO is a well-established technique [23, 24]. Carbon monoxide was used as a probe molecule to monitor potential geometric and/or electronic effects of its bonding modes on the metal surface.

CO adsorption on copper catalysts

Figure 7 shows the infrared spectra of CO adsorbed on 1wt% Cu/SiO₂ pre-treated by reducing in hydrogen. A band centred at 2098 cm⁻¹ is present at lower pressure of CO. With increasing pressures of CO, this band shifts to higher wave number (2103 cm⁻¹ at 80 torr). Evacuating the CO in the system reduces the intensity of the band and broadens it but the position remains unchanged. This indicates a contribution of the intensity to have been from gaseous CO. Also, at increased pressure of CO, a very weak shoulder appeared at 2114 cm⁻¹. These bands correspond to linear M–CO vibrations as reported by Pritchard *et al*, [25] on Cu ions. At the same time, another very low intensity band developed at 2067 cm⁻¹ which disappeared on evacuation of CO. This signal was also observed by Chesters *et al*. [26] at 2071 cm⁻¹ who assigned to linear CO adsorption on exposed Cu (111) and Cu (100) planes.

Figure 7: CO adsorption on 1wt%Cu/SiO₂ (a) after reduction in H₂ at different pressures of CO and (b) after in-situ calcination at different pressure of CO

For the *in situ* calcined sample of the same catalyst, adsorption of CO is less facile thus less intense bands are observed (**Figure 7**) for the silica and alumina supported copper samples respectively. Adsorption increased with increasing pressures of CO from 0.1 to 25.0 torr evidenced by the evolution of a band at 2120 cm⁻¹ with a blue shift to 2122 cm⁻¹ as the pressure increases. This band overlaps with the gaseous CO doublet but on evacuating, it shows the clear band without the gaseous CO. This band is typical for high index copper planes [27] and highly dispersed copper [27, 28]. This has also been reported to originate from adsorption on bulk CuO [29] and oxide supported copper [28, 30-38].

The 1wt% Cu/Al₂O₃ pre-treated *in situ* by calcination followed by exposure to CO showed very little adsorption at 2123 cm⁻¹ on increasing the CO pressure which is typical of oxidised copper species on the surface of the sample. Increasing the pressure of the CO led to the observation of the gaseous CO doublet bands (Figure 8).

Figure 8: CO adsorption on 1wt%Cu/Al₂O₃ after in-situ reduction at different pressure of CO

Catalyst Activity

Influence of temperature on Yield of products on the copper catalysts

Here the copper shows a higher yield of the target formaldehyde on the alumina-supported catalyst, which is at the lower temperature region.

Figure 9: Influence of temperature of products yield on (a) the alumina supported and (b) the silica supported copper catalysts

The alumina supported copper yields high DME at the higher temperature regions while the silica shows higher yield for methyl formate. The alumina-supported sample also shows higher yield of the COx.

Oxidation reactions over 1wt% Cu/Al₂O₃

The conversion of methanol over 1wt% Cu/Al₂O₃ and the selectivity to the various products with varying reaction conditions is as shown in Table 3. While *Figure 10* shows (a) the yield as a function of the various reaction temperatures and (b) the yield as a function of varying contact times.

Table 3: Summary of the conversions and selectivities on the 1wt% Cu/Al₂O₃ catalyst at 0.22 s

Temp/ °C	Conv/ %	Formaldehyde	Formic acid	DME	MF	CH ₄	COx
		Sel./%	Sel./%	Sel./%	Sel./%	Sel./%	Sel./%
250	15	48	5	20	6	11	2
290	48	39	8	29	10	5	22
350	64	27	10	35	15	4	19
400	78	14	30	40	6	1	10

It can be seen that with increasing temperature from 250 °C to 290 °C, there is an increase in yield of formaldehyde but further increase in temperature reduces the yield. Obviously, the trend for the selectivity in **Table 3** shows a continuous decrease in the selectivity. But since the conversion increases with temperature an optimum yield for the formaldehyde is observed at 290 °C, but with increasing contact time, the yield is highest at 0.22 s and levels out through to 2.2 s. a similar trend was observed for

the methane where the selectivity reduces with increasing temperature and with very low and almost stable yield with both contact time and temperature but with temperature having an increasing effect on the methane yield than the contact time. Formic acid has an opposite trend of selectivity from formaldehyde; it increases from 5% at 250 °C to 30% at 400 °C while the yield increases with temperature **Figure 4** but yields more with temperature increase as compared to contact time. For the DME, the selectivity trend shows an increase with increasing temperature and this is same for the yield with increase in both temperature and contact time. Selectivities for methyl formate and the COx increase with temperature but reduce at 400 °C and the trend is same for the yields with both temperature and contact time increase.

Figure 10: Yield of the various products of methanol oxidation over 1wt% Cu/Al₂O₃ with varying temperatures at (a) residence time = 0.22 s and (b) at 250 °C and varying contact times

Oxidation reactions with 1wt% Cu/SiO₂

For the 1 wt% Cu/SiO₂ catalyst **Table 4**, the conversion ranged 13 to 73% between 250 and 400 °C respectively being lower in all temperatures when compared to the copper supported alumina catalyst. Selectivity to formaldehyde was of the same trend, reducing over increasing temperature while the formic acid had an almost stable selectivity of ~20% over the temperature range with DME increasing from 8% at 250 °C to ~15% over the higher temperatures, methyl formate increasing from 12 - 40 % over the temperature range with methane and COx being low at ~5 % at the higher temperatures and 2 % at 250 °C for methane.

Table 4: Summary of the conversions and selectivities and yields on the 1wt% Cu/SiO₂ catalysts at GHSV = 16,615

Temp/°C	Conv/%	Formalde hyde	Formic acid	DM E	MF	CH ₄	COx
		Sel./%	Sel./%	Sel./%	Sel./%	Sel./%	Sel./%
250	13	59	18	8	12	2	3
290	36	36	20	15	23	2	4
350	61	23	21	18	25	5	5
400	73	13	20	15	40	6	4

The yield as shown in **Figure 11** for formaldehyde in the case of the copper silica catalysts was highest of all products being 8, 13 and 14 % at 250, 290 and 350 °C respectively but decreases at higher temperatures to 9 % at 400 °C. All the other products increased in yield with increasing temperature with methyl formate having the highest yield of 29% at 400 °C.

Figure 11: Yield of the various products of methanol oxidation over 1wt% Cu/SiO₂ with varying temperatures at (a) residence time = 0.22 s and (b) at 250 °C and varying contact times

For the yields of products as a function of varying contact times, formaldehyde decreases with increase in contact time while all the other products followed the same trend opposite to formaldehyde. Methyl formate and formic acid competitively increase in yield with increasing contact time.

Discussion

In the development of catalysts for catalytic reactions, understanding their nature as synthesised and their likely nature under reaction conditions is of grave importance. The target catalysts in this research of the oxidation of methanol were supported copper catalysts.

Nature of the catalysts

The nature in terms of electronic and chemical states and the dispersion of the loaded component of a supported catalyst are factors that could contribute to the activity of these catalysts. Information about these could give insight into the performance or behaviour of the catalyst. As the catalysts employed in this research were supported and their preparation could yield agglomerated and/or well-dispersed catalytic systems, they were thus characterised and found to be well-dispersed. This is a positive attribute since well-dispersed supported catalysts are required to be in a way that reactant molecules can interact more effectively with the active catalyst materials and it is known that smaller particles of the active phase of the catalysts are known to maximise the use of the metal through maximising the surface area [39, 40].

From their XRD patterns, these metal particles can be deduced to exist as well-dispersed crystallites with no copper metal agglomeration. The results showed no crystalline phases of the loaded metals since these metal particles were small and well dispersed on their various supports. The alumina supported catalysts showed patterns that were typical of the gamma-alumina phases with no reflections corresponding to those of either of the loaded metals. Lippits *et al.* [41] attributed this non-detection of the loaded metals to being consequent to the metal particulates having small sizes, while other studies have reported that the amount of copper that could reach these particulate size limits for diffraction as being approximately 4% by weight of Cu for every 100 m²g⁻¹ surface area of Al₂O₃ in the case of alumina supported copper catalysts [42, 43]. For the catalysts used here, their 1 wt % loadings (in the case of the copper for instance) was well below this limit considering an alumina support of 105 m²g⁻¹ and a metal loading of 1 wt%. Nitrogen adsorption studies show the presence of these small particulates loaded as the pure supports showed a slight reduction in the surface area when loaded with the catalyst. Silica with a surface area, about two and a half times that of alumina might be envisaged to show similar or even better dispersion of the supported metals, if the extent of metal precursor-support interactions is not considered.

Following calcination at 400 °C, these samples showed the presence of only few agglomerated metal/metal oxide clusters as suggested by their TPR profiles where the intensities of peaks indicative of the smaller or well-dispersed clusters were higher than those of peaks attributed to larger clusters. This deduction is made on the basis that small particles reduction is identified by their lower temperature reduction peaks as compared to the very low intensity peaks of the larger clusters which occur at a higher reduction temperature as speculated in the literature [43]. These larger peaks which have been proposed to originate from reduction of the small particulates on the support are thus assumed to correspond to higher consumption of the reducing gas (hydrogen), while the peaks assumed to be due to larger clusters were smaller in size and intensity as shown by the peaks at higher reduction temperatures the copper catalyst

had peaks centred around 267 and a shoulder at 297 °C were attributed to highly dispersed Cu clustered species whilst the 297 °C shoulder is attributed to reduction of Cu species contained within slightly larger three-dimensional clusters, while a very weak feature at 717 °C will thus be indicative of larger clusters which may as well be as a result of the metal–support interaction, causing reduction to be harder, so taking place at higher temperatures. The sizes of these peaks were also a direct reflection of their corresponding amount of hydrogen consumed, and this could be seen to indicate greater presence of the smaller clusters of the loaded metals which reduced at lower temperatures as reported. A trend in the reduction profiles on these supported materials was that the silica supported samples also showed more facile reduction as compared to their alumina supported analogue. This could be as a result of the metal support effect, where alumina shows a greater metal-support interaction with most metals and their precursors than silica as widely reported in the literature [16, 19, 44-46]. Thus, metal oxides on the alumina will ordinarily be expected to reduce at higher temperatures compared to the silica supported ones. However, the copper silica samples reduced at slightly higher temperatures when compared to the alumina ones.

Characterisation by CO adsorption showed intense bands for the CO adsorbed on well-dispersed clusters of the metals. For instance, the band at 2120 cm⁻¹ observed for copper catalysts has been thought to be due to dispersed copper [27, 28].

Product distribution showed initially highest selectivity to DME (46%) after which a transition occurred to give predominantly highest selectivity to formaldehyde (58%). All of the other products also show some variation at inception but then became constant with time on stream.

From the data presented from the characterisation, it was evident that catalyst samples after calcination were oxidised but it is also evident that they got reduced under reaction condition with the action of the methanol, thus producing the partial oxidation products like formaldehyde.

Copper has affinity for atomic oxygen species which cause dissociative adsorption of methanol for the oxidation reactions. Copper is metallic in character owing to its high reactivity. This attribute can however, be detected only under reaction conditions (reduction action of the reactant methanol), so were not detected in the characterisation of the catalyst materials which showed only the presence of oxides of Cu, which are believed to contain the sites responsible for deep oxidation in this reaction [47] However, results from the catalyst test reactions show production of partial oxidation products at steady state.

This route which is known from the general reaction scheme (refer to

Introduction) of methanol oxidation to form formaldehyde could also decompose to form CO_x and H₂ or hydrogenate to form formic acid, although the sites responsible for this was not determined by characterisation. Since the available O atoms in the system could be in active competition with other species to be scavenged for other processes as shown in all the reaction schemes for the process, gaseous methanol will normally be in excess compared to oxygen, under the conditions of operation here.

Key features of the reaction

From the product distribution on these catalysts, formaldehyde showed a higher yield at temperatures up to 350 °C then declines (**Figure 9**) for the alumina catalyst while the reverse was the case at the highest temperature. The silica supported catalysts had the same trend but the conversions were comparatively lower than the alumina ones having the higher selectivity.

The Cu/SiO₂ (73%) and Cu/ Al₂O₃ (81%), as can be seen in the reactivity results (**Table 4**) where the

selectivity to formaldehyde was highest for the silica supported catalysts reaction at 250°C, lest for the alumina supported ones that showed lower selectivity. These highest selectivities however, took place where conversions were generally lower at the lowest temperature (250 °C) and lower contact time (0.22 s). Conversion on all the silica supported catalysts was generally lower than for the alumina ones.

Oxi-dehydrogenation

Dehydrogenation

The supports materials also showed marked effects from the products formed, such as in the case of the alumina which is known to be a good catalyst for the dehydration of methanol to DME, and this is reflected in the products formed from samples supported on alumina. At higher conversion consequent to increase in temperature, the copper

catalysts selectivities of DME increased while with contact time and temperature. For the silica supported samples, methyl formate (MF) formation increased with higher conversion consequent to increase in temperature and contact time on the copper catalysts. This observation is quite unexpected as high selectivity to DME is normally expected at lower conversion of methanol as the route for the production of DME requires the abundance of gaseous methanol and this has been reported to take place at low temperatures and lower conversion. At higher conversion of methanol (i.e. at higher temperature and lower space velocity) there was high selectivity for DME. Fisher and Bell [48] had reported similar formation of DME at higher temperature in a methanol oxidation reaction. Also, the DME formation mechanism which involves an adsorbed surface methoxy group derived from methanol adsorption reacts with another adsorbed methanol molecule to form dimethyl ether. This, however, cannot be said with certainty. Schauermaun *et al.* [49] have also reported desorption of methanol at high temperature as being related to methanol preferentially adsorbing at defect sites on an alumina support. From catalyst test result of this work, it was shown that methanol and methoxy groups coexist on the surface of the catalysts during methanol adsorption experiments. This subject can be explained where the surface of the alumina supported catalysts contain both the Lewis and Brønsted acid sites and it is reported that Brønsted acid sites on $\gamma\text{-Al}_2\text{O}_3$ are able to catalyse the dehydration of methanol [50, 51].

DME and methyl formate from proposed reaction schemes of this reaction will require molecular methanol to react with methoxy and formate intermediates, respectively, were formed at higher conversion and from the methanol adsorption experiments; bands due to methanol adsorbed on the supports employed in this work were identified. Although these adsorption experiments were not performed at these higher temperatures, it can be assumed that these supports acted in such cases in parallel for the formation of those products. Chantaravitoon *et al.* [52] have reported less than 40% of the methanol dehydrated in a methanol dehydration reaction (between 270 and 620 °C) gives rise to dimethyl ether, showing the possibility of this as it appears to be observed in this work. The high selectivity to methyl formate; 40% also prominent on the silica supported catalysts may be in line with what has been suggested by Millar *et al.* [32] and Monti *et al.* [53] that methyl formate is formed *via* the interaction of adsorbed methoxy species and formaldehyde species.

Key features of the mechanism

Copper [54, 55] has the capability to adsorb methanol dissociatively only in the presence of adsorbed oxygen atoms. The formate and methoxy species formed, adsorb on the surfaces of these metals, where the formate adsorbs after the loss of two H atoms from the methanol molecule on two adjacent metal sites while the methoxy does the same in a monodentate form by the loss of one H atom from the methanol molecule (**Figure 1**).

The above description forms the basis of mechanisms proposed by many for the methanol oxidation reaction, which show two pathways; methoxy and formate, leading to the formation of the various possible products.[7, 56];

The different adsorption sites assumed to be present for these catalysts are associated with the partially reduced oxides of the metals (in the presence of reactants) characterized as prepared by the TPR data that showed the presence of highly dispersed Cu (II), CuO, clusters which were also confirmed in the CO adsorption results. This is further supported by the reactivity of the catalysts with the methanol forming the various products which all have their various pathways defined by the relative proportions in relation to the selectivity between partial and total oxidation products.

Pre-adsorbed oxygen atoms on the oxides of copper enhances the formation of a methoxy species intermediate which could further dehydrogenate to form formaldehyde or a further oxidation giving rise to the formate intermediate that yields other further products as represented in the mechanisms proposed in the literature. It is however, not straightforward to distinguish the oxidative-dehydrogenation and the direct dehydrogenation processes which require different sites which are characterized by acidic adsorbed oxygen on the copper metal [54, 57-59] or more basic oxygen sites implying weaker and/or stronger bonds with the copper/silver on the catalyst and/or different reaction conditions as these different adsorbed oxygen atoms operate better at different reaction parameters of temperature range;

The specific oxygen involved in the reactions could not be identified in this work through characterisation, making it more ambiguous to ascertain the types involved in any specific route claimed to be taking place. From the products and literature reports of the trends in formation of these products assumptions were made [60]. IR spectroscopy can give insight into the nature and types of adsorbed species that are present on the

surface of these materials used in the oxidation of methanol. From these experiments' formation of methoxy and formate on the copper surfaces which have been reported by other researches [48, 60-64] were assumed during methanol oxidation on these catalysts.

This could be argued further with the generally low yields of the CO_x in all the reaction profiles, implying the absence of further oxidation of the formate to CO_x but rather to formic acid, since the yield of formic acid increased at higher degrees of conversion.

With this, it can be seen that the reaction takes place in the transitional kinetic controlled range at the lower temperatures, demonstrated low contact time that showed basically similar activity of the reaction. These copper catalysts were very active at the initial stage. Reactions taking place where there is extremely low conversion at the lowest temperature (250 °C) and at the very short contact time that favours the partial oxidation with high selectivity to formaldehyde [61]. Also, at this lowest temperature, increasing the conversion by increasing the contact time did not favour the production of formaldehyde as shown in the case of Cu/SiO₂. This can be supported by the observation that the higher temperature dynamics of the reaction system influenced the lower amount of the formaldehyde and higher amounts of the side products formed equally. This implies that the major or primary reaction process and the side reactions are equally influenced by contact time and temperature. This decrease in the formaldehyde yield can be caused by enhanced participation of the methoxy intermediates in the other consecutive reactions where the methoxy rather undergoes further oxidation to the formate which was the case in some of the profiles (e.g. high formation of the formic acid at high conversion through both temperature and contact time increase) shown, as reflected in the product distribution. From the observed trends, a model for the reaction under study drawn out is in agreement with already existing models for the oxi-dehydrogenation pathway (**Figure 12**) for the reactions that have taken place where the target formaldehyde is selective at the temperature boundaries of the oxi-dehydrogenation region [64], while the alumina supported catalysts simultaneously dehydrate, the silica promote the methoxy route that favours the formation of methyl formate as a result of the methoxy reaction with formaldehyde desorbed. The only striking thing observed is that at these wide parameters of investigation, there was little formation of the CO_x .

Figure 12: Schematic representation of the proposed reaction process for methanol oxidation and the various steps that were enhanced by the different sample catalysts.

The scheme represented above (**Figure 12**) is proposed considering the formation of the various products under the varied conditions of temperature and contact time. The primary product was considered mainly to be formaldehyde and proceeded through the **Route I**. **Route II** which is meant to be an alternative route to **Route I**, however yielded products that could be related to a different reaction pathway required for this route. These are deemed so, considering that for an initial increase in temperature (from 250 – 290 °C) for instance favoured the formation of formaldehyde which eventually reduced and formation of the other products (secondary) were subsequently seen for all the catalysts. At the highest temperature however, a reverse in trend was the case where the formation of the secondary products dominated;

Conclusion

The oxi-dehydrogenation route for the oxidation of methanol over synthesised and characterised supported copper catalyst reported to be an exothermic reaction, giving rise to formaldehyde and other products of DME, Formic acid and MF and CO_x the reactions considering the temperature range of operation and the concurrent formation of products that are reported for the oxi-dehydrogenation route. Formation of the various products from variations in temperature and space velocity/contact time were investigated and also conformed to these assumptions and a scheme was proposed.

Characterisation of these materials through nitrogen and CO adsorption studies showed metal oxides on the supports while XRD and TPR studies provided evidence that the materials had been produced with good dispersion. The TPR results also showed the existence of the reduction peaks for the copper present.

Generally, the supports showed a very marked effect on the selectivities of the products where the alumina based samples were very selective to DME while the silica ones were selective to methyl

formate. Methanol adsorption studies on the surface of these materials revealed the existence of the adsorbed species which may have been involved in product formed.

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