Mechanism of methanol synthesis on copper/zinc oxide/chromia catalyst

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The methanol synthesis catalyst Cu/ZnO/Cr₂O₃ is studied using IR and diffuse reflectance spectroscopy (DRS) and temperature programmed desorption (TPD) techniques. DRS shows copper to be present as Cu⁺ and Cu²⁺. IR spectrum of adsorbed CO shows two bands, one due to linear adsorption on a single site and the other due to bridge-type adsorption. The TPD of adsorbed CO shows two desorption regions, one in the temperature range of 300 - 400K and another above 540K with readsoption taking place between 400 and 550K. The TPD of H₂ also shows two desorption regions. CO is considered to be adsorbed on Cu and H₂ on ZnO. The TPD of co-adsorbed CO and H₂ indicates interaction between CO and H₂. IR spectroscopic study of methanol decomposition suggests that the decomposition involves methoxide and formate intermediates. A mechanism is proposed for the synthesis reaction.

Methanol is produced from syngas using Cu/ZnO/Al₂O₃ or Cu/ZnO/Cr₂O₃ catalyst. A number of mechanisms have been suggested for the formation of methanol. Rozovskii and coworkers, in a series of publications on the kinetics and ¹⁴C isotope labelled studies, concluded that the hydrogenation of CO₂ is the source of methanol rather than the commonly believed hydrogenation of CO. Their proposal, however, has not received acceptance, although their results have been reproduced. In a recent publication, Bowker and coworkers have reported that the mechanism by which methanol is formed on a Cu/ZnO/Al₂O₃ catalyst from CO₂/H₂ feed is by the co-adsorption of H₂ and CO₂ on the copper component of the catalyst to form a formate species, the hydrogenation/hydrogenolysis of which is the rate-determining step in the synthesis. Deluzarche et al. proposed that the reaction proceeded via a formate intermediate formed from the insertion of CO into a surface hydroxyl species. Herman et al. suggested that CO was hydrogenated via a hydroxycarbene type of intermediate. Kung suggested a formyl intermediate in which both the carbon and oxygen interact with the catalyst. Saussey and coworkers, from their infrared spectroscopic study, suggested the formation of formyl species under synthesis conditions. Trapping of surface intermediates by reactive chemicals has been reported and the results indicate that an aldehydic or hydroxy carbene intermediate is involved in methanol formation. Recently, Saussey and Lavalley have reported that on Cu/ZnAl₂O₃ catalyst, CO + H₂ form bidentate formate intermediate on ZnAl₂O₃ while CO₂ + H₂ form formate intermediate on copper sites.

In view of the conflicting views regarding the mechanism of the reaction, a study of the catalysts employed in methanol synthesis was undertaken to throw light on their adsorption behaviour and the mechanism of the synthesis reaction. We report here the results of infrared spectroscopic study of CO adsorption, temperature programmed desorption (TPD) of CO and H₂, diffuse reflectance spectral (DRS) studies and investigations of the decomposition of methanol on a Cu/ZnO/Cr₂O₃ catalyst.

Materials and Methods

Catalyst precursor was prepared by coprecipitation⁹, and had the composition Cu/ZnO/Cr₂O₃(60/30/10 wt %). A bluish-green precipitate was obtained by adding an aqueous solution of sodium carbonate to an aqueous solution containing cupric nitrate, zinc nitrate and chromium nitrate in appropriate quantity. The final pH of the solution was 7. The precipitate was dried overnight at 383K followed by calcination at 623K for 3 hr. For the TPD studies, oxide form of the catalyst (0.5 to 1.0g) was reduced at 573K for 4 hr in flowing hydrogen at atmospheric pressure, degassed at 603K till the pressure reached 10⁻⁵ torr. and the evacuation continued for 3 hr at 10⁻⁵ torr. All the adsorption measurements were carried out at ambient temperature(303K). The TPD was carried out in a closed system by monitoring the pressure change. When the adsorption equilibrium was attained, the gas phase CO or hydrogen was pumped out slowly at 10⁻⁵ torr and heating started at a rate of 10°/min. The desorbed species were collected in a sample loop and analyzed by gas chromatogra-
phy with a molecular sieve 5A column using a thermal conductivity detector.

Hydrogen gas (Karnataka Oxygen Ltd) was purified by passing through (i) a copper trap at 573K to remove oxygen, (ii) silica gel and fused calcium chloride traps to remove moisture, and (iii) a carbon trap at liquid nitrogen temperature to remove other impurities like hydrocarbons, CO2 etc. The CO was prepared from calcium carbonate and zinc dust according to the procedure described by Weinhouse12. Methanol (E Merck, AR; 99.5%) was further purified by distillation under reduced pressure.

IR spectra were recorded on a Perkin-Elmer 983G spectrophotometer. The oxide form of the catalyst was made into a thin wafer, loaded into a cell with NaCl windows which had provisions for heating, evacuation and gas treatment. The sample was reduced by keeping it under H2 atmosphere for 4 hr at 573K. The degassing procedure was the same as used for TPD experiments. CO was adsorbed at 200 torr and methanol vapor at 100 torr.

The diffuse reflectance spectra were recorded at room temperature on a Hitachi 150-20 UV-visible spectrophotometer provided with an integrating sphere. The powder sample was made into a pellet of 1 mm thickness and loaded into the cell having a quartz window. The cell had provisions similar to those of the IR cell.

Results

Adsorption of CO

IR spectra of CO adsorbed at 303K on the reduced catalyst exhibits four bands at 2170, 2120, 2090 and 1940 cm\(^{-1}\). The first two bands disappeared when the gas phase CO was removed by evacuating to 10\(^{-2}\) torr pressure. The band at 2090 cm\(^{-1}\) is assigned to on-top (carbonyl type) adsorption of CO, while the weak band at 1940 cm\(^{-1}\) to the adsorption of CO in the bridged configuration.

TPD studies

The TPD traces for CO and H2 adsorbed at 303K and 200 torr are shown in Fig. 1. In both the cases two desorption regions are observed. In the case of CO, the first desorption is from 300 to 390K and the second desorption from 560K and continues even after 630K. Readsoption of the desorbed species is observed from 400 to 500K. The first desorption is assigned to CO adsorbed in the linear form (IR band at 2090 cm\(^{-1}\)) and second desorption to the CO adsorbed in the bridged mode (band at 1940 cm\(^{-1}\)).

The TPD trace for hydrogen shows the first desorption from 300 to 410K and a second desorption region from 540K, which continues even after 630K. The readsoption of desorbed species takes place from 425 to 525K. Since, for both CO and H2, the second desorption continues even after 630K, the maximum temperature employed for TPD was 630K as the calcination temperature of the catalyst was 623K and all the other pretreatment temperatures were less than 630K. At temperatures above 670K the copper species on the surface of the catalyst coalesce to form large crystallites and the catalytic activity is lost13.

Co-adsorption studies were carried out by exposing the surface to a pressure of any one gas sufficient to cause a partial coverage of the surface first, quickly pumping off the unadsorbed gas and then saturating with the other gas. A series of experiments was carried out for both the sequences, i.e. CO and H2 precovered surfaces. The results are summarized in Table 1.

The amount of CO adsorbed on a H2 precovered surface decreases as the coverage by H2 increases up to a fraction of 0.4 and thereafter remains constant. The amount of H2 adsorbed on a CO preadsorbed surface is not affected and remains constant with increase in the partial coverage by CO.

The TPD traces for both sequences of co-adsorption are shown in Figs 2 and 3. In both the cases two desorption regions are observed irrespective of the sequence of adsorption and the type of coverage. The first desorption starts invariably from 300K in all the cases. In the case of H2 precovered surfaces, the temperature at which the first desorption ends is shifted from 390 to 405K with increase in coverage by H2. But for the CO precovered surfaces this temperature is shifted from 405 to 390K with increase in the coverage by CO. The increased amounts of desorption in the first

Fig. 1—TPD traces for CO and H2 adsorbed on Cu/ZnO/Cr2O3 (60/30/10 wt %) catalyst [1, H2; 2, CO]
Table 1—Amount of CO/H₂ adsorbed on Cu/ZnO/Cr₂O₃ catalyst with H₂/CO preadsorbed

<table>
<thead>
<tr>
<th>Amount of H₂ (µmol g⁻¹) adsorbed on</th>
<th>Amount of CO (µmol g⁻¹) adsorbed on</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare surface CO preadsorbed surface</td>
<td>H₂ preadsorbed surface Bare surface</td>
</tr>
<tr>
<td>0.00</td>
<td>25.64</td>
</tr>
<tr>
<td>11.16</td>
<td>24.81</td>
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<tr>
<td>16.52</td>
<td>25.27</td>
</tr>
<tr>
<td>20.09</td>
<td>24.62</td>
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<tr>
<td>24.55</td>
<td>24.70</td>
</tr>
<tr>
<td>30.36</td>
<td>26.04</td>
</tr>
</tbody>
</table>

Fig. 2—TPD traces for CO adsorbed on H₂ preadsorbed Cu/ZnO/Cr₂O₃ (60/30/10 wt %) catalyst [1, θ₅₃₉ = 0.0; 2, θ₅₃₉ = 0.29; 3, θ₅₃₉ = 0.43; 4, θ₅₃₉ = 0.53; 5, θ₅₃₉ = 0.65; 6, θ₅₃₉ = 0.80]

Desorption region in both sequences are probably due to the increased amounts of weakly adsorbed CO and H₂. These species desorb immediately on starting the heating. The second desorption starts from 550K in both the sequences. This temperature slowly shifts to higher temperatures. This shift is clearly seen in the CO preadsorption series.

In Fig. 4 the diffuse reflectance spectra of reduced CuO, ZnO and the reduced Cu/ZnO/Cr₂O₃ catalyst are shown. Pure ZnO shows absorption around 365 nm and pure CuO after reduction around 555 nm. For the reduced Cu/ZnO/Cr₂O₃ catalyst, there is no clear absorption band corresponding to ZnO in the region of 300-400 nm. This is an indication of the strong interaction between ZnO and copper species present in the catalyst. Similar observations have been reported by Herman et al. on binary Cu/ZnO system. The band at 560 nm in the reduced catalyst is assigned to charge transfer transition. The absorption edge around 620 nm and the absorption continuum up to 850 nm is characteristic of Cu(1) species dissolved in ZnO lattice.

**Methanol decomposition**

Methanol was introduced onto the catalyst at 300K and 200 torr. After recording the IR spectrum at room temperature (300K), the catalyst was heated to different temperatures. Figure 5 shows the IR spectra obtained over the temperature range of 300-523K. The spectra have been vertically displaced along the transmittance axis for clarity. The spectrum at 300K was recorded immediately after adsorption of CH₃OH and exhibits bands at 2930 and 2840 cm⁻¹ assignable to the ν₁, C-H and ν₅, of the adsorbed methoxy species. Two broad bands in the regions of 3660-3700 and 3520-3560 cm⁻¹ correspond to

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vOH. The δC-H normally expected at 1470 cm\(^{-1}\) is likely to be obscured by residual carbonate features in this frequency region. As the temperature was increased the first changes in the IR spectra were observed at 470K. New bands appeared at 2870, 1580 and 1370 cm\(^{-1}\) which are assigned to ν\(_{\text{as}}\)C-H, ν\(_{\text{s}}\)C-H and νO-C-O modes of surface formate species\(^{11,14-16}\). The in-plane δC-H bending mode, expected in the region of 1375-1385 cm\(^{-1}\) may be obscured by the surface carbonate species which gives a strong band at 1384 cm\(^{-1}\). The intensities of the formate bands continue to increase with temperature up to 523K with a corresponding decrease in the intensities of the νOCH\(_3\) mode.

Discussion

**IR band assignment for CO adsorption**

The intense band at 2090 cm\(^{-1}\) observed when CO is adsorbed at 300K on Cu/ZnO/Cr\(_2\)O\(_3\) catalyst is assigned to carbonyl type adsorption of CO. This absorption is similar to π-bonded carbonyls on metallic copper (2080-2110 cm\(^{-1}\))\(^{16}\). In the IR spectra of copper (I) organo-metallic complexes these carbonyl frequencies appear in the region of 2050-2117 cm\(^{-1}\) (ref. 16). The band at 2090 cm\(^{-1}\) is assigned to νCO of the CO species adsorbed on a reduced copper site whose oxidation state may be either +1 or zero. The relationship between the oxidation state of copper and the νCO for adsorbed CO has been reported by Saussey and Lavalle\(^{11}\). The lower the wavenumber the higher the oxidation state of copper. So the band at 2090 cm\(^{-1}\) is most probably due to the carbonyl-type adsorption of CO on Cu\(^{+}\) sites. The weak band at 1940 cm\(^{-1}\) is assigned to CO adsorbed in the bridged configuration. Because, the difference in ν(C-O) is attributed to different kinds of ad-CO, species, the spectral regions of 2130-2000, 2000-1880, 1880-1800 and less than 1800 cm\(^{-1}\) correspond respectively to on-top CO, two-fold bridged CO, three-fold bridged CO and four-fold bridged CO (ref. 17). The results of diffuse reflectance spectroscopic studies (discussed later) show that Cu and ZnO are in intimate contact and interact strongly, i.e. Cu has oxygen as its adjacent neighbour. So the bridged configuration of CO adsorption is considered to involve a copper site and surface oxygen site. Also, it is reported that on Cu/ZnO methanol synthesis catalyst, copper site alone is the centre for adsorption and activation of CO, and ZnO sites adsorb hydrogen. The adsorbed CO and hydrogen interact to give methanol\(^7\).

**TPD studies**

The TPD results of both individual and co-adsorbed CO and H\(_2\) showed two desorption regions and in all the cases there is readsoption of the desorbed species. On a surface like Cu/ZnO/Cr\(_2\)O\(_3\), with a variety of cation sites present, CO desorption with different desorption energies in the TPD spectrum can be expected. TPD studies with pure ZnO showed a single desorption peak at 210K\(^{18}\). The desorption temperature range for CO adsorption on metallic copper is 250-300K (refs 19-21). The CO adsorbed on metallic Cu in Cu/ZnO catalysts also desorbs at temperatures less than 300K (ref. 22). Thus the observed CO desorption from 300 to 400K is probably due to the species adsorbed on copper cations. The catalyst has been reduced before CO adsorption. So the presence of Cu\(^{2+}\) on the surface is not likely. Also, the diffuse
reflectance and IR spectral results show that the surface contains Cu(I) and not Cu(II) ions. Thus the CO desorbed in the temperature range of 300-400K is considered to be that adsorbed in the linear form (carbonyl type) on Cu + sites. The bonding mechanism is through the $5\sigma$ electron pair of the CO molecule forming a donor-acceptor bond with the vacant 4$s$ orbital of Cu cation.

$$\text{Cu}^+ + \text{O}_2^- \rightarrow \text{Cu}^\bullet + \text{C}=\text{O}$$

The species that desorbs at high temperatures (above 540K) is probably the species that exhibits IR absorption at 1940 cm$^{-1}$. The high energy CO states over 540K is probably the species that exhibits absorption at 1940 cm$^{-1}$. The high energy CO states may result from an alternate bonding mechanism:

$$\text{CO} + \text{O}_2^- (s) \rightarrow \text{CO}_2^{2-} (s)$$

This process results in electron transfer to the ZnO conduction band and may give rise to high energy adsorbed CO states which will desorb above 500K (ref. 22). The IR band at 1940 cm$^{-1}$ has been assigned to CO adsorbed in the bridged configuration on Cu + site and surface oxygen site. This bonding mechanism is in accordance with the suggestion that a surface oxygen site is also involved in the bridged adsorption of CO.

Hydrogen adsorption can take place on Cu +, Cu 0 or ZnO. The desorption temperatures observed by us are significantly higher than the values found in the literature for desorption from Cu crystal surfaces and bulk metallic copper$^{23,24}$. In addition, adsorption on bulk copper must be taking place through hydrogen atoms, while the adsorption on Cu/ZnO catalyst can be through molecular hydrogen$^{22}$. The desorption observed presently may not be due to H2 adsorbed on metallic copper. The amount of hydrogen adsorbed on a CO preadsorbed surface is not altered with coverage. This suggests that the adsorption sites for CO and H2 are different. The IR and TPD studies of CO adsorption show that CO is adsorbed on Cu + centres. So the probable site for adsorption of H2 is a Zn-O pair site. Herman et al.$^{27}$ reported that CO adsorbs on copper sites and H2 on Zn-O sites. The temperature and hence the energy of desorption observed presently is significantly higher than the literature values for pure ZnO (refs 25, 26). Still, this desorption may be from the Zn-O pair site, because the properties of ZnO in the Cu/ZnO/Cr2O3 are different from those of pure ZnO as seen from the diffuse reflectance studies. The absorption due to ZnO is totally absent, suggesting a change in the properties of ZnO. The high temperature desorption above 540K is due to high energy adsorbed states of hydrogen which are probably the hydrogen adsorbed on the Zn-O sites adjacent to Cu + sites. The interaction between adjacent Cu + and Zn-O sites will be more intense when compared with that of the other Zn-O sites. This interpretation is consistent with previous results showing that H2 adsorption on Zn-O pair sites is strengthened by increased electron density at the adsorption site$^{27}$.

The analysis of desorbed species in the TPD of CO adsorbed CO and H2 showed the presence of only CO and H2. But the temperature of desorption is shifted by about 20-30° to a higher temperature when compared with individual adsorption. This is an indication of the interaction between the adsorbed species.

**Methanol decomposition**

The IR studies show that formate is formed from the adsorbed methoxide species. Based on these studies Scheme 1 is proposed for the decomposition of methanol on Cu/ZnO/Cr2O3 catalyst.

In this reaction sequence transformation of aldehydeic species to the formate species is a facile process. This was confirmed by treating the catalyst with formaldehyde at room temperature (300K) when only the formation of formate type species was observed. The fact that only methoxide species could be observed on the adsorption of methanol at room temperature and that the transformation could be effected only on heating to 473-523K shows that the rate-determining step in this reaction sequence could be the transformation of methoxide species. Formaldehyde type species is not observed in these studies because it is stable only at low temperatures (210K).

![Scheme 1](#)

Based on the results of the decomposition of methanol, a reaction sequence (Scheme 2) can be deduced for methanol synthesis. CO and H2 adsorbed on the surface interact in such a way as to produce formate type, aldehyde type and methoxide species and finally methanol$^{11,16}$. CO adsorbed on metal ion (Cu +) sites can also interact and bond to adjacent oxide ions to give rise to an adsorbed CO with some kind of bridged configuration as shown by IR and TPD results. This adsorbed species gets hydrogenated by the adsorbed hydrogen atoms probably through the reaction sequ-
Conclusions

Carbon monoxide adsorbs on Cu/ZnO/\(\text{Cr}_2\text{O}_3\) catalyst at the \(\text{Cu}^+\) sites dissolved in the ZnO lattice in the carbonyl type and bridge type of adsorption. The bridged type of adsorption involves \(\text{Cu}^+\) and surface oxygen sites. Hydrogen adsorbs on Zn-O pair sites.

Copper species and ZnO in the Cu/ZnO/\(\text{Cr}_2\text{O}_3\) catalyst are in intimate contact resulting in strong interaction. The decomposition of methanol proceeds through methoxide, formaldehyde and formate type surface intermediates in sequence. Transformation of methoxide into formaldehyde type species is the rate-controlling step in the decomposition of methanol.

The synthesis of methanol from CO and hydrogen on Cu/ZnO/\(\text{Cr}_2\text{O}_3\) catalyst takes place by the interaction of co-adsorbed CO and He reaction involves formate, formaldehyde and methoxide intermediates in sequence. The hydrogenation/hydrogenolysis of the formate intermediate is the rate-controlling step.

References