Different routes to methanol: inelastic neutron scattering spectroscopy of adsorbates on supported copper catalysts

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We have investigated methanol synthesis with model supported copper catalysts, Cu/ZnO and Cu/MgO, using CO/H₂ and CO₂/H₂ as feedstocks. Under CO/H₂ both catalysts show chemisorbed methoxy as a stable intermediate, the Cu/MgO catalyst also shows hydroxyls on the support. Under CO₂/H₂ the catalysts behave differently, in that formate is also seen on the catalyst. For the Cu/ZnO catalyst hydroxyls are present on the metal whereas for the Cu/MgO hydroxyls are found on the support. These results are consistent with a recently published model for methanol synthesis and highlight the key role of ZnO in the process.

Introduction

In commercial low-pressure methanol synthesis Cu/ZnO/Al₂O₃ catalysts have been successfully used for more than 50 years to convert synthesis gas (H₂, CO, CO₂) into methanol due to their high activity and excellent stability under typical reaction conditions of 250 °C and 50–100 bar. Despite the successful application of this catalyst and the development of promising Cu-based catalysts on a variety of different oxide supports the exact mechanism of this reaction is still not fully understood. In the past years, considerable efforts were made by experimentalists and theoreticians to elucidate the reaction mechanism and active center of methanol synthesis over conventional and the newly developed Cu-based catalysts. Work from the late 1970’s proposed CO hydrogenation (eqn (1))

\[ \text{CO} + 2\text{H}_2 \rightarrow \text{CH}_3\text{OH} \]  

as the primary reaction pathway for methanol synthesis until isotope labeling experiments identified CO₂ as the main carbon source according to eqn (2)

\[ \text{CO}_2 + 3\text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}, \]  

formed by the water gas shift reaction \(^{10,11}\) (eqn (3))

\[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2. \]

In accordance with this finding, the great majority of state-of-the-art methanol synthesis plants derive their synthesis gas from reforming or partial oxidation of natural gas close to stoichiometric composition with respect to formation of the end-product (i.e. CO₂:CO ratio 1:0.75). In the last few years, in addition to fossil-derived synthesis gas, also non-fossil synthesis gas received increasing attention, i.e. CO-rich gas derived from biomass gasification processes (CO₂:CO ratio 0.75:1), or the hydrogenation of pure anthropogenic CO₂ with “green” H₂ derived from excess energy from renewable resources. Some of the authors recently published a model of the active site and proposed bi-metallic stepped facets, such as CuZn(211), as the CO₂-converting centers, emphasizing the crucial role for Zn as a component of the active surface ensemble, which has been observed and debated in many previous literature reports.

Within this study and many others, formate (HCOO) was identified as a very stable reaction intermediate in the hydrogenation of CO₂ (eqn (2)) via the formation of HCOOH (eqn (6)) and H₂COOH (eqn (7)) according to the following scheme:\(^3\)

\[ \text{H}_2(\text{g}) + 2^* \leftrightarrow 2\text{H}^* \]  
\[ \text{CO}_2(\text{g}) + \text{H}^* \leftrightarrow \text{HCOO}^* \]  
\[ \text{HCOO}^* + \text{H}^* \leftrightarrow \text{H}_2\text{COOH}^* + \ast \]  
\[ \text{H}_2\text{COOH}^* + \ast \leftrightarrow \text{H}_2\text{CO}^* + \text{OH}^* \]
ZnO as the oxide support. In earlier experiments, Cu/MgO was found to be different for catalytic systems, which contain MgO rather than ZnO, pointing towards the weaker metal-oxide interaction owing to the less reducible nature of MgO. Considering Cu/ZnO, which was attributed to the weaker metal-oxide interaction, enrichment at the very outermost catalyst surface, but a generally pronounced Zn enrichment at the surface of the catalyst was explained by Grabow et al. by its very high binding energy of $-2.68$ eV for the Cu(111) facet. On the (211) surface, the binding was found to be even stronger, rendering formate a very stable species on highly active surfaces and suggesting the further hydrogenation of formate to methoxy and methanol to be the rate-determining step in methanol synthesis from CO$_2$ over the industrial Cu/ZnO/Al$_2$O$_3$ catalysts. The surface OH groups and the final product have lower binding energies and are removed as water ($BE_{Cu(111)} = -0.21$ eV) and methanol ($BE_{Cu(111)} = -0.28$ eV). Again, DFT calculations have revealed a further increase of the adsorption strength also of other intermediates such as H$_2$COOH and H$_2$CO by alloying of Zn into the Cu-nanoparticles surface steps, one aspect of the hotly debated Cu–ZnO synergy.

The evolution of such bimetallic, stepped surface facets is believed to be the result of a strong metal-support interaction (MSI). For the industrial catalyst systems, indeed a pronounced Zn enrichment at the surface of the catalyst was observed by depth-sensitive XPS measurements, while no alloy formation in the bulk was observable under conventional synthesis conditions of 250 °C and 60 bar. This situation is different for catalytic systems, which contain MgO rather than ZnO as the oxide support. In earlier experiments, Cu/MgO catalysts showed a significant activity in CO/H$_2$ containing feed gases. These results were more recently confirmed by laboratory performance studies carried out at 230 °C and 30 bar with a highly active Cu/MgO catalyst in CO/H$_2$ feed gas. XPS depth-profiling experiments carried out on this catalyst revealed a Mg enrichment at the very outermost catalyst surface, but a generally much lower tendency of overlayers formation compared to Cu/ZnO, which was ascribed to the weaker metal-oxide interaction owing to the less reducible nature of MgO. Considering that Cu/MgO is a very good CO hydrogenation catalyst, while Cu/ZnO is preferably hydrogenating CO$_2$, the results indicate that the oxide support does not act only as a structural promoter, but also plays a determining role in the preferred pathway for the two routes of methanol synthesis from CO$_2$/H$_2$ or CO/H$_2$ as the carbon source. In the many spectroscopic studies performed on Cu/ZnO or Cu/ZnO/Al$_2$O$_3$ in its unreduced state and in the reduced state, the most abundant surface species found were formyl, methoxy and formate.

In this work, we investigate the role of the oxide support of catalysts for methanol synthesis and in particular test the working hypothesis that methanol formation occurs through different mechanisms and intermediates depending on whether Zn is present or absent. For this purpose, we have prepared a conventional Al$_2$O$_3$-promoted Cu/ZnO (CZ) catalyst and a Cu/MgO catalyst without ZnO (CM), operated them both in CO/H$_2$ and CO$_2$/H$_2$ syngas feeds and studied the post-reaction surface adsorbates by inelastic neutron scattering (INS) using the MAPS spectrometer at the ISIS Facility of the STFC Rutherford Appleton Laboratory. In contrast to comparable methods (e.g. FT-IR, DRIFTS), INS can be readily used on realistic nanostructured and black catalysts, probes a representatively large sample of $20$ g, furthermore it exhibits high sensitivity towards hydrogen-containing adsorbates on the catalyst across the entire mid-infrared, $0$–$4000$ cm$^{-1}$, range. The successful application of this method for catalyst characterization was formerly demonstrated by the groups of Albers, Lennon and Parker.

### Experimental

The catalytic reactions were carried out on previously described gas handling system that is designed to provide the large samples needed for INS spectroscopy. Approximately $35$ g of the catalysts were loaded into a stainless steel tubular reactor and reduced in H$_2$/He mixture (total flow $1.65$ L min$^{-1}$) RT to 523 K at ambient pressure. Following the reduction, the reactor was pressurized to 8 bar in feed gas at 523 K until a methanol signal was clearly visible in the on-line mass spectrometer. After the products had reached a steady state, the reactor outlet was closed to pressurize it to 20 bar. When the pressure was reached, the heating of the reactor was switched off, to let it cool to 308 K within 2 h. Afterwards, the reactor was purged with inert gas. The reactor was transferred into a glove box and the catalysts were loaded into an aluminum sachet and placed in a thin-walled, indium-sealed aluminum can. To obtain reasonable resolution across the whole spectral range three incident energies ($E_i$) were used: $4840$, $2420$ and $1210$ cm$^{-1}$. These focus on the C–H/O–H stretch, the C–H deformation and the O–H deformation regions respectively. Three spectra were acquired for 4 h and summed up at each energy. Unless otherwise stated, all the spectra presented of the catalysts are difference spectra: $[(\text{catalyst} + \text{adsorbate}) - \text{(reduced catalyst)}]$. The catalysts, their synthesis and physico-chemical characterization has been described in detail previously. In the reduced state, CZ and CM exhibit similar specific Cu surface areas of $14.7$ and $13.6$ m$^2$ g$_{\text{cat}}^{-1}$, respectively, as determined by H$_2$-TPD.

### Results

#### Methanol formation from CO/H$_2$

Fig. 1 shows the exhaust gas composition as a function of time on stream for methanol formation over the CZ, Fig. 1a, and CM catalysts, Fig. 1b. It is clear that CO forms CO$_2$, presumably by reaction with hydroxyl groups located on the oxide (ZnO or MgO), as in the case of hydrous palladium oxide.

$$\text{CO} + 2\text{OH} \rightarrow \text{H}_2\text{O} + \text{CO}_2$$  \hspace{1cm} (15)

The presence of hydroxyls is seen in the INS spectra of the reduced catalysts before methanol synthesis occurs, Fig. 2.
Fig. 1 Gas analysis during methanol synthesis at 6.31 bar and 523 K over the CZ (a) and CM (b) catalyst in CO/H2 feed gas (composition: 37.5 ml min⁻¹ CO, 150 ml min⁻¹ H2 and 1500 ml min⁻¹ He). Due to a technological problem, the m/z = 2 trace in (a) is erroneous and not shown. The true evolution of the hydrogen concentration is expected to be similar to the trace shown in (b).

The assignments of INS bands encountered in this study are compiled in Table 1.

For the reduced CZ catalyst Fig. 2a, there are too few hydroxyls to allow detection of the O–H stretch, however, the stronger bending mode at 760 cm⁻¹ is seen, Fig. 2b. For the CM catalyst Fig. 2c, the much higher density of hydroxyls enables both the stretch (3600 cm⁻¹) and bend (690 cm⁻¹) to be observed. Close inspection of Fig. 1a and b shows an increase in the water signal simultaneously with the CO₂ spike, consistent with eqn (15).

Fig. 3 shows the background subtracted spectra of the catalysts (CZ Fig. 3a and CM Fig. 3b) after methanol synthesis in CO/H2 at 6.31 bar and 523 K. For comparison, the spectrum of solid methanol is also shown Fig. 3c. For the CZ catalyst, strong features are seen at 2940, 1450, 1160 and 95 cm⁻¹. These are assigned as the C–H stretch, the C–H deformations, methyl rock and methyl torsion respectively of chemisorbed methoxy.20,21 These can be unambiguously assigned to methoxy rather than physisorbed methanol by the absence of the features relating to the O–H group of methanol: the O–H stretch at 3200 cm⁻¹ and the C–O–H bend at 750 cm⁻¹, that are seen in the reference spectrum, Fig. 3c. The same features are also seen for the CM catalyst, Fig. 3b, although there are additional features that are due to surface hydroxyls, cf. Fig. 2c, generated in the reaction. The hydroxyl bending mode occurs in the same region as the methanol C–O–H bend mode, so complicates the distinction between methoxy and physisorbed methanol. However, the shape of the C–H stretch on the CM catalyst at 2940 cm⁻¹ is very similar to that seen on the CZ catalyst and distinctly different to the overlapping C–H and O–H stretch modes of solid methanol. Thus it is highly probable that methoxy is the dominant species on the CM catalyst as well. Methoxy typically adsorbs in an on-top mode on copper single crystal surfaces,26–38 but might be found in a bridged form on the supposedly important step sites as suggested by DFT.6

Methanol formation from CO₂/H₂

Fig. 4 shows the evolution of the product gas concentrations, CO as a product of the reverse water gas shift reaction and methanol and water as products of methanol synthesis from CO₂, as a function of time on stream over the CZ, Fig. 4a, and CM catalysts, Fig. 4b. Unfortunately, there were experimental difficulties, so the profiles are not as clean as for the CO/H₂ reaction, nonetheless, methanol formation is clearly observed over both catalysts. In good agreement with previous kinetic studies,2,15 the methanol productivity of the CM catalyst however is much lower than CZ. CM rather produces CO from the reverse water gas shift. This behaviour has been related to the absence of SMSI in this catalyst and its inability to convert formate to methanol in the absence of Zn.15

Fig. 5 shows the background subtracted spectra of the catalysts (CZ Fig. 5a and CM Fig. 5b) after methanol synthesis in CO₂/H₂ at 6.31 bar and 523 K. A reference spectrum of Cu(HCOO)₂·4H₂O is also shown, Fig. 5c. For both catalysts, features are again seen at 2940, 1450, 1160 and 95 cm⁻¹. As before, these are assigned to chemisorbed methoxy rather than physisorbed methanol, the downshift of the torsional mode from 110 cm⁻¹ in methanol to 95 cm⁻¹ in the chemisorbed species supports this assignment.

In contrast to the reaction in CO/H₂, formate is also present on the surface. Both catalysts show the characteristic22,23 in-plane C–H deformation mode at 1375 cm⁻¹, the weaker out-of-plane deformation is just visible at 1055 cm⁻¹ in the CZ sample, Fig. 5a. Unfortunately, the mode of formate coordination (mono- or bidentate) cannot be distinguished here as the diagnostic modes are the symmetric and asymmetric C–O stretches which are invisible to INS. A second difference between the reactions is the CZ sample shows the presence of hydroxyls, bands at 3430 and 915 cm⁻¹ for the O–H stretch and bend respectively. No clear indication of adsorbed water is seen.
in the spectra, but its presence cannot be unambiguously excluded and a small amount of water might be present.

**Discussion**

This work shows a clear distinction between the catalysts and different behaviour depending on the feedstock for methanol synthesis. Chemisorbed methoxy is observed in all cases, although the quantity varies considerably: CZ(CO/H$_2$) $\approx$ CM(CO$_2$/H$_2$) = 2.5 CM(CO$_2$/H$_2$) = 2 CZ(CO$_2$/H$_2$). This indicates that the methoxy is bonded to the copper in all cases. The spectra from the CO$_2$/H$_2$ reaction represent a saturated monolayer on the catalyst that with the similar copper areas for both CZ and CM give similar intensities as there is no other species present on the catalyst, (the similarity of the hydroxyl spectra on CM before and after reaction shows that they are on the MgO). For the CO$_2$/H$_2$ reaction this is not the case and an additional species, formate, competes for space, again suggesting that the formate is on the copper. For the CM catalyst the total area of (methoxy + formate) is lower, supporting the idea of adsorption on the copper.

For the CZ catalyst in CO$_2$/H$_2$ the area occupied by the two carbonaceous intermediates is different in the two reactions, the combined area is less than half that of the CO/H$_2$. In addition to formate, hydroxyls are also seen at 3460 and 920 cm$^{-1}$ for the O–H stretch and bend respectively, these do not appear in the spectra for the CO/H$_2$ reaction.
not occur for the reaction under CO/H₂. The position of the bending mode is significantly higher than was found for hydroxyls on the ZnO support, Fig. 2b. Comparison with hydroxyls in Cu(OH)₂ and on RANEY Cu, Fig. 6, shows that the hydroxyl bending mode for the CZ catalyst occurs in the region found for OH bonded to Cu. Together with the reduced total area of (methoxy + formate), this suggests that the hydroxyls are on the Cu component of the catalyst, rather than on the ZnO support, which is consistent with the observed product inhibition by the coupled product H₂O during methanol synthesis from CO₂ on Cu/ZnO catalysts. 39

As described in the Introduction, methanol synthesis has been the subject of extensive theoretical work. 6,15 Fig. 7 shows the Gibbs free energy calculated by DFT for the CO/H₂, Fig. 7a, and the CO₂/H₂, Fig. 7b, reactions. 15 Our results are completely consistent with this model. For the CO/H₂ reaction, it can be seen that on both the Cu-only and the Cu-Zn surfaces the only stable hydrogens intermediate is methoxy. In contrast, for the CO₂/H₂ reaction, both formate and methoxy are stable intermediates. The calculations also show that hydroxyls should be present on the metal surface, these are seen for the CZ catalyst but not for the CM, presumably these are more stable on the MgO and so spillover onto the MgO. It is noted that a kinetic model calculated for differential conversion showed formate to be the only dominating surface species on CZ. 15 The is due to the stronger bonding compared to the other intermediates and the overall lower amount of the product-like intermediate methoxy under such conditions. Thus, co-adsorption is characterized by a competition between hydroxyl and methoxy with formate and the coverage will depend on the chemical potentials given be the pressure and conversion. In this experiment, due to the closure of the exhaust gas stream and the build-up of pressure before the INS measurements, we are likely away from differential conversions explaining the observed substantial amount of methoxy and hydroxyls compared to previous kinetic modelling.

Conclusions

We have investigated methanol synthesis with model supported copper catalysts using CO/H₂ and CO₂/H₂ as feedstocks. Under CO/H₂ both catalysts show chemisorbed methoxy as a stable intermediate, the CM catalyst also shows hydroxyls on the support. Under CO₂/H₂ the catalysts behave differently, in that formate is also seen on the catalyst. For the CZ catalyst hydroxyls are present on the metal whereas for the CM material hydroxyls are found on the support. These results are consistent with a recently published model² for methanol synthesis, in which reduced Zn species on stepped copper surfaces are responsible to the hydrogenation of formate to methanol copper and, thus, highlight the key role of ZnO in the process.
Acknowledgements

The authors would like to thank Julia Schumann, Stefan Zander, Nygil Thomas and Florian Ribicki for sample preparation, discussions and assistance. The STFC Rutherford Appleton Laboratory is acknowledged for the allocation of neutron beam time. This research project has been supported by the European Commission under the 7th Framework Programme, NMI3-II Grant number 283883, CP-CSA_INFRA-2008-1.1.1.

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