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Application Note 1378

In Situ Investigation of Catalytic Reactions on CuO-Based Catalysts by Raman and Diffuse Reflection Infrared Spectroscopy

Guisheng Wu, Department of Chemical Engineering, Research Institute of Applied Catalysis, Shanghai Institute of Technology, 200235 Shanghai, People's Republic of China

Introduction

Raman spectroscopy and mid-infrared diffuse reflection (DR) spectroscopy have different, and highly complementary, roles in the study of catalytic reactions. In general, Raman spectroscopy does not have enough sensitivity to allow the investigation of molecules that are adsorbed on the surface of powdered oxide catalysts, but is usually sensitive enough to allow the bulk structure of such catalysts to be characterized *in situ*. On the other hand, numerous previous studies have demonstrated that DR mid-infrared spectroscopy allows the reactants, intermediates, and products present on the surface of heterogeneous catalysts to be observed. In this note, we report how Raman and mid-infrared spectroscopy have been used to investigate the reactions that occur when methanol is adsorbed on the surface of copper oxide based catalysts.

It is known that methanol can decompose to form either CO and H_2 or formaldehyde and H_2 by a combination of dehydration and oxidation processes with a variety of catalysts.[1-3] These methanol steam reforming reactions are potentially important for hydrogen production. The mechanism and rate of the reaction depend strongly on the composition of the catalyst and the reaction temperature. We have monitored the composition of copper oxide based catalysts by Raman spectroscopy with a Renishaw Model 2000 Raman spectrometer equipped with a ~100-mW, 785 nm diode laser. The powdered samples were held in a Harrick HVC high-temperature reaction chamber (Raman configuration, see Figure 1a), the temperature of which was controlled by a Harrick temperature controller. Diffuse reflection spectra were measured in situ using the Harrick HVC high-temperature reaction chamber (infrared configuration, see Figure 1b) mounted into the Harrick Praying Mantis DR accessory (see Figure 7 on page 4); these were installed into a Thermo-Nicolet 670 FT-IR spectrometer equipped with a DTGS detector. The sample temperature was controlled with the same Harrick temperature controller used for the Raman measurements. Using both Raman and mid-infrared DR spectroscopy, we

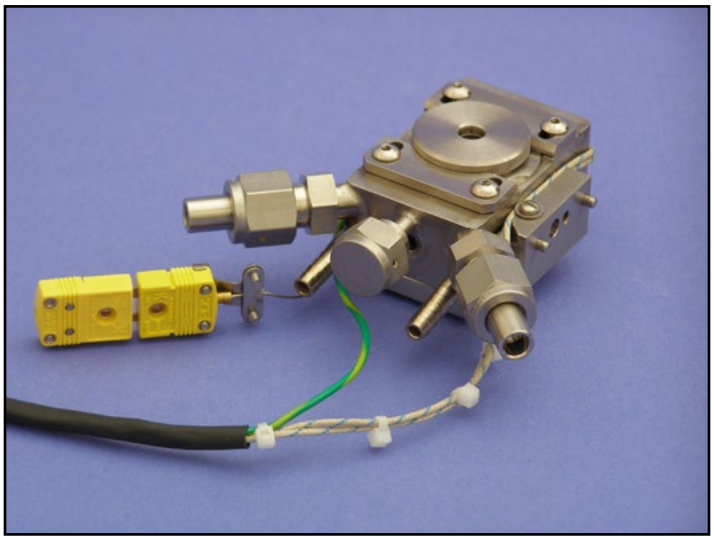

Figure 1a. Harrick HVC Reaction Chamber in Raman configuration with flat-planar window assembly; window material is fused-silica UV-quartz.

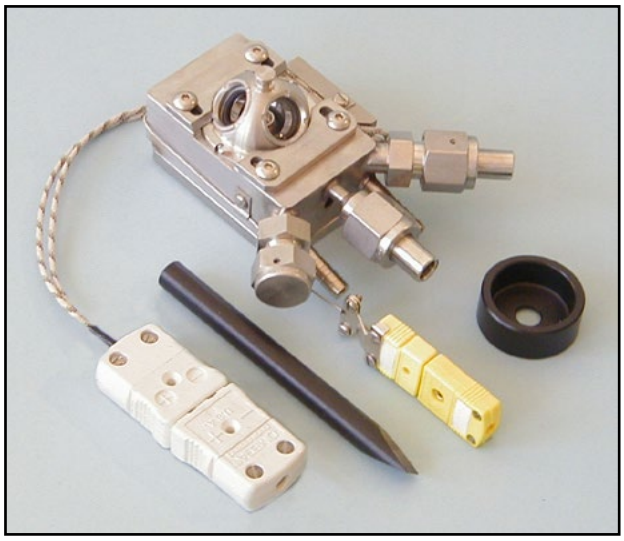

***Figure 1b**. Harrick HVC Reaction Chamber in DR infrared configuration with three-window dome assembly. Two windows (typically ZnSe or KB) are for the infrared radiation that enters and exits the chamber; a third window is used to irradiate the sample for photochemistry studies.*

have been able to follow the pretreatment of CuO-based catalysts at different temperatures, and to monitor both the adsorbed species and the composition of the vapor-phase species above the catalyst at temperatures up to 350°C. It might be noted that both the Renishaw Raman and Thermo-Nicolet FT-IR spectrometers are well over 15 years old; significantly improved performance might be expected from more current instruments.

Experimental

Cupric oxide was prepared by the decomposition of $Cu(NO_3)_2$ powder at 450°C in air for 4 h. ZrO_2/CuO was obtained by impregnating CuO formed in this way in a 0.5 M solution of $Zr(NO_3)_4$ for 10 h, followed by air drying at 120°C overnight followed by air calcinations at 400°C for 4 h. To prepare the catalyst, it was loaded into the sample cup, and a mixture of 5% H_2 and 95% N_2 was passed through it. The sample temperature was increased at the rate of 10°C/min to various set values and maintained for 30 min. The sample was then allowed to cool back to ambient temperature at which point the Raman spectrum was measured. The chamber was then pumped to 10^{-3} Pa for 30 min, methanol vapor was introduced in short pulses, and the IR spectra were recorded at different temperatures.

Results and Discussion

The Raman spectra show that the CuO catalyst as prepared above gives rise to bands at 291, 355 and 626 cm^{-1}, as shown in Figure 2a. These bands are respectively assigned to the A_g, B_g^1 and B_g^2 optical phonon modes of CuO, which has the space group C^6_{2h}.[4,5] After H_2 reduction at 300°C for 30 min, the Raman spectrum is hardly changed; see Figure 2b. On continuing H_2 reduction at this temperature for a further 30 min, however, the intensities of the three bands listed above are reduced significantly, and two additional bands are observed at 146 and 213 cm^{-1}; see Figure 2c. These bands are respectively assigned to the Γ^-_{15} and Γ^-_{12} optical phonon modes of Cu_2O, which has the space group symmetry O^4_h.[6,7] Thus these Raman spectra showed that when H_2 was passed over CuO at 300°C there was an induction period of between 30 and 60 min, after which the CuO was slowly reduced to Cu_2O.

The spectra of ZrO_2/CuO as prepared are similar to those of CuO and do not show any bands assignable to ZrO_2, indicating that ZrO_2 is highly dispersed; see Figure 3a. When ZrO_2/CuO is reduced at 300°C for 30 min, the Raman bands due to CuO completely disappear and weak new bands appear at 148 and 220 cm^{-1} for which we currently have no explanation; see Figure 3b. After reduction for 60 min, new bands are seen at 202, 334, 489 and 633 cm^{-1}, which have been previously reported in the Raman spectrum of tetragonal ZrO_2;[8] see Figure 3c. This result appears to indicate that zirconium atoms migrate to the surface of the copper oxide catalyst at high temperature, forming a layer of tetragonal ZrO_2.

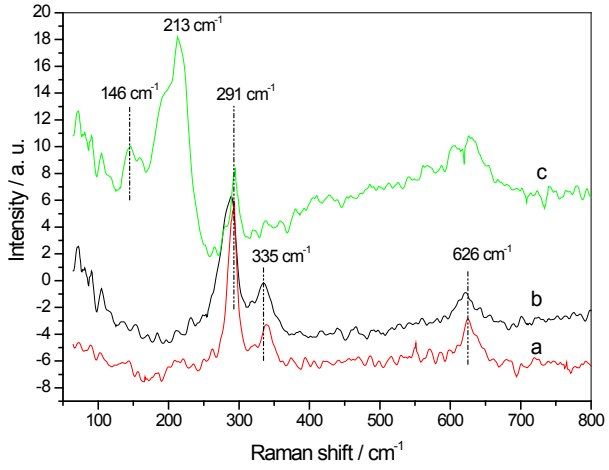

Figure 2. The Raman spectra of CuO catalysts, a: CuO as prepared; b: CuO reduced at 300 °C for 30 min; c: CuO reduced at 300°C for 60 min

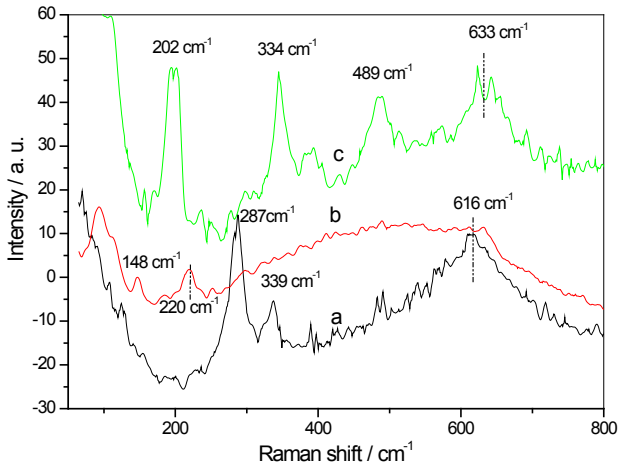

Figure 3. The Raman spectra of ZrO_2/CuO catalysts. a: ZrO_2/CuO as prepared; b: ZrO_2/CuO reduced at 300°C for 30 min; c: ZrO_2/CuO reduced at 300°C for 60 min.

When CO is adsorbed on the surface of the CuO catalyst that has been reduced at 300°C for 1 h, the characteristic bands of Cu_2O decrease rapidly, and a new broad band appears between 450 and 650 cm^1. This band has been assigned to the Cu-C stretching mode of Cu-CO.[9] However, the C=O stretching mode of this moiety, which would be expected to be seen strongly in the mid-infrared DR spectrum between 1900 and 2100 cm^{-1} is absent; thus this assignment should be taken as very tentative. If CO is adsorbed on the reduced ZrO_2/CuO catalyst, the bands assigned to ZrO_2 disappear and the broad band between 450 and 650 cm^1 is intensified.

To investigate the effect of these catalysts on the decomposition of methanol, CuO was first reduced at 280°C; methanol was then introduced with the catalyst at ambient temperature. After 10 min, the only features in the spectrum that could be measured were due to methanol vapor, see Figure 4a; there was no evidence of either adsorption or of any reaction products. When the temperature of the catalyst was increased to 200°C and the spectrum measured after 1 min (see Figure 4b), several new bands were observed below 1500 cm^{-1}, suggesting either the presence of adsorbed methoxide or a change in structure of the catalyst on increasing the temperature. For reasons that will become evident in the next paragraph, we favor the latter explanation. Also readily apparent from this spectrum is the formation of CO_2 as evidenced by the strong doublet around 2350 cm^{-1}. When the sample temperature was raised to 220°C, there was no evidence of any methanol remaining in the cell, with the only vapor-phase species remaining in the cell being CO_2 (see Figure 4d). The 2350-cm^{-1} CO_2 band was very intense, so that even the two very weak combination bands of CO_2 between 3500 and 4000 cm^{-1} can be seen in this spectrum. Thus under these conditions neither the formation of CO and H_2 nor formaldehyde and H_2 is indicated.

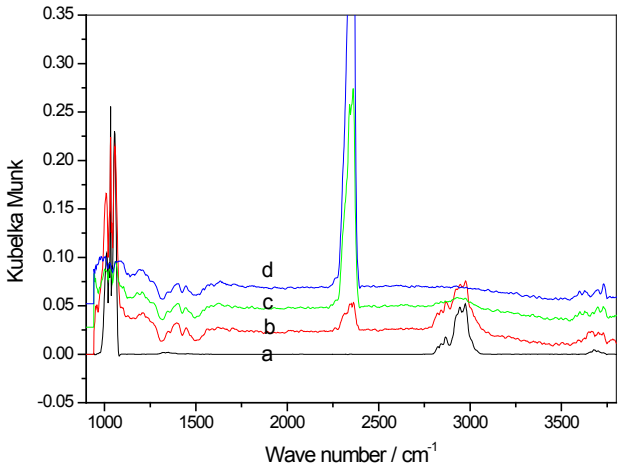

Figure 4. IR spectra measured after methanol was introduced to the CuO catalyst that had been reduced at 280 °C. Following the introduction of methanol vapor, the temperature of catalyst was first maintained at 22°C for 10 min (a); the sample temperature was raised to 200°C and the spectrum measured after 1 min (b) and 7 min (c). The temperature was then raised to 220°C and the spectrum measured after 1 min (d).

Significantly different results were obtained when methanol was passed into a cell containing the CuO catalyst that had been reduced at 350°C. When the catalyst was at room temperature, there was again no evidence for adsorption or reaction of methanol and the only features that could be seen in the spectrum were the bands due to methanol in the vapor phase, as can be deduced from the contours of the rotational transitions, see Figure 5a. When the temperature of the catalyst was raised to 200°C, the intensity of the vapor-phase CH_3OH bands decreased with time. Initially, a band at ~1750 cm^{-1} is observed, which must be caused by the formation of formaldehyde (Figure 5b). The apparent fact that this band is a doublet almost certainly means that the CH_2O is in the vapor phase. Also seen in this spectrum is a band at ca. 1200 cm^{-1}. From the contour of this band, it does not appear to be due to a small molecule in the vapor phase; we believe that it is more likely caused by the presence of adsorbed methoxide. It is likely that this methoxide is dehydrogenated on the catalyst surface to form formaldehyde. In the spectrum measured 7 min after methanol was introduced (Figure 5c), the formation of CO_2 is evident from the appearance of the band around 2350 cm^{-1}; it is also clear that the formaldehyde concentration has decreased. Thirty min after the introduction of methanol, most of the reactant had been converted to CO_2; a small amount of methanol remained and there was no evidence of formaldehyde in the cell, see Figure 5d.

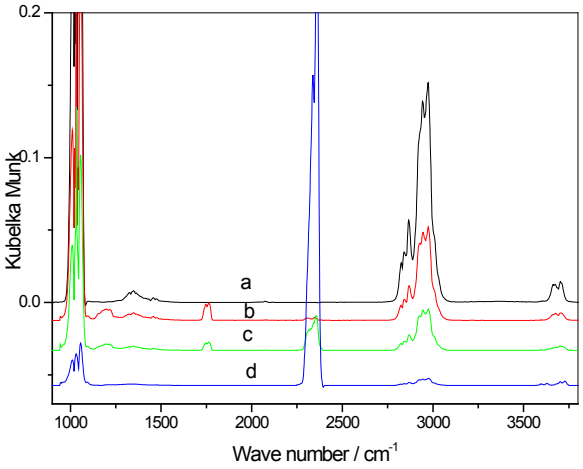

Figure 5. IR spectra measured after methanol was introduced to the CuO catalyst that had been reduced at 350°C. Following the introduction of methanol vapor, the temperature of catalyst was maintained at 18 °C for 10 min (a), at 200°C for 1 min (b), 7 min (c) and 30 min (d).

When analogous measurements were made with the ZrO_2/CuO catalyst, similar results to the ones shown in Figure 4 were found when the catalyst was prepared at 280°C, but when the catalyst was prepared at 350°C, no evidence of formaldehyde formation was observed; see Figure 6. While the concentration of methanol vapor clearly decreased as the temperature of the catalyst was increased, only a small amount of CO_2 was formed. A band at ca. 1580 cm^{-1} is best assigned to adsorbed formate, strongly suggesting that the Zr^{4+} ions act as oxidizing agents.

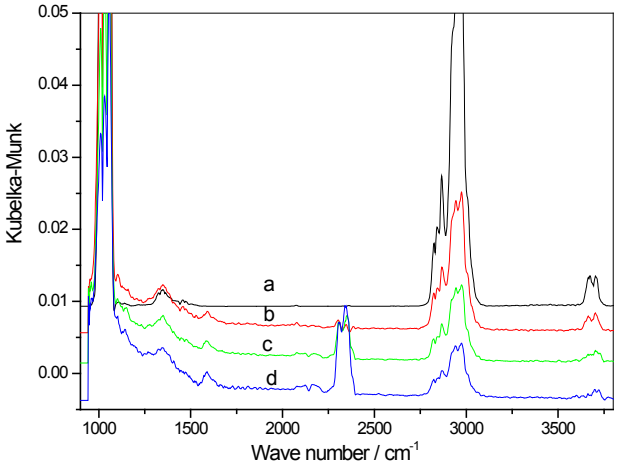

Figure 6. IR spectra measured after methanol was introduced to the ZrO_2/Cu catalyst that had been reduced at 350°C. Following the introduction of methanol vapor, the temperature of the catalyst was maintained at 18°C for 10 min (a), at 200°C for 20 min (b), at 230°C for 20 min (c) and at 250°C for 20 min.

Conclusion

These spectra not only serve to illustrate the complexity of these particular reactions, but also nicely illustrate the complementary information on catalysis phenomena that can be gained by acquiring both Raman and DR infrared spectra. We were surprised to observe one other beneficial piece of information: even though the total pathlength of the beam between the sample and the two cell windows is only of the order of 1 cm and the spectra were measured with a standard DTGS detector, the spectra of vapor-phase species were strongly evident in the spectra. Since species on the vapor and condensed phases are usually readily distinguished on the basis of the band frequencies and contours, this adds one more weapon to the arsenal of catalysis researchers.

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Figure 7. Harrick Praying Mantis diffuse reflection accessory (top right), with CHC Low/High Temperature Reaction Chamber with cryostat (top left); HVC High temperature Reaction Chamber (lower left); ambient micro and macro sample cups and alignment fixture (lower right).

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