

Comment on the “In situ IR studies on the mechanism of methanol synthesis from CO/H₂ and CO₂/H₂ over Cu-ZnO-Al₂O₃ catalyst” by Wang et al

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(Received 26 January 2011)

Wang et al. [1] have recently reported an in situ IR investigation of the mechanism of methanol synthesis from CO/H₂ and CO₂/H₂ mixtures over a Cu-based catalyst. Some IR bands were assigned by these authors to surface adsorbates such as formates and carbonates (Fig. 1(a)). These particular IR bands, as well as many others observed on this figure, appeared to be unusually narrow to be realistically those of species adsorbed on the catalyst. The full width at half-height of most of the narrow bands reported in Fig. 1(a) was lower than 6 cm⁻¹. Such a narrow width contrasts with that of IR bands of typical carbonates and formates [2–4] observed at the surface of catalysts that can be wider than 100 cm⁻¹. In fact, it is usually difficult to resolve the bands of carbonate and formate species.

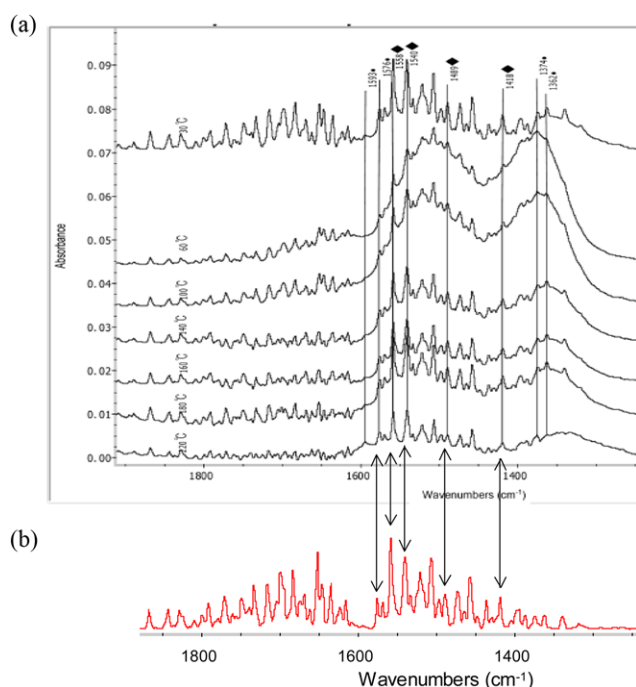


Fig. 1. (a) Detail of the first figure reported in the paper by Wang et al. [1] showing in situ IR spectra recorded during temperature-programmed methanol synthesis under CO/H₂, HCOO-Zn (●), carbonate (◆). (b) IR spectrum of gas-phase water recorded at ambient temperature.

A closer inspection of the set of narrow bands observed by Wang et al. [1] reveals that those exactly match the rovibrational bands associated with gas-phase water, which is given in Fig. 1(b), collected at the same resolution (i.e. 4 cm⁻¹). This observation strongly suggests that all the narrow bands observed by Wang et al. [1] are due to the absorption of water molecules, from ambient air and/or present in the cell due to the release/formation of water during the temperature-programmed reaction.

Similar narrow bands were also observed and assigned to formates and carbonates in the Fig. 5 reported by Wang et al. in their paper [1] and it appears again that those are all assignable to gas-phase water. Truly carbonate species can actually be observed on the spectra reported by the authors [1], i.e. the very broad bands at ca. 1,550 and 1,370 cm⁻¹ (Fig. 1(a)), which were not indexed by the authors.

In conclusion, we believe that the interpretation of the in situ IR data reported by Wang et al. [1] is partly flawed and the paper should be revised in part to ensure that the appropriate conclusions were reached.

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REPLY

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(Received 11 May 2011)

We have made the experiment to study the IR spectrogram about the gas-phase water with and without the catalysts in our reaction system under the same condition in line with our previous work. The

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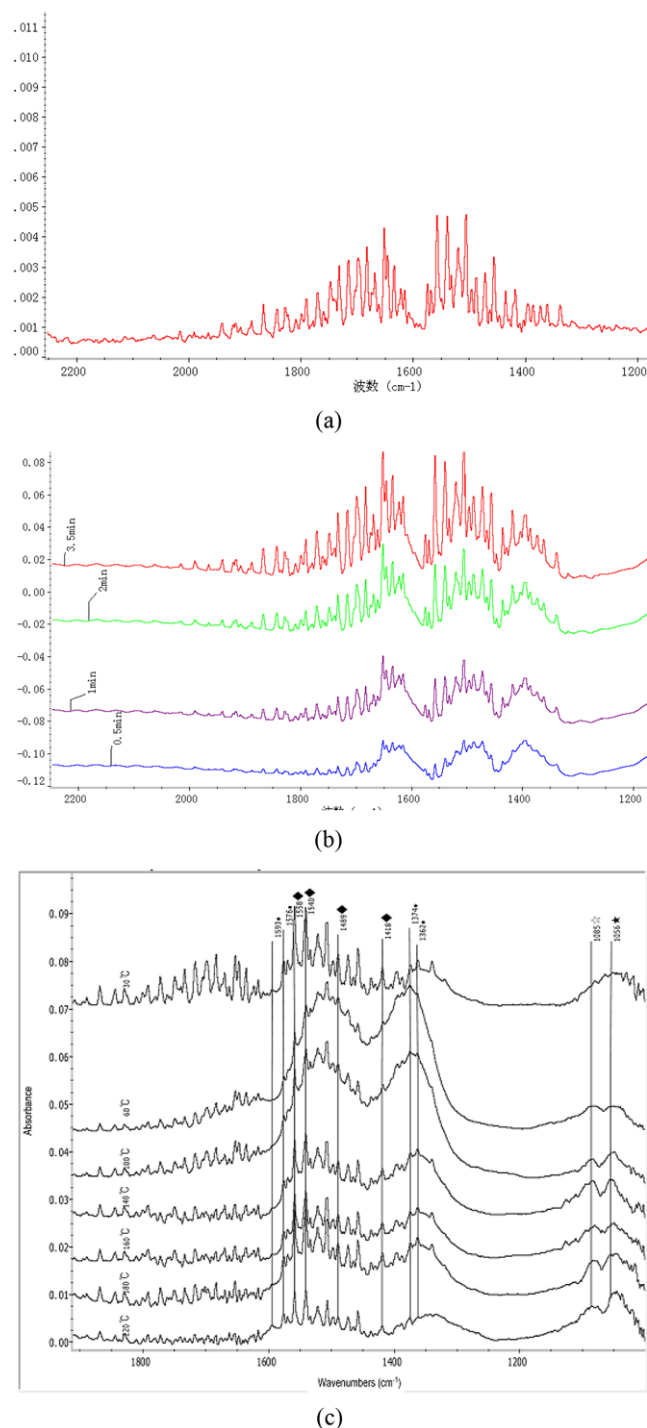


Fig. 1. In situ IR spectra for methanol synthesis from CO/H₂ recorded during temperature-programmed-reaction at low wave number area. HCOO-Zn (●), carbonate (◆), CH₃O-Zn (☆), CH₃OH (★).

gas-phase water is swept into the cell with nitrogen and the spectrograms are recorded. The spectrograms are shown below (A: without catalyst; B: with catalyst which reflect the bands' variation with the time at 60 °C). We also have done this work at different temperatures 30, 100, 140, 180 and 220 °C, the results are nearly the same as B. C is the picture in our previous work.

According to the spectrograms, it is obvious that the bands of gas-phase water (A) are located between about 2,000 cm⁻¹ and 1,300 cm⁻¹ and every peak is sharp. But the difference between B and A is evident. Yes indeed, the new LARGE band that you see at ca. 1,630/cm in Fig. 1(a) is ADSORBED molecular water, which contrary to gas-phase water (which can be inside and outside of the reaction cell) does not give the narrow rotational bands but a single large band. There are obviously three broad peaks which should belong to the water's characteristic absorption band in our reaction system. The three broad peaks can not be seen in the A. However, the spectrogram of C only show 2 broad peaks between 1,600 cm⁻¹ and 1,200 cm⁻¹, and not show the ones between 1,550 cm⁻¹ and 1,800 cm⁻¹. See my explanation above. Note that in my earlier comment I had indeed indicated that the large bands observed were due to adsorbed carbonates. So we have reason to believe that the bands between 1,600 cm⁻¹ and 1,300 cm⁻¹ which the Dr. Frederic Meunier tried to assign to gas-phase water should not be simply assigned to gas-phase water, or at least, could not completely be the gas-phase water. So we agree with the interpretation of the IR wavenumbers from the reference mentioned in our paper and believe our assignment of IR spectra is acceptable.