

COMMENTS

Comment on “Density Functional Theory Study of Triangular Molybdenum Sulfide Nanocluster and CO Adsorption on It”

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MoS₂ nanoparticles promoted by Co or Ni constitute the active phase of most commercial hydrotreating catalysts that aim at reducing the sulfur content of petroleum feedstocks.¹ In a recent article,² Zeng and co-workers have reported a theoretical investigation of CO adsorption on triangular MoS₂ clusters using DFT calculations. Such a study is valuable because it allows a straightforward comparison to be made with experimental infrared spectra of CO adsorbed on real, highly dispersed supported MoS₂ catalysts.^{3–9} Figure 1 shows infrared spectra recorded during CO adsorption at low temperature (100 K) on a MoS₂/Al₂O₃ catalyst. Experimental details can be found elsewhere.⁹ The high-frequency bands (above 2140 cm^{−1}) are due to CO adsorbed on the Al₂O₃ support. CO adsorption on the MoS₂ phase is characterized by the intense band at 2112 cm^{−1} and the broad, ill-defined shoulder at ~2070 cm^{−1} that develops at high CO coverage. In previous studies,^{9,10} we have compared experimental infrared spectra of CO adsorbed on MoS₂/Al₂O₃ catalysts with theoretical calculations of $\mu(\text{CO})$ stretching frequencies of CO adsorbed on (100) surfaces of MoS₂ using a periodic DFT approach. We concluded that the band at 2112 cm^{−1} could be assigned to adsorption of *monocarbonyl* species on sixfold coordinated Mo centers of the so-called molybdenum edge of MoS₂ crystallites, whereas the broad shoulder at ~2070 cm^{−1} was assigned to mono- and dicarbonyl species adsorbed on six- and fourfold coordinated Mo centers of the sulfur edge of MoS₂. Because we used a periodic model, however, we could not investigate the possibility of CO adsorption on corner sites of MoS₂. This has been done by Zeng et al. on triangular MoS₂ clusters, and their theoretical results led them to assign the band at 2112 cm^{−1} to the symmetric stretching (computed at 2102 cm^{−1}) of *dicarbonyl* species adsorbed on fourfold coordinated Mo centers located at the corner of MoS₂.² To the best of our knowledge, this is the only study suggesting that the main $\nu(\text{CO})$ band observed on MoS₂ could be due to adsorbed dicarbonyl species. In this respect, this proposal certainly deserves attention. In this comment, we discuss this assignment by comparing the theoretical results reported by Zeng et al. with experimental IR spectra of CO. We also present new experimental results demonstrating that the band at ~2110 cm^{−1} can definitely be assigned to monocarbonyl species.

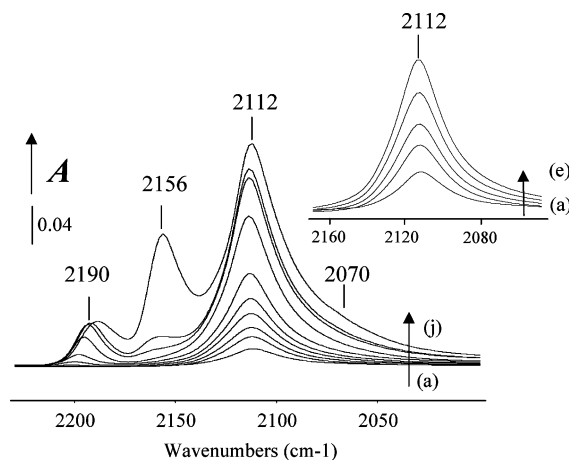


Figure 1. IR spectra of CO adsorbed (100 K) on sulfided Mo/Al₂O₃ catalyst (8.7 wt % Mo). Spectra a–i: doses of 20, 60, 130, 230, 390, 650, 1170, 1960, and 3000 μmol of CO per gram of catalyst. Spectrum j: 133 Pa of CO at equilibrium.

First, by comparing mono- and dicarbonyl adsorption on corner sites, Zeng et al. show that the adsorption energy per CO molecule is almost constant (27.6 kcal mol^{−1} vs 28.9 kcal mol^{−1}, respectively). In such a case, formation of monocarbonyl species should be statistically favored at low CO coverage (low CO pressure). Monocarbonyl species present a single $\nu(\text{CO})$ mode with a frequency (computed at 2049 cm^{−1} by Zeng et al.) that strongly differs from those of symmetric and antisymmetric stretching modes of dicarbonyl species (computed at 2102 and 2081 cm^{−1}, respectively). Therefore, according to the proposal of Zeng et al., experimental IR spectra obtained at low CO coverage should exhibit a single band at low wavenumbers (~2050 cm^{−1}) corresponding to monocarbonyl species, whereas higher frequency bands at ~2100 and 2080 cm^{−1} should progressively develop as the CO coverage increases.¹¹ This is not observed on experimental spectra obtained at low CO coverage that show a single, symmetrical band at 2112 cm^{−1} characteristic of CO adsorption on the MoS₂ phase (inset of Figure 1).

Second, as stated above, dicarbonyl species are generally characterized by two bands, corresponding to symmetric and antisymmetric $\nu(\text{CO})_2$ stretching modes.¹² According to the data reported by Zeng et al., these bands should be separated by ~20 cm^{−1}. Experimentally, the half-width at half-height (HWHH) of the $\nu(\text{CO})$ band at 2112 cm^{−1} is 15 cm^{−1} (Figure 1). Thus, assuming that the antisymmetric $\nu_{\text{as}}(\text{CO})_2$ band has a nonnegligible intensity, the symmetric and antisymmetric $\nu(\text{CO})_2$ modes should appear as two resolved bands. This is not observed experimentally because only a symmetrically shaped band at 2112 cm^{−1} is observed at low CO coverage. It should be noted that the shoulder at ~2070 cm^{−1} only arises at higher CO coverages (Figure 1) and cannot account for the antisymmetric $\nu_{\text{as}}(\text{CO})_2$ mode. It is worth noting, however, that examination of these experimental $\nu(\text{CO})$ spectra should not allow one to distinguish monocarbonyl from dicarbonyl species if the latter showed an antisymmetric band of very weak intensity.¹³ To investigate this possibility and to definitely assign the $\nu(\text{CO})$ band at 2110 cm^{−1} to either monocarbonyl or dicarbonyl species,

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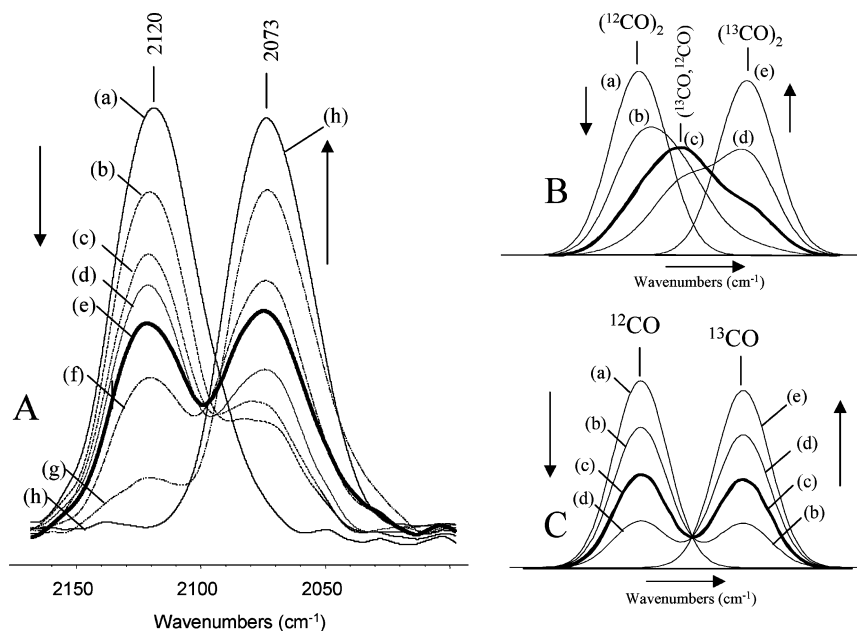


Figure 2. (A) IR spectra of $^{12}\text{CO}/^{13}\text{CO}$ mixtures adsorbed (298 K, equilibrium pressure of 1 Torr) on sulfided $\text{Mo}/\text{Al}_2\text{O}_3$ catalyst (8.7 wt % Mo). Spectrum a: pure ^{12}CO ; spectra b–g: mixtures of increasing ^{13}CO content. Spectrum h: pure ^{13}CO . (B and C) Simulated IR spectra for dicarbonyl and monocarbonyl adsorption, respectively. Spectra a: pure ^{12}CO ; spectra b–c: ^{12}CO – ^{13}CO mixtures: 75–25, 50–50, 25–75; spectra e: pure ^{13}CO .

we have carried out the adsorption of $^{12}\text{CO}/^{13}\text{CO}$ mixtures on $\text{MoS}_2/\text{Al}_2\text{O}_3$. Experiments were done at room temperature in order to avoid ^{13}CO adsorption on the support that would lead to $\nu(^{13}\text{CO})$ bands overlapping the $\nu(^{12}\text{CO})$ bands characterizing the sulfided phase.

Assuming the formation of monocarbonyl species, adsorption of the $^{12}\text{CO}/^{13}\text{CO}$ mixture should lead to the appearance of two bands corresponding to adsorbed ^{12}CO and ^{13}CO . By contrast, if dicarbonyl species are formed, then three bands are expected, corresponding to the symmetric stretching modes of $(^{12}\text{CO})_2$, $(^{12}\text{CO}, ^{13}\text{CO})$ and $(^{13}\text{CO})_2$ isotopomers. Figure 2A shows the infrared spectra recorded after the adsorption at room temperature of $^{12}\text{CO}/^{13}\text{CO}$ mixtures of various compositions on $\text{MoS}_2/\text{Al}_2\text{O}_3$ (1 Torr at the equilibrium). In these conditions (room temperature), CO only adsorbs on the sulfided phase. Adsorption of pure ^{12}CO (spectrum a) leads to a single band at 2120 cm^{-1} , upward shifted by 8 cm^{-1} as compared to adsorption at 100 K. Similarly, adsorption of pure ^{13}CO leads to a single band at 2073 cm^{-1} (spectrum h). The observed isotopic shift (47 cm^{-1}) corresponds to that expected from the variation of the reduced mass. The spectra obtained after adsorption of $^{12}\text{CO}/^{13}\text{CO}$ mixtures of intermediate compositions (spectra b–g) clearly result from the superimposition of the two bands at 2120 and 2073 cm^{-1} , that is, those obtained for pure ^{12}CO and ^{13}CO isotopes. In particular, no band at intermediate frequency that would correspond to the stretching mode of $(^{12}\text{CO}, ^{13}\text{CO})$ dicarbonyl species appear for $^{12}\text{CO}/^{13}\text{CO}$ mixtures of intermediate composition.

For comparison, we have simulated IR spectra that are expected for the adsorption of $^{12}\text{CO}/^{13}\text{CO}$ mixtures in the case of (i) dicarbonyl species (Figure 2B) and (ii) monocarbonyl species (Figure 2C). To obtain the theoretical spectra of dicarbonyl species, we have used the frequencies reported by Zeng et al. for the symmetric and antisymmetric modes (2102 and 2081 cm^{-1}) to compute the force constants in the harmonic approximation, which in turn were used to obtain the frequencies of the symmetric stretching modes of the three isotopic carbonyl species: 2102, 2080, and 2053 cm^{-1} for $(^{12}\text{CO})_2$, $(^{12}\text{CO}, ^{13}\text{CO})$, and $(^{13}\text{CO})_2$, respectively. It should be noted that the frequency

for $(^{12}\text{CO})_2$ computed by Zeng et al. (2102 cm^{-1}) is slightly lower than the $\nu(\text{CO})$ band observed experimentally (2020 cm^{-1} at room temperature, Figure 2A, spectrum a). Hence, for comparison with experimental data, the frequencies obtained for the three isotopomers (Figure 2B) should be shifted upward by $\sim 20 \text{ cm}^{-1}$. The relative intensities of these bands (Figure 2B) were computed assuming a statistic distribution of ^{12}CO and ^{13}CO molecules among the three isotopomers. The bandwidth was fixed to that observed experimentally (HWHH = 15 cm^{-1}). The simulated spectra for monocarbonyl species (Figure 2C) were computed assuming that the band at 2120 cm^{-1} corresponds to adsorbed ^{12}CO monocarbonyl species.

Assuming the formation of dicarbonyl species, Figure 2B clearly shows that adsorption of $^{12}\text{CO}/^{13}\text{CO}$ mixtures of increasing ^{13}CO content should first lead to the decrease in intensity of the high-frequency band due to $(^{12}\text{CO})_2$ species in favor of the band of intermediate frequency corresponding to $(^{12}\text{CO}, ^{13}\text{CO})$ species. This intermediate band has a maximum intensity for 50–50 $^{12}\text{CO}/^{13}\text{CO}$ mixtures (spectrum c) and further decreases in favor of the lowest frequency band, which is due to $(^{13}\text{CO})_2$ dicarbonyl species. By contrast, the spectra obtained assuming the formation of monocarbonyl species (Figure 2C) show a continuous decrease of the high-frequency band (^{12}CO monocarbonyl species) in favor of the low-frequency band (^{13}CO monocarbonyl species). Comparison of experimental (Figure 2A) and simulated spectra (Figures 2B and 2C) clearly shows that formation of dicarbonyl species cannot account for the experimental $\nu(\text{CO})$ spectra, because no frequency shift or broadening of the band at 2112 cm^{-1} is observed for the adsorption of $^{12}\text{CO}/^{13}\text{CO}$ mixtures. It should be noted that by contrast with simulated spectra of monocarbonyl species (Figure 2C) no clear isosbestic point is observed on experimental spectra (Figure 2A). This slight discrepancy is likely due to the heterogeneity of adsorption sites, which broadens the $\nu(\text{CO})$ bands toward low frequencies. In any case, synthetic spectra of Figure 2C are in good agreement with experimental observations. This, in our opinion, is clear and definitive spectroscopic evidence for the formation of monocarbonyl species on MoS_2 .

Finally, it is worth noting that Zeng et al. have considered

the possibility of a competitive adsorption between CO and H₂S on corner sites. Compared to H₂S, CO adsorption is energetically much favored and the authors thus conclude that H₂S should not compete with CO for the adsorption on these sites. However, the opposite is observed experimentally: CO/H₂S coadsorption experiments clearly show a strong decrease of the band at 2112 cm⁻¹ when CO is adsorbed after H₂S preadsorption on MoS₂ catalysts (see figure 4 of ref 9). This shows that H₂S adsorption on the sites giving rise to the band at 2112 cm⁻¹ is favored as compared to CO adsorption and contradicts the proposal of Zeng and co-workers.

In conclusion, the strong $\nu(\text{CO})$ band at 2112 cm⁻¹ is not due to dicarbonyl species. In a previous study, we have assigned this band to CO adsorbed as monocarbonyl species on the molybdenum edge of MoS₂. Evidently, this assignment based on periodic DFT calculations can still be discussed because many parameters, such as the influence of the support, are not taken into account in such calculations. In any case, however, the $\nu(\text{CO})$ band at 2112 cm⁻¹ can be assigned to monocarbonyl species adsorbed on MoS₂. Evidently, this does not exclude the possibility of dicarbonyl species in small amounts, which could contribute to the low-frequency band at ~ 2070 cm⁻¹.⁹

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References and Notes

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