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Spectroscopy, microscopy and theoretical study of NO adsorption on MoS_2 and Co–Mo–S hydrotreating catalysts

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ABSTRACT

Infrared (IR) spectroscopy using NO as a probe molecule has been one of the important methods for characterizing hydrotreating catalysts, since this technique provides information on the nature and quantity of active edge sites of these catalysts. However, due to the strong adsorption of NO, which may lead to significant edge reconstructions, it has not been clear, how the characteristics of the adsorption complexes may reflect the nature of the original edge sites. By combining IR spectroscopy measurements with scanning tunneling microscopy (STM) experiments and density functional theory (DFT) calculations, we present new atomic-scale insight into the nature of NO adsorption on MoS_2 and Co–Mo–S nanoclusters. The DFT calculations and STM experiments show that NO does not adsorb at fully sulfided MoS_2 edges not containing hydrogen. However, typical sulfided catalysts will have hydrogen present at the edge in the form of S–H groups. For such samples, the results indicate a "push–pull" type mechanism involving simultaneous vacancy creation, NO adsorption and H_2S release. This mechanism is observed to dominate in the IR experiments. In STM experiments, stable vacancies can be generated by dosing atomic hydrogen, and these vacancies are observed to adsorb NO dimers. The detailed nature of the adsorption is revealed by DFT. IR measurements recorded during temperature-programmed desorption (TPD) show the presence of several NO adsorption complexes and the assignment to specific species is achieved by comparison to calculated frequencies and adsorption energies obtained from DFT. The results show that mononitrosyl species dominate at the Mo-edges, whereas stable dinitrosyl species are found at both the unpromoted and the Co-promoted S-edges. Thus, based on the present results, it is possible to use NO as a probe molecule to obtain detailed atomic-scale information on hydrotreating catalysts and the origins of activity differences.

1. Introduction

In order to meet the increasing demands for the production of ultra clean transportation fuels [1], there is a need to obtain an atomic-scale understanding of the nature of the active sites involved in different hydrotreating reactions for both unpromoted and promoted MoS_2-based catalysts [2–8]. Specifically, a better insight into the sites involved in hydrogenation and hydrogenolysis reactions in both unpromoted and promoted MoS_2-based catalysts is desirable, since the relative significances of the two types of reactions depend strongly on both the feedstocks and the required conversions [2,9–13]. For many years, information regarding the surface binding sites in hydrotreating catalysts has mainly been obtained by the use of different spectroscopic techniques [2], and one of the most important approaches has been to follow the adsorption of different probe molecules such as NO [14–32] and CO [28,33–42] by means of infrared (IR) spectroscopy. For example, IR studies of NO adsorption made it possible to distinguish different adsorption complexes for both unpromoted and promoted catalysts [16–18,43]. This is a distinct advantage compared to other extensively used characterization methods like oxygen chemisorption [44]. Combined IR_NO studies and extended X-ray adsorption fine structure (EXAFS) spectroscopy experiments on sulfided Mo/Al_2O_3 catalysts showed that NO molecules were adsorbed on MoS_2 edges and not on the basal planes [45]. Typical IR spectra of Co/Al_2O_3, Mo/Al_2O_3 and Co–Mo/Al_2O_3 catalysts after sulfidation are shown in Fig. 1 (adapted from Ref. [43]). These spectra show that it is possible to distinguish between NO adsorption on the Co and Mo sites, since some of the bands do not overlap. In Fig. 1b, we show for a series of catalysts with constant Mo loading a plot of the NO-IR absorbance of the high-frequency band due to NO adsorbed on Co (around 1850 cm^{-1}) and the low-frequency

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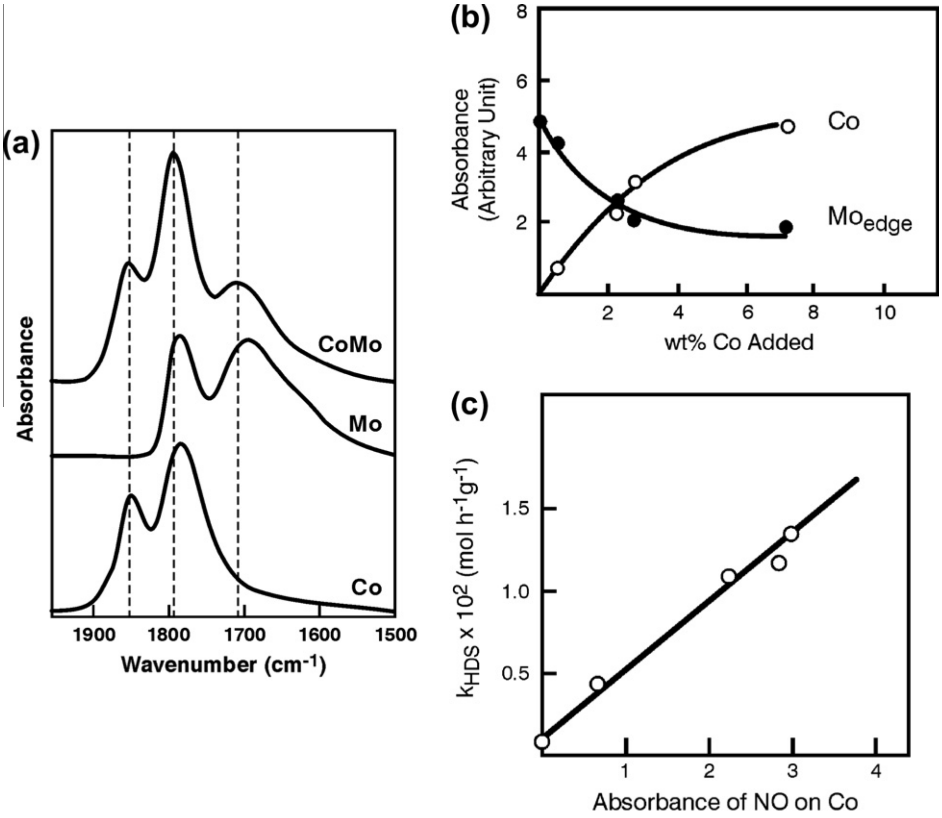

Fig. 1. (a) IR spectra of NO adsorbed on sulfided 2% Co/Al_2O_3, 8% Mo/Al_2O_3 and 2%Co 8%Mo/Al_2O_3. (b) Absorbance of IR bands of NO adsorbed on Co (1850 cm^{-1}) and Mo (1690 cm^{-1}) plotted as function of Co/Mo ratio at constant Mo loading. (c) Thiophene HDS activities vs. absorbance of IR band of NO adsorbed on Co. The figure is adapted from Ref. [43].

band due to NO adsorbed on Mo (around 1690 cm^{-1}) as function of Co loading. The simultaneous decrease in the absorbance of the Mo–NO band and increase in the Co–NO band revealed that the Co atoms are located at the MoS_2 edges, and this provided important new insight into the nature of the Co–Mo–S structure. Fig. 1c shows that there is a linear correlation between the absorbance of NO on the Co sites and the thiophene HDS catalytic activity. This correlation demonstrated clearly that NO probes the Co-promoted sites in Co–Mo–S, which are responsible for the activity increase. For the less-active unpromoted Mo/Al_2O_3 catalysts, IR results also showed correlations between the activity and the amount of MoS_2 edge sites titrated by NO [45]. NO adsorption is also a useful tool for characterizing industrial catalysts, and Fig. 2 shows data for NO absorbance on Co sites versus real feed catalytic activity for industrial-type hydrotreating catalysts. Even though the correlation is less clear than for the model catalysts, this example nonetheless illustrates the usefulness of NO adsorption to assess catalytically active sites and explains the popularity of this method.

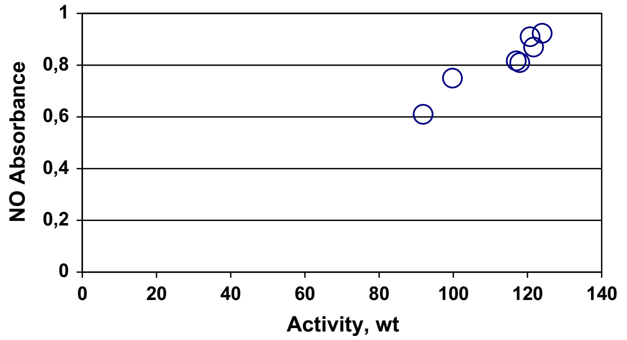

Fig. 2. Absorbance of IR band of NO adsorbed on Co site (1850 cm^{-1}) on sulfided CoMo/Al_2O_3 industrial catalysts versus real feed activity per weight.

In view of the usefulness of this technique, there has for many years been a strong interest in obtaining a detailed understanding of the nature and location of the different adsorption complexes. In an early approach for obtaining such knowledge, the observed IR frequencies for hydrotreating catalysts were compared to those observed for well-defined NO-containing inorganic metal sulfur clusters [46]. Such studies showed that the adsorption complexes had many similarities to dinitrosyl complexes exhibiting pseudotetrahedral coordination around the adsorbing atom. Also isotopic exchange studies [47] were consistent with a dinitrosyl behavior of the adsorption complex. More recently, detailed desorption [24], electron paramagnetic resonance [48] and magnetic studies [31] have also provided further insight, but many questions still remain. For example, in view of the strong bond of the edge sites with NO, it is possible that the local geometry of the adsorption complex differs from that of the original surface sites, such that significant reconstructions on the edges of the MoS_2 nanoclusters may take place [16–18]. In order to avoid substantial surface reconstructions, it may be advantageous to use CO as a probe molecule [40]. However, the frequencies of the NO adsorption bands are more sensitive toward changes in the catalyst structure, and the NO adsorption technique has found widespread use in the study of many catalyst systems [16–18,29]. Both CO and NO adsorption on hydrotreating catalysts have recently been studied by density functional theory (DFT). CO adsorption has been studied theoretically on MoS_2, Co–Mo–S and Ni–Mo–S catalysts [40,41,49–53] and NO adsorption on unpromoted MoS_2 catalysts [54,55].