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CO adsorption on highly dispersed MoP/Al_2O_3 prepared with citric acid

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Abstract

Calorimetry of CO adsorption was used for the first time to study the surface properties of alumina-supported molybdenum phosphide (MoP/Al_2O_3). To increase the dispersion of MoP active sites, the sample was prepared by novel citric acid-temperature programmed reduction (CA-TPR) method. Fourier transform infrared spectroscopy (FT-IR) of CO adsorption confirmed the formation of MoP by CA-TPR method. The calorimetry results proved that the novel method increased the amounts of active sites and led to the formation of a highly dispersed alumina-supported MoP, but the adsorption heat and the active sites distribution were not much affected by the preparation method. Furthermore, the energetic distribution of active sites depended on the MoP loading.

Keywords: Calorimetry; FT-IR; CO adsorption; Alumina-supported molybdenum phosphide; Citric acid

1. Introduction

Calorimetry of chemisorbed probe molecules is a powerful tool to study the solid surface [1,2]. It gives information on the energy of interaction of the reactive molecules with the surface active sites, which is related to the surface structure. Moreover, adsorption calorimetry can provide an energetic distribution of the surface active sites as a function of coverage and more accurate adsorption heat values than those obtained from other techniques. For example, calorimetry has been used to study the acid or base strength of oxides [3], metals [4,5], and metal nitrides [6]. However, adsorption calorimetry is scarcely applied to supported metal phosphides. There is only one report on calorimetry of CO and H_2 adsorption on amorphous nickel phosphide (Ni–P) alloy particles [7].

Much attention has recently been focused on molybdenum phosphide (MoP) due to its excellent catalytic properties in hydrodenitrogenation (HDN) and hydrodesulfurization (HDS) [8–11]. As an efficient catalyst, the active phase is always well dispersed over the surface of a support material and high dispersion can enhance the performance of the catalyst. However it should be mentioned that the dispersion of MoP on alumina is difficult to manage, because the molybdate as well as the phosphate interacts strongly with the alumina surface sites [11]. To overcome this problem, a new synthesis procedure with citric acid addition was designed. Adding citric acid as a chelating agent is a simple and efficient way to prepare highly dispersed metal or metal oxide heterogeneous catalysts [12], but no work has been done to synthesize a highly dispersed MoP/Al_2O_3 with citric acid.

In this paper, CO adsorption calorimetry is applied to study the surface states of alumina-supported molybdenum phosphide for the first time. The detailed schematic of this analysis system was developed in our laboratory and has been used to determine the chemical reactivity of the solid surface by exploring the strength of reactant and products chemisorption [13,14]. The MoP/Al_2O_3 samples were prepared by two different methods including the novel citric acid-temperature programmed reduction (CA-TPR) and the conventional temperature programmed reduction (TPR) [11]. Moreover, Fourier transform infrared (FT-IR) of CO adsorption was used to further investigate the surface chemical states and the active sites of the samples.

2. Experimental

2.1. Sample preparation

The Al_2O_3-supported MoP precursor was prepared by incipient impregnating Al_2O_3 (20–40 mesh, 184 $cm^2\,g^{-1}$, pore volume 1.1 $ml\,g^{-1}$) in a solution with chelating agent (citric acid). The solution was obtained as follows: after the complete

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dissolution of appropriate amounts of $(NH_4)_6Mo_7O_{24}\cdot4H_2O$ and $(NH_4)_2HPO_4$ with the theoretical MoP loading of 8% and 13%, citric acid (CA) was added with a molar ratio of CA:Mo:P = 2:1:1. The resulting materials were dried at 120 °C for 12 h, and then calcined in air at 500 °C for 5 h. After calcination, the samples were reduced via temperature programmed reduction at 850 °C with a heating rate of 2 °C min^{-1} for 2 h. Finally, the synthesized samples were passivated in a flow of 1% O_2/N_2 for 2 h at room temperature, and are denoted as 8% MoP-CA2.0/Al_2O_3 and 13% MoP-CA2.0/Al_2O_3.

The citric acid-free simples were prepared by conventional temperature programmed reduction. The detailed preparation procedure was described in an earlier study [11], and the samples are hereafter denoted as 8% MoP-CA0/Al_2O_3 and 13% MoP-CA0/Al_2O_3.

2.2. *Sample characterization*

The X-ray diffraction (XRD) patterns of the samples were obtained with a Rigaku powder X-ray diffractometer operated at 100 kV and 40 mA with Cu Kα monochromatized radiation. The specific surface areas were determined using the BET method based on N_2 adsorption isotherms in a Micromeritics-ASAP 2010. Thermal analysis measurements (thermogravimetry, TG) were carried out by a Shimadzu DT 20B thermal analyzer in an air flow with a rate of 10 ml min^{-1} at a heating rate of 10 °C min^{-1} up to 600 °C.

2.3. *Calorimetry of CO adsorption*

The dispersion of the active sites of MoP/Al_2O_3 was determined volumetrically by means of CO adsorption with simultaneous measurement of the evolved heats at 30 °C by a Tian–Calvet heat-flow calorimeter (Setaram, BT 2.15). The apparatus was similar to that described in our earlier studies [13,14]. The use of a capacitance manometer (MKS 689A) ensured a high degree of precision in determining the amount adsorbed.

A well-established stepwise procedure was followed as previously described [13]. The passivated MoP/Al_2O_3 was evacuated to 10^{-1} Pa and then reduced in a special treatment cell in flowing H_2 from room temperature to 700 °C in 1 h and held constant for 2 h. After reduction, the sample was outgassed in the quartz cell at 700 °C for 0.5 h under high vacuum, then transferred to a side-armed Pyrex flask and sealed in a Pyrex capsule. The capsule minimizes the possible contamination in the high vacuum system during the course of thermal equilibrium (6–8 h) with the calorimeter. After thermal equilibrium was reached, the capsule was broken by a vacuum feedthrough and the fresh sample was exposed. The calorimetric data were then collected by sequentially introducing small doses (1–10 μmol) of CO onto the sample. Through the measurement of the CO amounts adsorbed at increasing pressures and the heats evolved in the adsorption of the subsequent doses of CO, the differential heat versus CO coverage plots and adsorption isotherms can be simultaneously obtained. Dead volume of the volumetric apparatus was carefully calibrated by He expansion. The adsorbed CO was purified with several freeze-thaw cycles using liquid nitrogen.

The metal dispersion was obtained from the total amount of CO uptake at the monolayer. The monolayer uptake was determined by extrapolating the linear part of the isotherm fitted curve to zero pressure.

2.4. *FT-IR of CO adsorption*

The FT-IR of CO adsorption was conducted at room temperature on a Fourier transform infrared spectrometer (Bruker Equinox 55) with a resolution of 4 cm^{-1} and 64 scans in the region of 4000–1000 cm^{-1}. In this work, a passivated sample (ca. 20 mg) was pressed into a self-supporting wafer and put into a quartz IR cell with CaF_2 windows and treated again in the FT-IR cell. The FT-IR experiment was carried out as follows: the MoP/Al_2O_3 was rereduced from room temperature to 700 °C at a rate of 10 °C min^{-1}, and held constant for 2 h. To remove the weakly bonded species from the surface, the cell was evacuated to 10^{-3} Pa at 700 °C for 0.5 h. After the cell was cooled to room temperature, then CO was introduced. The spectrum was collected after the system was evacuated to 10^{-1} Pa.

3. Results and discussion

The specific surface areas of the MoP/Al_2O_3 samples are listed in Table 1. The surface areas decrease gradually with the incorporation of phosphides onto the support and the increase of the MoP loadings. It is also seen that all the MoP/Al_2O_3 samples prepared with citric acid have slightly higher surface areas. This means that adding citric acid is favorable to disperse the MoP active sites on the surface of support.

The XRD patterns of the alumina-supported MoP samples along with the PDF reference pattern (PDF 24-0771) are presented in Fig. 1. The figure shows that there is no characteristic peak found in the patterns of 8% MoP-CA0/Al_2O_3 and 8% MoP-CA2.0/Al_2O_3 samples, indicating the high dispersion of MoP phase on the support. While for the 13% MoP-CA0/Al_2O_3 and 13% MoP-CA2.0/Al_2O_3 samples, only the peak at $2\theta \sim 43°$ corresponding to MoP (1 0 1) occurs.

Fig. 2 shows the FT-IR spectra of CO adsorption on 8% MoP-CA0/Al_2O_3 and 8% MoP-CA2.0/Al_2O_3 samples. A characteristic IR band at 2048 cm^{-1} is observed for the samples, and is identical to the main band obtained before [15]. This band is assigned to linearly adsorbed CO on the surface Mo atoms of MoP. Therefore, the FT-IR spectra confirmed the formation

Table 1
Specific surface areas, CO uptakes, and MoP dispersions of MoP/Al_2O_3

	S_{BET} ($m^2 g^{-1}$)	N_{Ads}[a] (μmol g^{-1})	D (%)[b]
Al_2O_3	184.0	–	–
8% MoP-CA0/Al_2O_3	155.3	80	12.7
8% MoP-CA2.0/Al_2O_3	161.9	105	16.7
13% MoP-CA0/Al_2O_3	128.0	100	9.8
13% MoP-CA2.0/Al_2O_3	136.1	125	12.2

[a] Monolayer uptake of CO adsorption.
[b] CO uptake (μmol g^{-1} cat)/theoretical amounts of MoP (μmol g^{-1} cat).

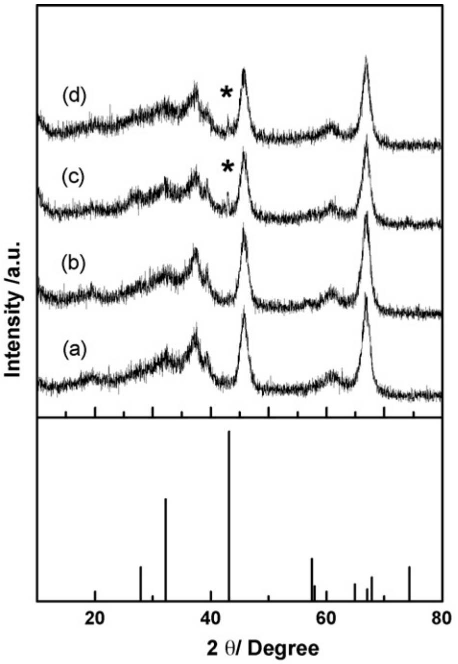

Fig. 1. X-ray diffraction patterns of the samples: (a) 8% MoP-CA0/Al_2O_3, (b) 8% MoP-CA2.0/Al_2O_3, (c) 13% MoP-CA0/Al_2O_3, (d) 13% MoP-CA2.0/Al_2O_3, and the reference of MoP (PDF24-0071).

of crystallinic MoP. The intensity of the band at 2048 cm^{-1} on MoP-CA2.0/Al_2O_3 is clearly stronger than that on MoP-CA0/Al_2O_3, demonstrating that the novel method leads to more active sites.

The plots of differential heats of CO adsorption at 30 °C for 8% MoP/Al_2O_3 and 13% MoP/Al_2O_3 samples prepared with and without citric acid are given in Fig. 3. It shows that the 8% MoP-CA0/Al_2O_3 sample exhibits an initial differential heat of CO adsorption of 117 kJ mol^{-1}. Then the differential heat falls sharply to a small plateau circa 95 kJ mol^{-1}, and decreases slowly to 40 kJ mol^{-1}. The 8% MoP-CA2.0/Al_2O_3 has a similar initial differential heat for CO adsorption but a smoother CO adsorption curve. This indicates a higher homogeneity of the active sites on the sample prepared with citric acid. But for the 13% MoP-CA0/Al_2O_3 and 13% MoP-CA2.0/Al_2O_3, a portion of the active sites with high energy (about 3 μmol g^{-1}) disappears with respect to the 8% MoP-CA0/Al_2O_3 and 8% MoP-CA2.0/Al_2O_3. The initial differential heats are 95 kJ mol^{-1}, which correspond to the plateau values of 8% MoP-CA0/Al_2O_3 and 8% MoP-CA2.0/Al_2O_3. The disappearance of the most active sites is likely the reason for the lower initial differential heat due to the strong interaction between the phosphate and alumina [11,16]. Moreover, the higher loading results in a complicated MoP/Al_2O_3 precursor, which is difficult to be reduced to obtain the final product [11]. It is likely that the introduction of more phosphate changes the surface of support.

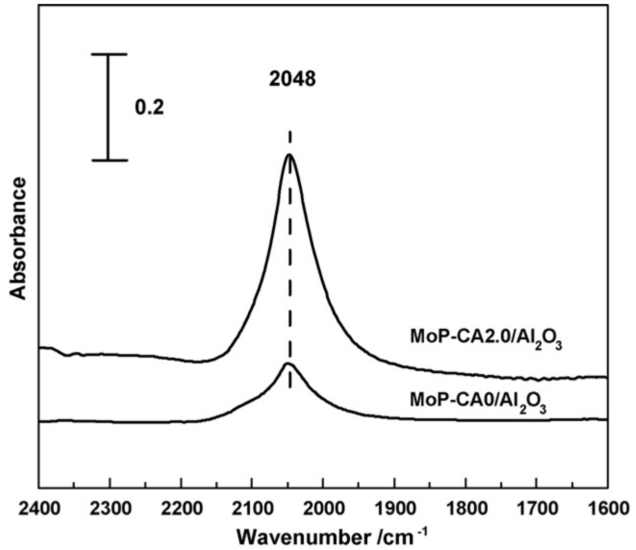

Fig. 2. FT-IR spectra of CO adsorption on 8% MoP-CA0/Al_2O_3 and 8% MoP-CA2.0/Al_2O_3 at room temperature.

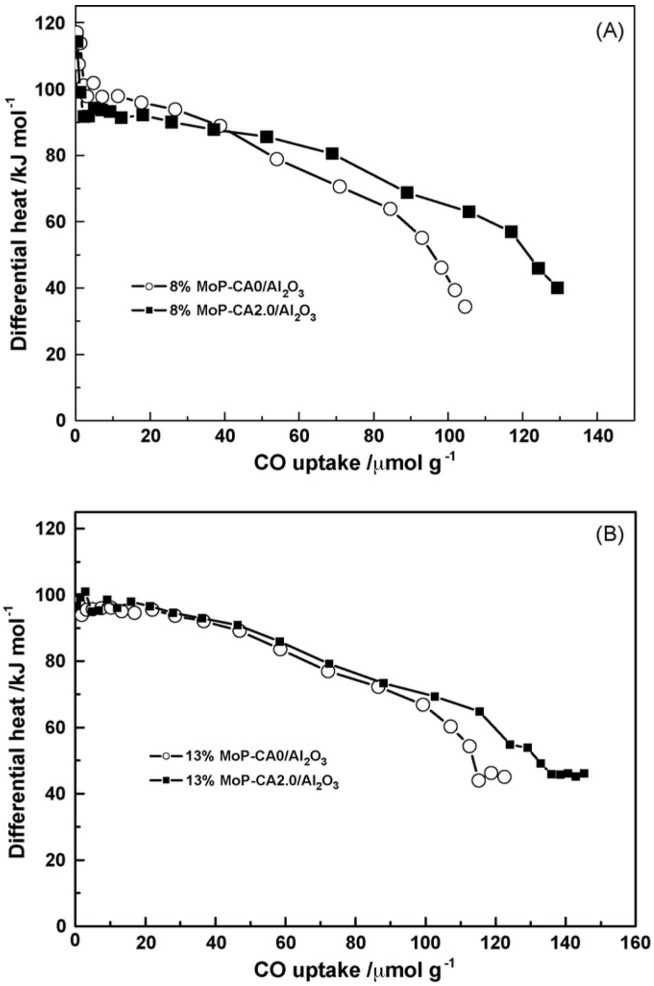

Fig. 3. Differential heats of CO adsorption on: (A) 8% MoP-CA0/Al_2O_3 and 8% MoP-CA2.0/Al_2O_3; (B) 13% MoP-CA0/Al_2O_3 and 13% MoP-CA2.0/Al_2O_3 at 30 °C.

To facilitate the comparison of the different MoP/Al_2O_3 samples, the curves representing differential heats of CO adsorption plotted as a function of CO coverage are shown in Fig. 4. Except for the slightly higher initial differential heats for samples with lower loading, the curves of the four samples are almost the same, which means that the novel CA-TPR method does not change the nature of the MoP surface sites. Therefore,

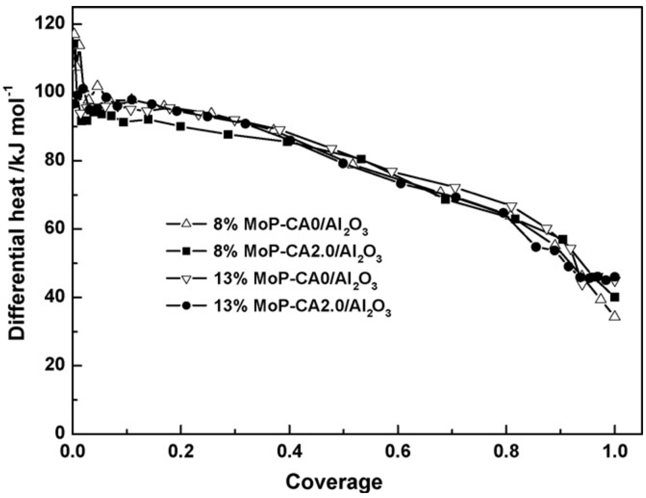

Fig. 4. Differential heats of CO adsorption as a function of surface coverage on MoP/Al_2O_3 samples at 30 °C.

the samples prepared with citric acid maintain the distribution of site strength for CO adsorption. In this sense, it is clear that the calorimetry of CO adsorption is a useful tool to detect the dispersion of the phosphide active sites on the support.

Fig. 5 displays the adsorption isotherms of CO adsorption on the MoP-CA0/Al_2O_3 and MoP-CA2.0/Al_2O_3 samples at 30 °C. The values for 8% MoP-CA0/Al_2O_3 and 8% MoP-CA2.0/Al_2O_3 are 80 and 105 μmol g^{-1}, respectively, while the monolayer uptakes of 13% MoP-CA0/Al_2O_3 and 13% MoP-CA2.0/Al_2O_3 are 100 and 125 μmol g^{-1}, respectively. Table 1 summarizes the CO uptakes and the MoP dispersions of MoP/Al_2O_3. The MoP dispersions of various samples are calculated by assuming a MoP/CO = 1 stoichiometry [15]. The dispersions of the samples prepared with citric acid are obviously higher than those of the samples prepared without citric acid. For example, for the 8% MoP/Al_2O_3 samples prepared without and with citric acid, the dispersions of active sites are 12.7% and 16.7%, respectively. Similar results are also observed for the 13% MoP-CA0/Al_2O_3 and 13% MoP-CA2.0/Al_2O_3 samples. It also shows that the dispersions of samples with higher loading are smaller than those of the samples with lower loading. This is consistent with the observation of crystalline phases for the phosphide, as evidenced by the XRD results.

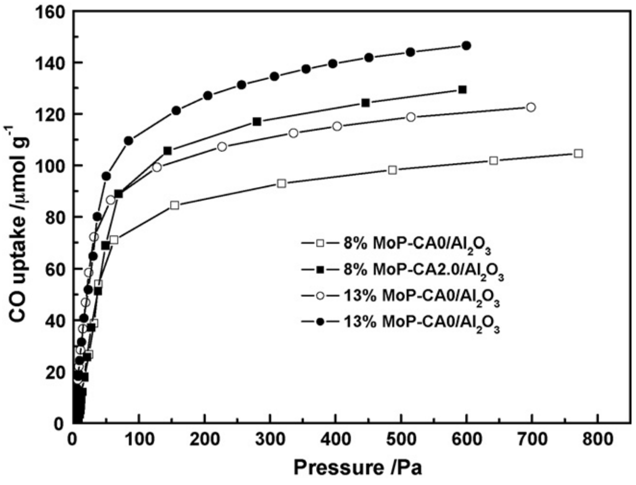

Fig. 5. Isotherms of CO adsorption on MoP/Al_2O_3 samples at 30 °C.

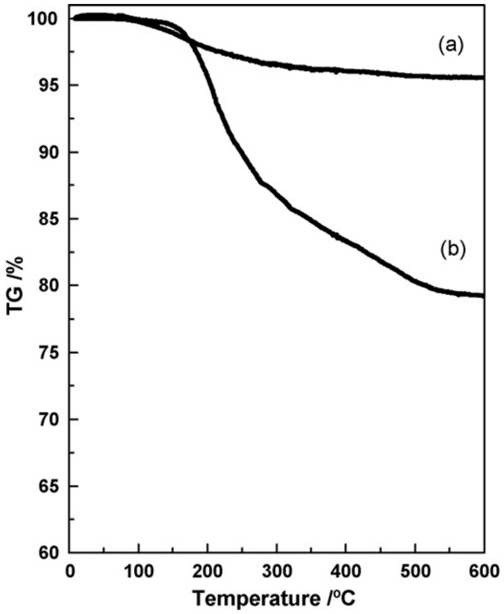

Fig. 6. TG curves of dried samples: (a) 8% MoP-CA0/Al_2O_3 and (b) 8% MoP-CA2.0/Al_2O_3.

To explain the effect of the citric acid, we carried out TG experiments. Fig. 6 shows the TG curves of the dried samples of 8% MoP-CA0/Al_2O_3 and 8% MoP-CA2.0/Al_2O_3. The total weight losses are 4.3% and 19.5% for two samples at 600 °C in the TG curves. The corresponding theoretical values are 5.2% and 22.4%, respectively. The calculation of theoretic weight loss for the sample without citric acid is based on the following reaction [10]:

$$\begin{aligned}&2(NH_4)_6Mo_7O_{24}\cdot 4H_2O\ +\ 14(NH_4)_2HPO_4\\&\quad\rightarrow\ 14MoO_3\cdot 7P_2O_5 + 40NH_3 + 35H_2O\end{aligned}$$

For the sample with citric acid, the calculation is based on the following reaction with an assumption that the citric acid completely decomposes in the calcination:

$$\begin{aligned}&2(NH_4)_6Mo_7O_{24}\cdot 4H_2O\\&\quad + 14(NH_4)_2HPO_4 + 28C_6H_8O_7 + 126O_2\\&\quad\rightarrow\ 14MoO_3\cdot 7P_2O_5 + 40NH_3 + 147H_2O\ +\ 168CO_2\end{aligned}$$

It also should be noted that the onset of the weight loss of the dried MoP-CA2.0/Al_2O_3 is significantly higher than that of the MoP-CA0/Al_2O_3, meaning that the complex of citric acid and Mo is stable and decomposes only at higher temperatures. Meanwhile, due to the gelation of citric acid, the viscosity of solution increases substantially upon gradual removal of the solvent [12]. The enhanced viscosity inhibits the redistribution of the impregnation solution during drying. The above two reasons favor a uniform distribution of the active component over the alumina support.

4. Conclusions

In this work, we successfully applied CO adsorption calorimetry to study the highly dispersed MoP/Al_2O_3 samples prepared by two methods, i.e., novel citric acid-temperature programmed reduction (CA-TPR) and conventional temperature programmed reduction (TPR). The calorimetric results showed that the MoP/Al_2O_3 prepared with citric acid exhibited a higher dispersion of active sites on the support. It was also found that the adsorption heat value and the active sites distribution of MoP/Al_2O_3 were independent of the preparation method. The increased viscosity of the solution and the slower decomposition of the complex of citric acid with Mo inhibited the redistribution of active sites over alumina during the preparation of the precursor.

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