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Journal of Catalysis 249 (2007) 397–400
JOURNAL OF CATALYSIS
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Research Note

Molybdenum phosphide, a new hydrazine decomposition catalyst: Microcalorimetry and FTIR studies

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Received 5 January 2007; revised 5 April 2007; accepted 8 April 2007

Abstract

Unsupported and Al_2O_3-supported molybdenum phosphides (MoP) were tested as catalysts for the decomposition of hydrazine (N_2H_4), in comparison with previously studied Mo_2N catalysts. The results showed that the activity increased with MoP loading on the MoP/Al_2O_3 catalysts and that the supported MoP catalysts were more stable during hydrazine decomposition compared with the supported Mo_2N catalysts. FTIR results indicated that N_2H_4 decomposed on the Mo sites on the MoP, similar to the case of Mo_2N. FTIR and microcalorimetric adsorption measurements showed that NH_3 was adsorbed only moderately on the MoP catalyst, giving it better catalytic stability than the Mo_2N, for which strong adsorption of NH_3 blocked the active sites and led to a sharp decrease in activity.

Keywords: Hydrazine decomposition; Molybdenum phosphide; Molybdenum nitride; Microcalorimetry; FTIR spectroscopy

1. Introduction

The catalytic decomposition of N_2H_4 is an important reaction used in microthrusters for satellite attitude control and maneuvering [1,2]. The conventional catalyst used in this reaction is Ir/Al_2O_3. However, due to its high price and relative scarcity, considerable research has been focused on the development of low-cost and widely available substitutes. It is known that transition metal nitrides and carbides catalyze many reactions that are typically catalyzed by noble metals [3–5]. Our previous work showed that Al_2O_3-supported Mo_2C and Mo_2N, with high mechanical strength, were as active as Ir/Al_2O_3 for N_2H_4 decomposition in a 10 N monopropellant thruster [6–9].

MoP is a metallic conductor with properties similar to intermetallic compounds. Some reports have been published concerning the use of MoP in hydroprocessing reactions [10–15]. Recently, we successfully synthesized a high-surface area MoP by combining citric acid with a temperature-programmed reduction (CA-TPR) method, and found that MoP also was active for N_2H_4 decomposition [16]. In the present work, we studied the catalytic performance and adsorption properties of the MoP in comparison with Mo_2N, with the aim of revealing the effect of metalloids on Mo atoms in N_2H_4 decomposition.

2. Experimental

2.1. Catalyst preparation

Unsupported MoP was prepared according to the procedure of Stinner et al. [11]. Stoichiometric amounts of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and $(NH_4)_2HPO_4$ were dissolved in deionized water. After water evaporation, the white solid was further dried at 393 K for 12 h and calcined in air at 773 K for 5 h. The sample was then reduced with H_2 at 923 K for 2 h, and finally passivated in a flow of 1% O_2/N_2 for 2 h at room temperature.

MoP/Al_2O_3 catalysts with loadings of 8, 13, and 20 wt% were synthesized by impregnating γ-Al_2O_3 support with an aqueous solution of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and $(NH_4)_2HPO_4$. To obtain 20 wt% MoP loading, double impregnations were used. After drying and calcining, the samples were reduced at 1123 K for 2 h and then passivated in a flow of 1% O_2/N_2 for 2 h at room temperature.

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doi:10.1016/j.jcat.2007.04.007

Unsupported Mo_2N and supported Mo_2N/Al_2O_3 were prepared by the temperature-programmed reaction of MoO_3 and MoO_3/Al_2O_3 (8.7 wt%) with NH_3 [8].

2.2. Catalyst tests

Catalytic tests were performed at atmospheric pressure in a microreactor [8]. A catalyst sample (40 mg for unsupported catalysts and 50 mg for supported catalysts) was diluted with silica and placed in the quartz reactor. Before the reaction, the catalyst was prereduced in H_2 at 923 K (for MoP) or 973 K (for MoP/Al_2O_3) for 0.5 h. Similarly, the unsupported Mo_2N and Mo_2N/Al_2O_3 were renitrided with NH_3 at 973 K for 0.5 h before the activity tests. The feed gas N_2H_4/Ar (3% V/V) was introduced into the reactor at a rate of 85 ml min^{-1}. N_2H_4 conversion and H_2 selectivity were used to evaluate the catalytic performance [17].

2.3. NH_3 microcalorimetry

The microcalorimetry of NH_3 adsorption was performed at 423 K using a Calvet-type microcalorimeter (Setaram BT 2.15) [18]. Before measurements, the samples were pretreated following the same procedures used for reaction tests. The samples were outgassed at the final temperature for 0.5 h, and then cooled to room temperature to allow sample transference. The microcalorimetric data were collected by successively introducing doses of NH_3 to the sample. The dead volume of the volumetric apparatus was carefully calibrated by He expansion.

2.4. FTIR studies

FTIR spectra were collected at room temperature with a Bruker Equinox 55 spectrometer at a resolution of 4 cm^{-1} using 64 scans. Before adsorption, the samples were pretreated following the same procedures used for the reaction tests, then cooled to room temperature and evacuated to about 10^{-3} Pa. The probing gases, including N_2H_4, CO, and NH_3, were purified with liquid nitrogen. N_2H_4 was dosed from a variable leak valve.

3. Results and discussion

3.1. Reactivity studies

Fig. 1 shows the N_2H_4 conversions at 303 K with time on stream over the various MoP and Mo_2N catalysts. The conversion of N_2H_4 over the unsupported MoP was >90% initially and gradually decreased with time on stream, to 85% after a 170-min run. It was 100% on the unsupported Mo_2N in the initial 20 min, but rapidly decreased to <80% after 170 min on stream. For the supported MoP catalysts, N_2H_4 conversion was enhanced with increased MoP loading and remained stable during the reaction period. For the Al_2O_3-supported Mo_2N catalyst, rapid deactivation behavior was observed during an 80-min run, indicating the supported MoP catalysts have better stability than the supported Mo_2N in N_2H_4 decomposition reaction.

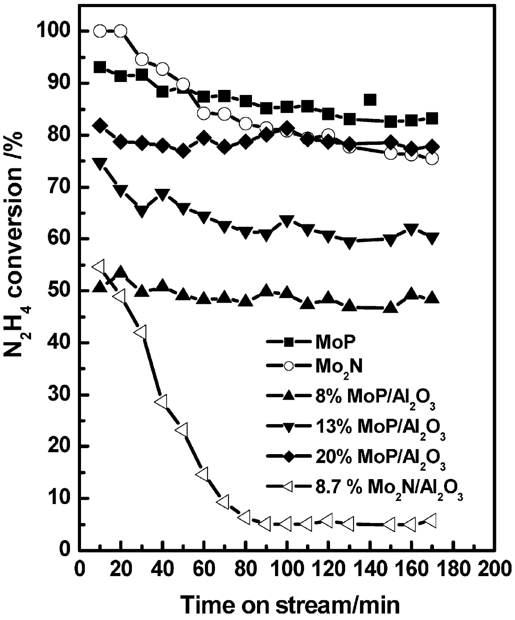

Fig. 1. N_2H_4 conversions at 303 K with the time on stream over supported and unsupported MoP and Mo_2N catalysts.

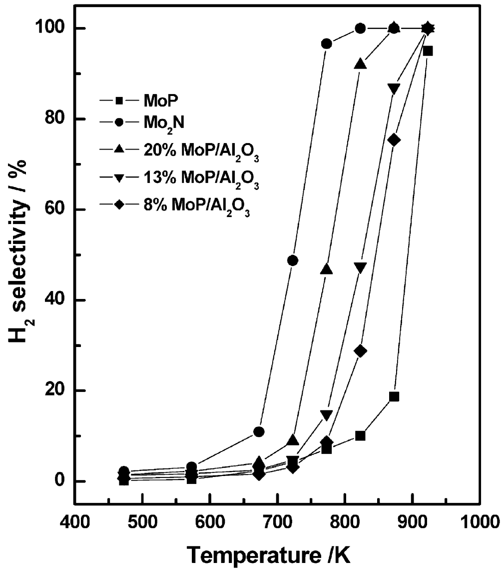

Fig. 2. Variation in H_2 selectivities with the reaction temperature over MoP, Mo_2N, and MoP/Al_2O_3 catalysts.

Fig. 2 presents the H_2 selectivities with the reaction temperature over the different catalysts. The selectivities on all catalysts were low below 673 K. With increasing the reaction temperature, the generated NH_3 could be further dissociated, leading to the production of H_2 [8,9,17]. The unsupported Mo_2N exhibited the highest H_2 selectivities among all the investigated samples, suggesting that Mo_2N is a good catalyst for NH_3 decomposition [3]. In contrast to Mo_2N, the unsupported MoP shows the lowest H_2 selectivity, indicating that it is a poor catalyst for NH_3 decomposition. H_2 selectivity was improved when supporting MoP onto Al_2O_3, and also increased with increasing MoP loading.

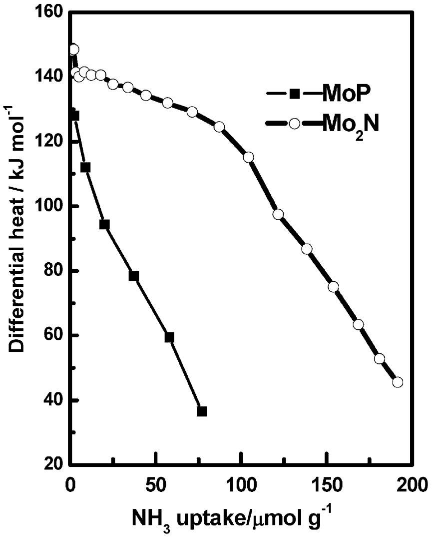

Fig. 3. Differential heats of NH_3 adsorption versus uptake on MoP and Mo_2N at 423 K.

3.2. NH_3 adsorption microcalorimetry

Because NH_3 is both a product and intermediate in hydrazine decomposition [2], it can be used as a probe to study the active sites of MoP or Mo_2N catalysts. Fig. 3 shows the differential heats versus the NH_3 adsorption uptake for MoP and Mo_2N at 423 K. For MoP, the heat of NH_3 adsorption was 130 kJ mol^{-1} initially and dropped dramatically to the range of physical adsorption (<40 kJ mol^{-1}). The trend of continuously decreasing differential heat indicates a highly heterogeneous surface of the MoP. The initial adsorption heat of NH_3 on Mo_2N was as high as 148 kJ mol^{-1}, and the differential heat curve showed a plateau above 130 kJ mol^{-1}. The adsorption heat then decreased gradually to 40 kJ mol^{-1}. These findings indicate that the NH_3 adsorption is much stronger on Mo_2N than on MoP.

The differences in NH_3 adsorption on MoP and Mo_2N shown in the microcalorimetric experiments could be due to the difference in surface sites. A $3p$-group element should not be as strong as a $2p$-group element as an electron acceptor. A theoretical study based on density functional theory (DFT) has shown that the Mo–P bond in MoP is less ionic than the Mo–N bond in Mo_2N [14]. Thus, the Mo in Mo_2N should have stronger Lewis acidity than the Mo in MoP, resulting in stronger adsorption of NH_3 on Mo_2N. For the decomposition of N_2H_4, such strongly bound NH_3 and/or nitrogen fragments left on the catalyst surface may poison the catalyst, possibly accounting for the declining activity of Mo_2N. The relatively weak NH_3 adsorption on MoP might be the reason for its low H_2 selectivity in the decomposition of N_2H_4.

3.3. FTIR

To gain insight into the nature of the N_2H_4 decomposition on the MoP catalysts and shed light on the difference between MoP and Mo_2N catalysts, FTIR studies were carried out with CO as a probe molecule and N_2H_4 as a reactant molecule.

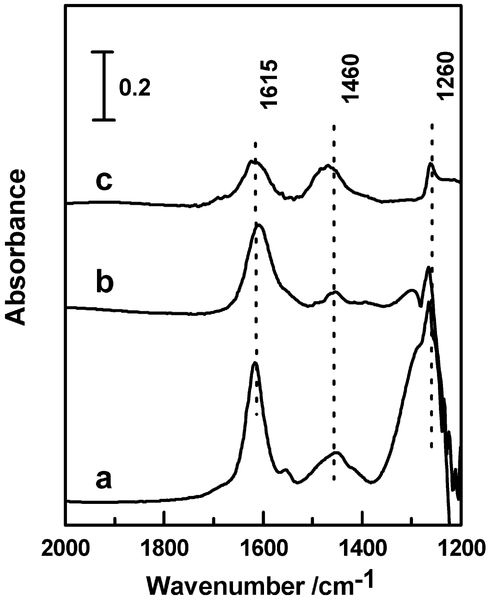

Fig. 4. IR spectra of (a) NH_3 adsorption on MoP/Al_2O_3; N_2H_4 adsorption on (b) MoP/Al_2O_3 and (c) Mo_2N/Al_2O_3 at room temperature.

3.3.1. NH_3 and N_2H_4 adsorption

Fig. 4 shows the IR spectra of adsorbed NH_3 on MoP/Al_2O_3 and adsorbed N_2H_4 on MoP/Al_2O_3 and Mo_2N/Al_2O_3 catalysts at room temperature. Adsorbed NH_3 on MoP/Al_2O_3 yielded IR bands at 1615, 1460, and 1260 cm^{-1}, corresponding to the characteristic frequencies of NH, NH_4^+, and molecularly adsorbed NH_3 [19]. Similar results were obtained when N_2H_4 was adsorbed on MoP/Al_2O_3 and Mo_2N/Al_2O_3, suggesting that the decomposition of N_2H_4 occurred at room temperature and produced NH_3.

3.3.2. CO and N_2H_4 coadsorption

Fig. 5 shows the IR results for the co-adsorption of N_2H_4 and CO on MoP/Al_2O_3 and Mo_2N/Al_2O_3. CO adsorption alone on MoP/Al_2O_3 gave an IR band at 2048 cm^{-1} (Fig. 5a); this can be attributed to linearly adsorbed CO on the Mo atoms [20,21]. Adsorption of N_2H_4 onto CO-preadsorbed MoP/Al_2O_3 produced three bands at 1615, 1460, and 1260 cm^{-1} due to adsorbed NH_3, accompanied by a red shift of ν_{CO} from 2048 to 1960 cm^{-1}. This suggests that the decomposition of N_2H_4 occurred on the Mo sites of the MoP. On the other hand, CO adsorption alone on Mo_2N/Al_2O_3 yielded an IR band at around 2200 cm^{-1} in addition to the band at 2048 cm^{-1}. The band at 2200 cm^{-1} can be assigned to the CO adsorbed on the surface N sites of Mo_2N/Al_2O_3 [20]. When N_2H_4 was adsorbed on the CO-preadsorbed Mo_2N/Al_2O_3, the aforementioned three bands due to NH_3 adsorption were present, the band at 2048 cm^{-1} disappeared, and the band at 2200 cm^{-1} shifted slightly to 2185 cm^{-1}. This finding again indicates that N_2H_4 decomposed on the Mo sites of the Mo_2N, and the NH_3 adsorption on the Mo sites of the Mo_2N was so strong so as to push away the preadsorbed CO on those sites.

Fig. 5B shows the IR results for adsorbed CO on N_2H_4-preadsorbed MoP/Al_2O_3 and Mo_2N/Al_2O_3. The band at 1970 cm^{-1} assigned to adsorbed CO was evident on the MoP/

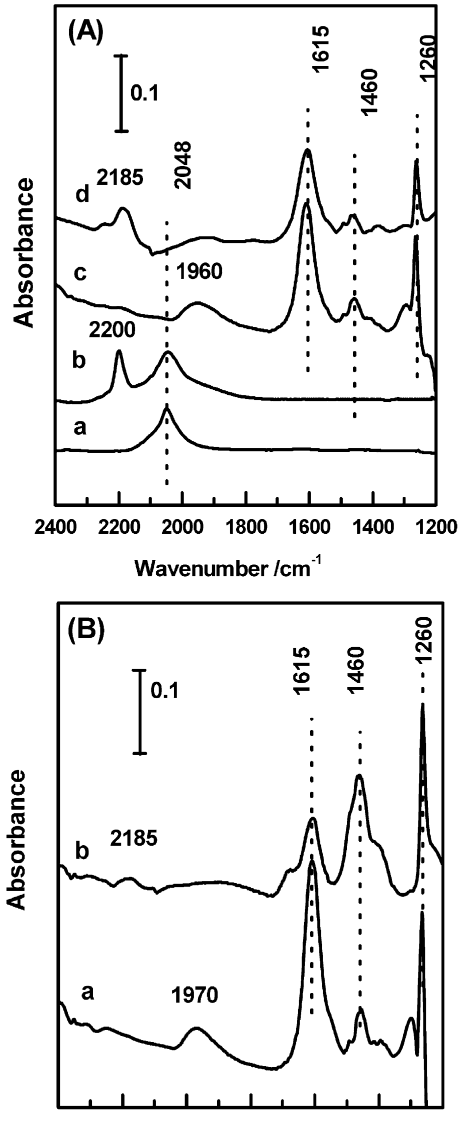

Fig. 5. (A) IR spectra of (a, b) CO adsorption on MoP/Al_2O_3 and Mo_2N/Al_2O_3; (c, d) N_2H_4 adsorption on CO-preadsorbed MoP/Al_2O_3 and Mo_2N/Al_2O_3; (B) IR spectra of CO adsorption on N_2H_4-preadsorbed MoP/Al_2O_3 (a) and Mo_2N/Al_2O_3 (b).

Al_2O_3, whereas it was no longer observed on the Mo_2N/Al_2O_3. This finding again confirms that hydrazine decomposition occurred on the Mo sites and that CO and N_2H_4 were competing for the same Mo sites on the catalysts. Due to the stronger adsorption of NH_3 on the Mo sites of the Mo_2N compared with those of the MoP, CO could not be adsorbed on those N_2H_4-preadsorbed sites of the Mo_2N catalyst.

Consistent with the results of microcalorimetric NH_3 adsorption, FTIR offered more evidence showing that NH_3 was more readily adsorbed on Mo_2N/Al_2O_3 than on MoP/Al_2O_3. Thus, the NH_3 and/or the nitrogen fragments were not easily desorbed from the Mo_2N/Al_2O_3 surface and may have blocked the active sites, leading to decreased activity during N_2H_4 decomposition.

4. Conclusion

This study found that both supported and unsupported MoP were active and stable for the decomposition of N_2H_4 at room temperature, but less active for the decomposition of NH_3. N_2H_4 adsorbed and decomposed on the Mo sites for both MoP and Mo_2N, but the metalloid elements in MoP and Mo_2N had a significant effect on the N_2H_4-derived NH_3 adsorption. MoP/Al_2O_3 exhibited relatively weaker adsorption for NH_3 than Mo_2N/Al_2O_3. As a result, in the decomposition of N_2H_4, the strongly bound nitrogen adspecies on Mo_2N accumulated, and the intermediates on MoP were readily desorbed from the active sites, leading to a relatively better stability of MoP. The moderate adsorption of NH_3 might also be the reason for the poor H_2 selectivity for the N_2H_4 decomposition over the MoP at high temperatures.

Acknowledgments

This research was supported by grants (20325620, 20303017 and 20573108) from the National Natural Science Foundation of China (NSFC).

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