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Catalytic decomposition of hydrazine over supported molybdenum nitride catalysts in a monopropellant thruster

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The catalytic decomposition of hydrazine over a series of MoN_x/γ-Al_2O_3 catalysts with different Mo loadings was investigated in a monopropellant thruster (10 N). When the Mo loading is equal to or higher than the monolayer coverage of MoO_3 on γ-Al_2O_3, the catalytic performance of the supported molybdenum nitride catalyst is close to that of the conventionally used Ir/γ-Al_2O_3 catalyst. The MoN_x/γ-Al_2O_3 catalyst with a loading of about 23 wt% Mo (1.5 monolayers) shows the highest activity for hydrazine decomposition. There is an activation process for the MoN_x/γ-Al_2O_3 catalysts at the early stage of hydrazine decomposition, which is probably due to the reduction of the oxide layer formed in the passivation procedure.

KEY WORDS: hydrazine decomposition; supported molybdenum nitride; passivation; monopropellant thruster.

1. Introduction

Hydrazine is widely employed as a fuel or a monopropellant in gas generators, fuel cells, micropropulsion systems and so on. The most important application of hydrazine is as the monopropellant to control and adjust the orbit and attitude of a spacecraft, based on the decomposition of hydrazine to nitrogen, hydrogen and ammonia, which can produce much larger volumes of gases from a relatively small volume of liquid hydrazine. The conventionally used catalyst for hydrazine decomposition is Ir/Al_2O_3 catalyst with high loading of Ir up to 20–40 wt% [1]. To develop a low cost, readily available and active catalyst for hydrazine decomposition has long been an important objective for many years.

Since the Pt-like behavior of tungsten carbide [2] was reported in 1973, transition metal nitrides and carbides have received a great deal of attention. Much work focused on synthesis and characterization [3–9] of these materials. It has been found that transition metal nitrides and carbides exhibit excellent performances in many reactions, for instance, NH_3 synthesis [10], NH_3 decomposition [11], ethane hydrogenolysis [12], CO hydrogenation [12,13], hydrodenitrogenation [14–16], and hydrodesulfurization [17,18]. In 1997, molybdenum nitride and tungsten carbide were reported as the possible substitutes of the iridium catalyst for hydrazine decomposition [19]. They were tested in a hydrazine microthruster (2 N). The thrusts produced by tungsten carbide and Ir/Al_2O_3 catalyst were compared. For the same consumption of hydrazine for both catalysts, the tungsten carbide catalyst yielded a thrust higher than that of the commonly used Ir/Al_2O_3 catalyst. Recently, Brayner *et al.* [20] reported that the catalytic activity of niobium oxynitride with macropores was lower than that of tungsten oxynitride in laboratory scale at 333 K. The performance of niobium oxynitride was also inferior to that of tungsten oxynitride and Ir/Al_2O_3 catalyst in the 2 N thruster.

To increase the specific surface area and dispersion of nitride, transition metal nitrides can be dispersed on the supports with high specific surface area, such as Al_2O_3 and SiO_2. Compared with the bulk Mo nitride, alumina-supported Mo nitride has some advantages, such as relatively low Mo loading, large surface area, strong mechanical strength and easy molding. This kind of supported catalyst has potential applications in space technology. Pure molybdenum nitride has been tested for hydrazine decomposition, but no study on catalytic decomposition of hydrazine over supported molybdenum nitride has been reported. In this work, a series of MoN_x/γ-Al_2O_3 catalysts with different loadings were prepared. The performances of hydrazine decomposition over the MoN_x/γ-Al_2O_3 and commercial Ir/γ-Al_2O_3 catalysts were compared.

2. Experimental

2.1. Catalyst preparation

A series of MoO_3/γ-Al_2O_3 precursors were prepared by repeated impregnation using aqueous solution of

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$(NH_4)_4Mo_7O_{24}\cdot 4H_2O$ and γ-Al_2O_3 ($S_{BET} = 198\,m^2/g$, 20–30 mesh), followed by a drying at 393 K for 12 h and a calcination at 773 K for 4 h.

The nitridation of MoO_3/γ-Al_2O_3 samples was carried out in a quartz tube reactor by temperature-programmed reaction with NH_3 (99.99%). The reaction involves three stages: the temperature was increased from room temperature to 573 K in 1 h; then from 573 K to 973 K at a rate of 1 K/min, then kept at 973 K for 2 h. The space velocity of NH_3 was maintained at $6000\,h^{-1}$. The nitrided sample was cooled down to room temperature in flowing ammonia and then passivated in a mixture of 1% O_2/N_2 so as to avoid the violent oxidation of the nitrided catalyst. Alumina-supported Mo nitride catalysts with different loadings (8.7, 12.9, 15.4, 23.0 and 26.9 wt% Mo) were prepared.

2.2. BET surface area

BET surface areas of the catalysts before the reaction and after the reaction were measured at liquid nitrogen temperature using a Micrometritics ASPA-2000 adsorption analyzer.

2.3. XRD measurement

The XRD patterns of the passivated samples were taken on a Rigaku Rotaflex (Ru-200b) powder X-ray diffractometer (Cu K_α radiation).

2.4. Evaluation of catalytic activities

The catalytic activity of hydrazine decomposition was tested using a specially designed experimental apparatus as schematically described in figure 1. About 9 g of catalyst was charged into the monopropellant thruster of 10 N. The diameter of the catalyst bed was 16 mm, and the length was 40 mm. The thruster is placed in a vacuum system (evacuated to 0.5 Torr). The hydrazine injection pressure (P_i) was 1.5×10^6 Pa, and was kept constant during the hydrazine decomposition in order to give almost constant hydrazine feeding rate. When the electromagnetic valve was opened, hydrazine was pressed into the thruster by the N_2 gas and the decomposition reaction took place as soon as hydrazine contacted the catalyst. The initial temperature in the catalyst bed was 373 K and the opening time of the electromagnetic valve lasted 30 s except by special notification. After continuous feeding of hydrazine for 30 s, the catalyst bed was cooled down to 373 K, and then another 30 s startup–shutdown test started.

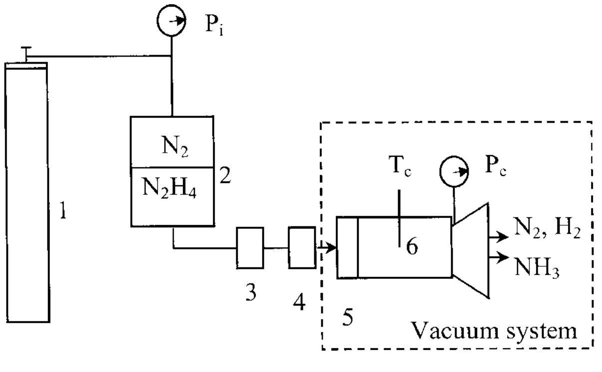

Figure 1. Experimental apparatus for the catalytic decomposition of hydrazine: (1) N_2 gas cylinder, (2) hydrazine tank, (3) feed rate measurement, (4) electromagnetic valve, (5) injector and (6) catalyst in a 10 N thruster.

Chamber pressure (P_c), catalyst bed temperature (T_c) and ignition delay (t_0 and t_{90}) were recorded automatically by a computer. P_c and T_c are the parameters correlated with the hydrazine conversion extent. t_0 and t_{90} are the times that the chamber pressures reach 10% and 90% of the stable-state pressure of the chamber, respectively. They directly reflect the initial catalytic activity. The smaller the values of t_0 and t_{90}, the higher the initial activity of the catalyst. In this work, the specific activity at the steady stage is defined as the chamber pressure produced by per unit weight of hydrazine feeding.

3. Results and discussion

The surface areas of the MoN_x/γ-Al_2O_3 catalysts and the Ir/γ-Al_2O_3 catalyst before the reaction are given in table 1. It is seen that the BET surface area slightly decreases as the loading of Mo increases to 23 wt%. When the Mo loading is up to 26.9 wt%, the BET surface area dramatically decreases to $154\,m^2/g$. This result is mainly due to the Mo_2N particles on the surface of γ-Al_2O_3.

Figure 2 shows the XRD patterns of the catalyst samples. The XRD patterns of the MoN_x/γ-Al_2O_3 catalysts with Mo loadings <23 wt% exhibit only some broad peaks, and it is difficult to distinguish the γ-Mo_2N phase from the γ-Al_2O_3 phase because some peaks overlap. However, when the loading of Mo is higher than about 23 wt%, the XRD patterns of bulk γ-Mo_2N can be observed. The theoretical monolayer capacity of the MoO_3/γ-Al_2O_3 sample is 0.12 g MoO_3/100 m^2 of γ-Al_2O_3 surface [21]. Monolayer coverage of MoO_3 on alumina with $198\,m^2/g$ corresponds to a loading of about 12.9 wt% Mo. Because it was difficult to detect the highly dispersed small Mo_2N particles by XRD, the absence of γ-Mo_2N peaks suggests that γ-Mo_2N on the surface of alumina is highly dispersed and/or in amorphous state. Results are similar to those reported previously by Colling *et al.* [16].

Figure 3 compares the catalytic behaviors of the MoN_x/γ-Al_2O_3 catalysts of different Mo loadings with that of the 31.6 wt% Ir/γ-Al_2O_3 catalyst ($164.9\,m^2/g$) in the first 30-s continuous feeding of hydrazine. Data for the MoN_x/γ-Al_2O_3 catalyst (8.7 wt% Mo) are not shown because its activity is very low (see table 1). As

Table 1
Performances of the catalysts for the hydrazine decomposition during the first startup–shutdown cycle. The initial temperature in the catalyst bed was 373 K

Catalyst	Metal content (wt%)	BET surface area (m^2/g)		Flow rate of hydrazine (g/s)	t_0 (ms)	t_{90} (ms)	T_c (K)	P_c (MPa)	Specific activity (MPa/g/s)
		Before reaction	After reaction						
MoN_x/Al_2O_3	8.7	190.9	188.7	11.3	–	–	408	0.088	0.008
	12.9	183.7	164.1	6.15	152	353	1103	1.11	0.180
	15.4	182.9	153.3	5.11	150	480	1048	1.19	0.233
	23.0	187.3	138.8	4.77	110	330	1169	1.13	0.237
	26.9	154.0	133.8	4.70	90	240	1181	1.10	0.234
Ir/Al_2O_3	31.6	164.9	123.4	4.63	20	371	1071	1.07	0.232

seen in figure 3, P_c increases quickly, and then reaches a maximum level. There is no obvious difference between the steady-state chamber pressures of the MoN_x/γ-Al_2O_3 catalysts and the Ir-based catalyst under the same conditions. These results indicate that alumina-supported Mo nitride catalysts are very effective for catalytic decomposition of hydrazine and their activities are comparable with that of the Ir/γ-Al_2O_3 catalyst.

Table 1 summarizes the experimental results of steady P_c and T_c, ignition delay (t_0 and t_{90}) and specific activity. The specific activity for hydrazine decomposition over supported Mo nitrides varies significantly with the Mo loadings. The specific activity of hydrazine decomposition over the MoN_x/γ-Al_2O_3 catalyst with a loading of 8.7 wt% Mo (lower than the monalayer coverage) is 0.008, while its T_c is 408 K. When the Mo loading is 12.9 wt% (monolayer coverage), the specific activity increases from 0.008 to 0.180. The activity is further increased when the Mo loading is increased to 15.4 wt%, which is beyond the monolayer coverage of MoO_3 on alumina. The specific activity is no longer changed very much when the Mo loading is higher than 15.4 wt%. The specific activity of the supported Mo nitride with a loading of 23.0 wt% Mo reaches its highest among the prepared nitride catalysts, and its T_c is up to 1169 K. The specific activities of supported Mo nitride catalysts with high loadings are even higher than or at least comparable with that of Ir/Al_2O_3 catalyst. The low specific activity of the MoN_x/γ-Al_2O_3 catalyst with the loading of 8.7 wt% Mo is probably

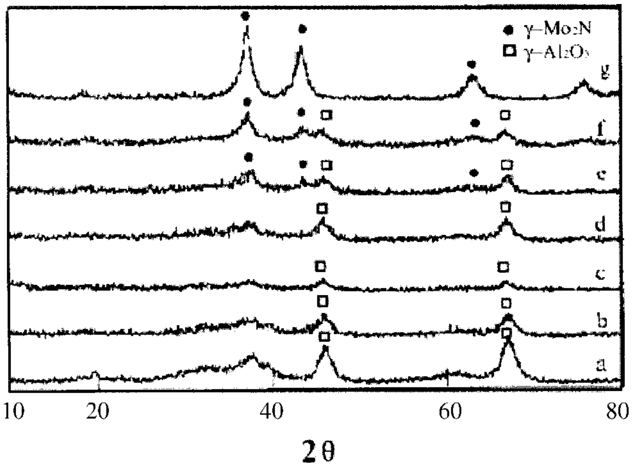

Figure 2. XRD patterns of (a) γ-Al_2O_3, the MoN_x/Al_2O_3 catalysts with different Mo loadings, (b) 8.7 wt%, (c) 12.9 wt%, (d) 15.4 wt%, (e) 23.0 wt%, (f) 26.9 wt%, and (g) pure phase γ-Mo_2N.

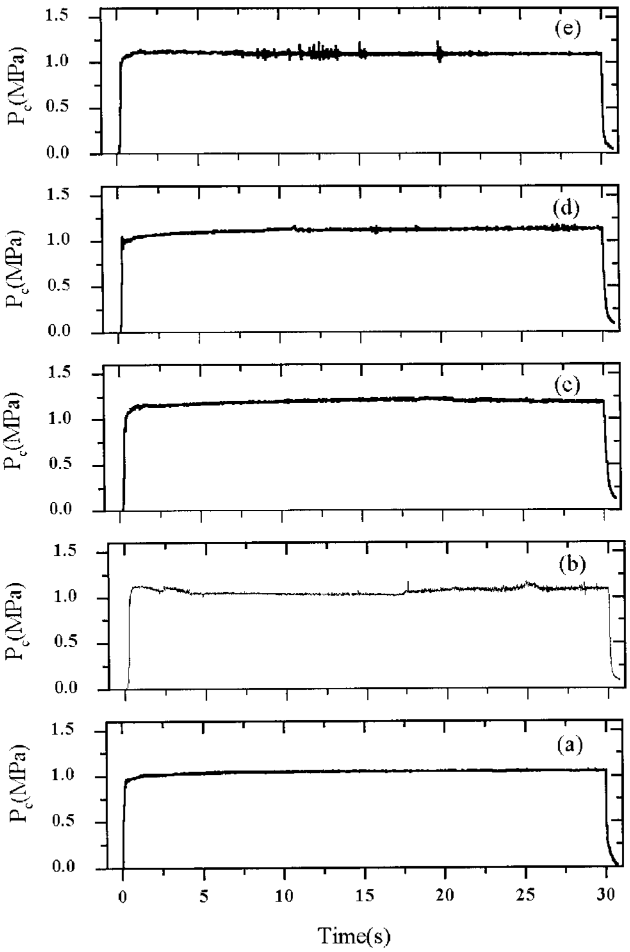

Figure 3. Comparison of catalytic performance of hydrazine decomposition over (a) Ir/Al_2O_3 catalyst, and the MoN_x/Al_2O_3 catalysts with different Mo loadings, (b) 12.9 wt%, (c) 15.4 wt%, (d) 23.0 wt%, (e) 26.9 wt% in a 10 N thruster. The initial temperature of the catalyst bed was 373 K.

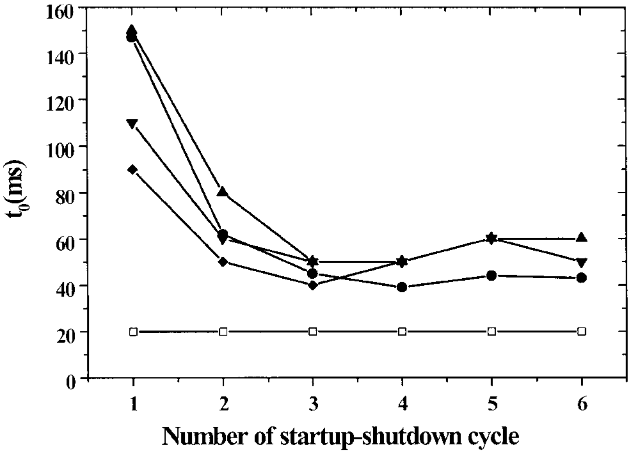

Figure 4. Comparison of the t_0 values of the Ir/Al_2O_3 (□) and the MoN_x/Al_2O_3 catalysts with different Mo loadings (●) 12.9 wt%, (▲) 15.4 wt%, (▼) 23.0 wt%, (◆) 26.9 wt% during a series of startup–shutdown cycles. The initial temperature of the catalyst bed was 373 K.

due to the MoO_3 loading below monolayer coverage, which may be difficult to nitride because of strong interaction between the MoO_3 and γ-Al_2O_3. Another reason is that the highly dispersed γ-Mo_2N on alumina is oxidized back to molybdenum oxide again after the passivation treatment and then exposure to air. The higher specific activities of the MoN_x/γ-Al_2O_3 catalysts with the loadings of 15.4, 23.0 and 26.9 wt% Mo are mainly attributed to the γ-Mo_2N phase.

The t_0 value also depends on the Mo loading and it becomes shorter as the Mo loading increases. In other words, the initial catalytic activity increases with the increase of Mo loading. These results also verify that the active phase for hydrazine decomposition is the γ-Mo_2N phase. Figure 4 shows the t_0 values of catalysts during a series of startup–shutdown cycles. For the MoN_x/γ-Al_2O_3 catalysts, the t_0 value is shortened with the number of startup–shutdown cycles. After three cycles the t_0 value reaches a stable level in the range of 40–60 ms, which is a little larger than that of Ir/γ-Al_2O_3 catalyst. These results indicate that the initial activities of supported MoN_x/γ-Al_2O_3 catalysts are somewhat lower than that of Ir/γ-Al_2O_3 catalyst. There is an activation process for the MoN_x/γ-Al_2O_3 catalysts. As mentioned in section 2, all the MoN_x/γ-Al_2O_3 catalysts were passivated before exposing to air. It has been found that there is a thin oxide layer on the surface of the MoN_x/γ-Al_2O_3 catalyst by the XPS method [22,23]. This oxide layer is reduced gradually by hydrazine and ammonia during the hydrazine decomposition reaction at high temperatures. This causes the lower initial activity of the alumina-supported Mo nitride than that of the Ir/γ-Al_2O_3 catalyst.

As described in section 2, t_{90} is the time between the opening of the electromagnetic valve and the time at which the pressure is up to 90% of the final stable pressure in the chamber. Generally speaking, the t_{90} value is more important than t_0 for the practical application. The higher the initial activity of the catalyst, the smaller the t_{90} value. As listed in table 1, the t_{90} value of Ir/γ-Al_2O_3 catalyst is about 371 ms for the first cycle of reaction. The t_{90} values of the Mo nitride catalysts sometimes are close to or less than that of Ir/γ-Al_2O_3 catalyst especially during the first startup–shutdown cycle (see table 1). Figure 5 illustrates the t_{90} values during a series of startup–shutdown cycles. The t_{90} value increases slightly at the early stage of hydrazine decomposition and then becomes stable after three startup–shutdown cycles. There is no significant difference in t_{90} values between the MoN_x/γ-Al_2O_3 and Ir/γ-Al_2O_3 catalysts. This implies that the catalytic performances of the MoN_x/γ-Al_2O_3 catalysts are almost comparable with that of the Ir/γ-Al_2O_3 catalyst, the current commercial catalyst for hydrazine decomposition.

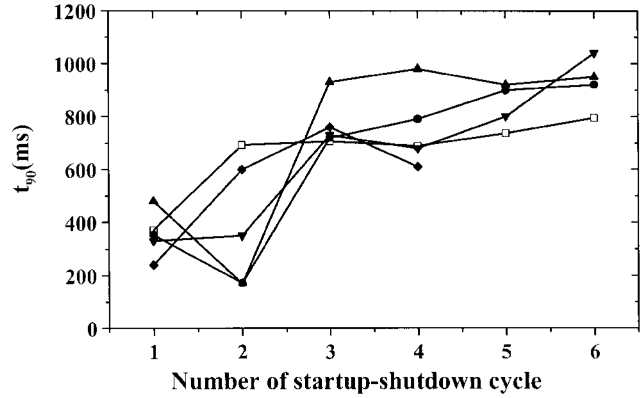

Figure 5. Comparison of the t_{90} values of the Ir/Al_2O_3 (□) and the MoN_x/Al_2O_3 catalysts with different Mo loadings (●) 12.9 wt%, (▲) 15.4 wt%, (▼) 23.0 wt%, (◆) 26.9 wt% during a series of startup–shutdown cycles. The initial temperature of the catalyst bed was 373 K.

Table 1 also lists the BET surface areas of the MoN_x/γ-Al_2O_3 catalysts and Ir/γ-Al_2O_3 catalyst after six startup–shutdown cycles, which lasted about 180 s. Compared with the BET surface area of this catalyst before the reaction, the BET surface area of the MoN_x/γ-Al_2O_3 catalyst with the Mo loading of 8.7 wt% after the reaction does not change very much. As mentioned before, the activity of this catalyst for hydrazine decomposition is very low, and the temperature in the catalyst bed during hydrazine decomposition is only 408 K. However, the BET surface areas of other catalysts, including the Ir/γ-Al_2O_3 catalyst, considerably decrease. The temperature in the catalyst bed is usually at the range 1000–1200 K. Therefore the decrease of the BET surface areas of the catalysts after reaction is probably due to the decrease of surface area of the alumina at high temperatures.

Because the catalytic activity of hydrazine decomposition at low temperature is very important to the application, we investigated the activity for the MoN_x/γ-Al_2O_3 catalyst with the loading of 23.0 wt% Mo at 313 K, about 15 K above room temperature. At first, continuous

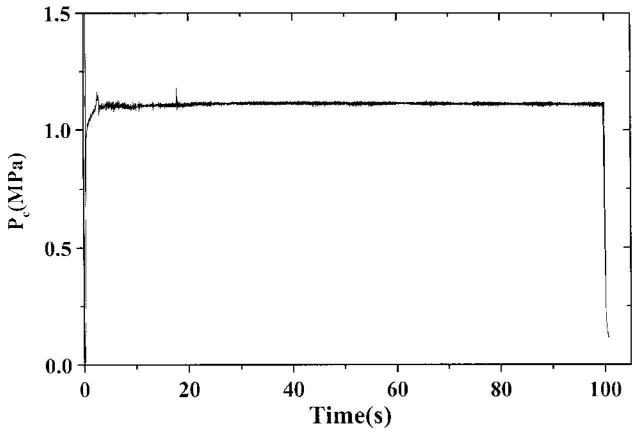

Figure 6. Catalytic decomposition of hydrazine over the MoN_x/Al_2O_3 catalyst with the loading of 23.0 wt% Mo of a continuous feeding of hydrazine for 100 s in a 10 N thruster. The initial temperature of the catalyst bed was 313 K.

feeding of hydrazine for 30 s removed the oxide layer over the surface of the catalyst at 373 K, and then exhibited very high activity at 313 K (see figure 6). The specific activity is 0.239, which is similar to that of Ir catalyst. t_0 is about 180 ms, and t_{90} is about 460 ms. After five startup–shutdown cycles of 100 s continuous feeding of hydrazine, the mass loss of the catalyst bed is only about 5%. This catalyst shows stable activity during long duration tests at 313 K. These results suggest that the supported Mo nitrides are promising candidates to substitute Ir/γ-Al_2O_3 catalysts for hydrazine decomposition.

4. Conclusion

Alumina-supported molybdenum nitride catalyst, MoN_x/γ-Al_2O_3, is applied to the hydrazine decomposition for the first time. It is found that the catalytic performance of the MoN_x/γ-Al_2O_3 catalyst with an Mo loading of more than 12.9 wt% is as good as that of Ir/γ-Al_2O_3 catalyst (31.6 wt% Ir), which has been used in space technology. The γ-Mo_2N phase of MoN_x/γ-Al_2O_3 catalyst is mainly responsible for the high catalytic activity for the hydrazine decomposition. The catalyst experiences an activation process at an early stage of the reaction to reduce the oxynitride layer formed during the passivation of the catalyst.

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