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# A novel catalyst for hydrazine decomposition: molybdenum carbide supported on $\gamma$-$Al_2O_3$

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**An alumina-supported $Mo_2C$ catalyst is found to be as active as a conventionally used Ir/$\gamma$-$Al_2O_3$ catalyst for catalytic decomposition of hydrazine tested in a monopropellant thruster.**

The catalytic decomposition of hydrazine has been of interest for many years since this process has been successfully used in a monopropellant thruster to control and adjust the orbits and altitudes of spacecrafts. The traditionally used catalyst for hydrazine decomposition is a 20–40 wt% Ir/$\gamma$-$Al_2O_3$ catalyst.[1-4] The Ir-based catalyst is very expensive because iridium is a rare and noble metal. Therefore it is highly desirable to develop an inexpensive, active, stable and readily available catalyst for hydrazine decomposition.

Transition metal carbides and nitrides have received a great deal of attention because of their excellent catalytic behavior resembling group VIII metals in a number of reactions,[5,6] such as hydrogenolysis, hydrogenation, hydrotreating (hydrodenitrogenation and hydrodesulfurization), $NH_3$ synthesis and decomposition. Pure phases of $\gamma$-$Mo_2N$, $W_2N$, NbN and $W_2C$ have been tested as possible substitutes for the Ir/$\gamma$-$Al_2O_3$ catalyst for hydrazine decomposition in space technology.[7,8] Their behaviors were similar to or inferior to that of the Ir/$\gamma$-$Al_2O_3$ catalyst.

Until now, no studies on the catalytic performance of molybdenum carbide for hydrazine decomposition have been reported. Supported $Mo_2C$ on alumina catalysts were prepared in order to obtain highly dispersed molybdenum carbide on the alumina with a high surface area. Compared with the bulk molybdenum carbide, alumina-supported molybdenum carbide has some advantages, such as relatively low Mo loading, large surface area, strong mechanical strength and easy molding. In this work, for the first time it has been found that the supported $Mo_2C$ catalysts are very active for hydrazine decomposition.

The theoretical monolayer capacity of the $MoO_3$/$\gamma$-$Al_2O_3$ sample is 0.12 g $MoO_3$/100 $m^2$ of $\gamma$-$Al_2O_3$ surface.[9] The theoretical monolayer coverage of $MoO_3$ on $\gamma$-$Al_2O_3$ with 198 $m^2$ $g^{-1}$ corresponds to a loading of *ca.* 12.9 wt% Mo. The $MoO_3$/$\gamma$-$Al_2O_3$ precursor (Mo in the catalyst is 12.9 wt%) was first prepared by the incipient wetness method using an aqueous $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ solution and $\gamma$-$Al_2O_3$ ($S_{BET}$ = 198 $m^2$ $g^{-1}$, 20–30 mesh), followed by drying at 393 K for 12 h and calcination at 773 K for 4 h. The $Mo_2N$/$\gamma$-$Al_2O_3$ precursor was prepared by temperature-programmed reaction (TPR) of $MoO_3$/$\gamma$-$Al_2O_3$ with ammonia. 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 $min^{-1}$; and then kept at 973 K for 2 h. The nitrided sample was cooled down to room temperature in flowing ammonia and passivated in a mixture of 1% $O_2/N_2$ so as to avoid the violent oxidation of the $Mo_2N$/$\gamma$-$Al_2O_3$ precursor. Supported molybdenum carbides with the same Mo loading but different structures were prepared by TPR between the precursors ($Mo_2N$/$\gamma$-$Al_2O_3$ or $MoO_3$/$\gamma$-$Al_2O_3$) and 20% $CH_4$/$H_2$ (v/v). A four-stage heating ramp was used: the temperature was first heated from room temperature to 573 K in 0.5 h; then to 823 K at a rate of 0.5 K $min^{-1}$; further from 823 to 973 K at a rate of 1 K $min^{-1}$; and finally maintained at 973 K for 1 h. The $\alpha$-$Mo_2C$/$\gamma$-$Al_2O_3$ catalyst with a face-centered cubic structure (fcc) was prepared by carburizing the produced $Mo_2N$/$\gamma$-$Al_2O_3$, whereas the $\beta$-$Mo_2C$/$\gamma$-$Al_2O_3$ catalyst with a hexagonal-close packed structure (hcp) was synthesized from $MoO_3$/$\gamma$-$Al_2O_3$ directly.[10–13] Both of the supported $Mo_2C$/$\gamma$-$Al_2O_3$ catalysts with different structures were passivated by 1% $O_2/N_2$ for 10 h to form a protective oxide layer on the surface.

The catalytic activity of hydrazine decomposition was evaluated in an experimental apparatus similar to that used by Tian *et al.*[14] and Rodrigues.[7,8] A monopropellant thruster of 10 Newtons containing a catalyst bed (40 mm long with a diameter of 16 mm), was placed in a vacuum chamber (evacuated to 0.5 Torr). In this thruster the theoretical chamber pressure ($P_c$) produced by hydrazine decomposition was *ca.* 1.02–1.05 MPa (at flow rate of hydrazine of 4.41 g $s^{-1}$). Approximately 9 g of catalyst was used for each batch. The hydrazine injection pressure ($P_i$) was controlled by pressurized $N_2$ and was kept constant (1.5 MPa) during the hydrazine decomposition to obtain an almost constant hydrazine feeding rate. When the electromagnetic valve was opened, the hydrazine was pressed into the catalytic chamber by $N_2$. Almost at the same time, the hydrazine was vaporized and decomposed by the catalyst bed, generating the gases of nitrogen, hydrogen and ammonia. The initial temperature in the catalyst bed was 373 K. The continuous feeding of hydrazine lasted 30 s, and then the catalyst bed was allowed to cool to 373 K before the next 30 s test began. Chamber pressure ($P_c$), catalyst bed temperature ($T_c$) and ignition delay ($t_0$) were recorded with a frequency of 1 kHz and calculated automatically by computer. The performance of hydrazine decomposition over the $Mo_2C$/$\gamma$-$Al_2O_3$ catalysts with different structures and commercial 31.6 wt% Ir/$\gamma$-$Al_2O_3$ catalysts were compared.

The $Mo_2C$/$\gamma$-$Al_2O_3$ catalysts (12.9 wt% Mo) prepared by different methods both show broad XRD peaks which make it difficult to distinguish the $Mo_2C$ phase from $\gamma$-$Al_2O_3$. However, the bulk materials synthesized under similar preparation conditions give strong and sharp XRD peaks due to $\alpha$-$Mo_2C$ (fcc) and $\beta$-$Mo_2C$ (hcp) phases. These results suggest that the $\alpha$-$Mo_2C$ and $\beta$-$Mo_2C$ particles are well dispersed on $\gamma$-$Al_2O_3$ under these preparation conditions.

Hydrazine decomposition is a volume expansion and exothermic reaction. When hydrazine was fed into the thruster and contacted with the catalyst, it was decomposed immediately. Consequently, the chamber pressure ($P_c$) increases quickly, and then reaches a maximum value. Fig. 1 compares the catalytic behaviors of the commercial 31.6 wt% Ir/$\gamma$-$Al_2O_3$, $\alpha$-$Mo_2C$/$\gamma$-$Al_2O_3$ and $\beta$-$Mo_2C$/$\gamma$-$Al_2O_3$ catalysts in the first 30 s continuous feeding of hydrazine. It can be seen that $P_c$ attains a steady value within a short time. The higher the catalyst activity, the more rapid the increase of the chamber pressure. These results indicate that both the $\alpha$-$Mo_2C$/$\gamma$-$Al_2O_3$ and $\beta$-$Mo_2C$/$\gamma$-$Al_2O_3$ catalysts are effective for the catalytic decomposition of hydrazine. Furthermore, there is no obvious difference between the stable-state chamber pressures of the $Mo_2C$/$\gamma$-$Al_2O_3$ catalysts with different structures and the Ir/$\gamma$-$Al_2O_3$ catalyst under the same reaction conditions. The steady $P_c$ produced by hydrazine decomposition is close to or greater than the

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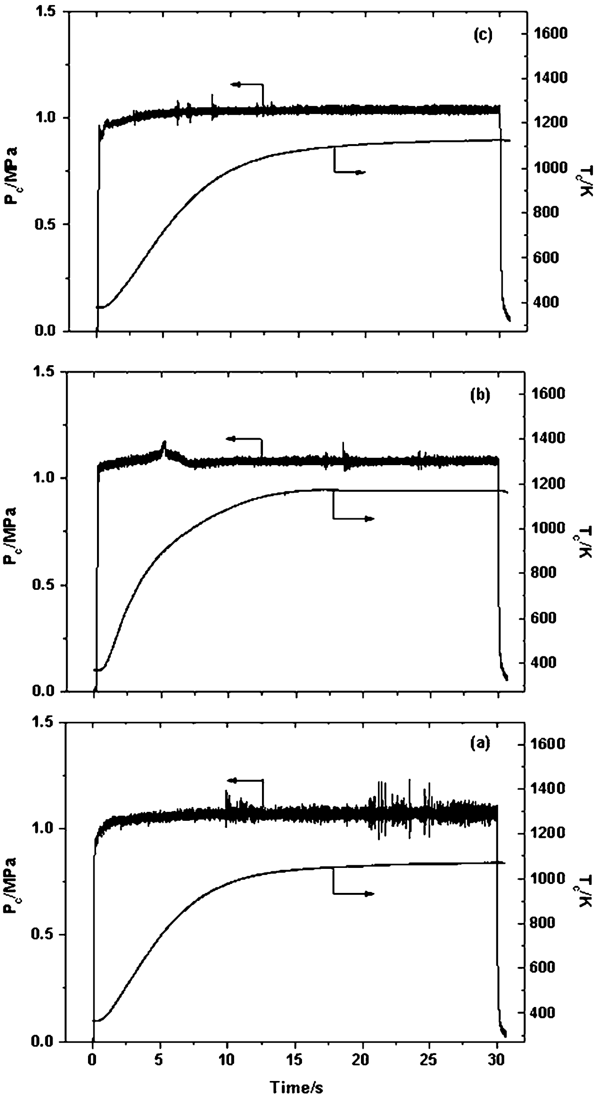

**Fig. 1** Comparison of catalytic performance of hydrazine decomposition over (a) Ir/γ-$Al_2O_3$, (b) α-$Mo_2C$/γ-$Al_2O_3$ (fcc) and (c) β-$Mo_2C$/γ-$Al_2O_3$ (hcp) catalysts with a continuous feeding of hydrazine for 30 s in a thruster of 10 N. The initial temperature of the catalyst bed was 373 K.

theoretical $P_c$. The activities of supported molybdenum carbide catalysts for hydrazine decomposition are comparable to that of the Ir/γ-$Al_2O_3$ catalyst.

Table 1 summarizes the experimental results of steady chamber pressure ($P_c$), catalyst bed temperature ($T_c$) and ignition delay ($t_0$). The parameter $t_0$ is the time when the pressure of the chamber reaches 10% of the stable-state pressure of the chamber. It reflects the initial activity of the catalyst and depends mainly upon the intrinsic activity of the catalyst at the initial time. The smaller the values of $t_0$, the higher the initial activity of the catalyst. The $t_0$ value of the Ir/γ-$Al_2O_3$ catalyst is the shortest with an average of 28 ms, whereas the $t_0$ values of the α-$Mo_2C$/γ-$Al_2O_3$ and β-$Mo_2C$/γ-$Al_2O_3$ catalysts are longer than that of the Ir-based catalyst with the average of 56 and 46 ms, respectively. The results indicate that the initial activity of the Ir/γ-$Al_2O_3$ catalyst is higher than that of the $Mo_2C$/γ-$Al_2O_3$ catalysts, but is within the same order of magnitude. The difference in the $t_0$ value of these two $Mo_2C$/γ-$Al_2O_3$ catalysts of the same chemical composition is small and is probably due to their different phases.

**Table 1** Performance of the catalysts with a continuous feeding of hydrazine for 30 s in a thruster of 10 N. The initial temperature in the catalyst bed was 373 K

| Catalyst | Hydrazine flow rate/g $s^{-1}$ | Average $t_0$/ms | $T_c$/K | $P_c$/MPa |
|---|---|---|---|---|
| α-$Mo_2C$/γ-$Al_2O_3$ (fcc) | 4.70 | 56 | 1171 | 1.08 |
| β-$Mo_2C$/γ-$Al_2O_3$ (hcp) | 4.42 | 46 | 1123 | 1.04 |
| Ir/γ-$Al_2O_3$ | 4.63 | 28 | 1071 | 1.07 |

The chamber pressure ($P_c$) and catalyst bed temperature ($T_c$) at the steady states remains almost unchanged for six tests of the 30 s continuous feeding of hydrazine. This indicates that these two $Mo_2C$/γ-$Al_2O_3$ catalysts are stable for hydrazine decomposition.

The ammonia component of the resultant mixture produced by hydrazine decomposition may further dissociate into $H_2$ and $N_2$ at elevated temperatures. The ammonia decomposition is endothermic and the hydrazine decomposition is exothermic. Hence the catalyst bed temperature ($T_c$) is the parameter of the ammonia and hydrazine conversion. As shown in Fig. 1, $T_c$ increases when hydrazine decomposes, and rises to a stable level finally. The $T_c$ of the Ir/γ-$Al_2O_3$ catalyst is lower than those of the $Mo_2C$/γ-$Al_2O_3$ catalysts with different phases. The results suggest that the ammonia conversion over the Ir/γ-$Al_2O_3$ catalyst is higher than that of the $Mo_2C$/γ-$Al_2O_3$ catalysts.

In conclusion, alumina-supported molybdenum carbides have been applied to hydrazine decomposition for the first time. The $Mo_2C$/γ-$Al_2O_3$ catalysts exhibit excellent catalytic performances for hydrazine decomposition. They show comparable activities to that of the Ir/γ-$Al_2O_3$ catalyst. Alumina-supported molybdenum carbide catalysts are therefore promising substitutes for the Ir-based catalyst for hydrazine decomposition in space technology because of their low cost, high activity, strong mechanical strength and easy preparation.

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