

Ammonia Decomposition over Bimetallic Nitrides Supported on γ -Al₂O₃

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Abstract: A series of monometallic nitrides and bimetallic nitrides were prepared by temperature-programmed reaction with NH₃. The effects of Co, Ni and Fe additives and the synergic action between Fe, Co, Ni and Mo on the ammonia decomposition activity were investigated. TPR-MS, XRD were also carried out to obtain better insight into the structure of the bimetallic nitride. The results of ammonia decomposition activity show that bimetallic nitrides are more active than monometallic nitrides or bimetallic oxides.

Keywords: Nitrides, transition metal, γ -Al₂O₃, ammonia decomposition.

Transition metal nitrides belong to a class of interstitial compounds, in which nitrogen atoms replace oxygen. They possess some technologically useful properties as packaging materials, structural materials and catalytic materials. Since Boudart¹ succeeded to prepare high specific surface area γ -Mo₂N in 1985 using the NH₃ temperature-programmed reduction method, transition metal nitrides have attracted much attention as potential catalysts owing to their similarity with the group VIII metals. It seems reasonable to suppose whether transition metal nitrides could take the place of noble metals catalysts in many industrial processes. So far, molybdenum and vanadium nitride have been studied extensively. They have shown specific activity in a lot of reactions such as Fischer-Tropsch reaction², hydrodesulfurization (HDS)³, hydrodenitrogenation (HDN)⁴, ammonia synthesis⁵. Recently, it has shown that the catalytic activity of molybdenum nitrides is enhanced by addition of another transition metals such as cobalt, nickel, and iron⁶ *etc.*

However comparing with the reactions presented above, the study of ammonia decomposition over transition metal nitrides was still few, and most of which focused on monometallic nitrides such as Mo₂N and VN, bimetallic nitrides were studied relatively few.

In this study, nitride catalysts were prepared through temperature-programmed reaction of the corresponding precursors with flowing NH₃. The effects of Co, Ni and Fe additives on the ammonia decomposition activity were investigated. TPR-MS, XRD were also carried out to obtain better insight into the structure of the bimetallic nitride.

Experimental

γ -Al₂O₃-supported bimetallic nitrides were prepared by incipient wetness impregnation

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of $\gamma\text{-Al}_2\text{O}_3$ (with specific surface area $180\text{ m}^2/\text{g}$) using aqueous solutions (de-ionized water) of ammonia heptamolybdate and corresponding nitrate of nickel, iron, or cobalt. Molybdenum oxide was impregnated followed by nickel, iron, or cobalt nitrate. Each impregnation was followed by drying at room temperature and 120°C each for 5 h. Eventually the sample was calcined at 500°C for 4 h. The nominal molybdenum loading was 10 wt%; the molar ratios of nominal nickel/iron/cobalt loadings to the nominal molybdenum loading were 0.5 to 1.0 (Ni/(Ni+Mo)), 0.6 to 1.1 (Fe/Mo) and 0.5 to 1.0 (Co/Mo), respectively.

The bimetallic nitrides were performed in a quartz tube reactor (ID. 6 mm) using a temperature-programmed reaction of their corresponding metal oxide precursors with anhydrous NH_3 . About 3 mL of catalyst with particle size of 30-40 mesh (0.45-0.6 mm) was heated from room temperature to 450°C at a heating rate of $4^\circ\text{C}/\text{min}$, and then heated to 700°C at a rate of $1^\circ\text{C}/\text{min}$, subsequently held that temperature for 2 h in flowing ammonia gas with a rate of 160 mL/min. Eventually, the sample was cooled down to room temperature in flowing ammonia gas and then passivated by exposure to the mixture gas of 1% $\text{O}_2/99\%\text{N}_2$ (v/v).

Ammonia decomposition reaction over the sample was carried out in the same apparatus with pure ammonia with GHSV 7600 h^{-1} under atmospheric pressure, after the passivated sample was reduced in the mixture gas of H_2/N_2 with molar ratio of 3:1. The reduction program was as follows: the sample was heated to 500°C from room temperature in 30 min, and held that temperature for 1 h; then heated from 500°C to 600°C in 10 min; eventually held 600°C for 3 h. The effluent gas from the reactor was neutralized by sulfuric acidic solution (0.5 mol/L) containing an indicator (methyl red).

The XRD patterns of the passivated samples were performed with powder X-ray diffractometer on a Rigaku D/max-2550 PC (Cu K_α radiation). TPR-MS experiment was carried out using a QMS 200(Omnistar). A 50 mg of sample was heated to 300°C and held that temperature for 1 h in flowing helium gas to remove adsorbed physical water and other impurities on the surface of sample. After cooling down to room temperature, the sample was heated to 1000°C at a heating rate of $10^\circ\text{C}/\text{min}$ in reducing gas of 10% $\text{H}_2/90\%\text{Ar}$ (v/v %) with a flow rate of 40 mL/min. The effluent gas was passed a cooler to remove the produced water in the reaction and then monitored by thermal conductivity detector and mass spectrometer detector.

Results and Discussion

The XRD patterns of the passivated samples and their corresponding precursor oxides are shown in **Figure 1**. In XRD spectra of the passivated samples, no marked diffraction peaks of crystalline $\text{Ni}_3\text{Mo}_3\text{N}$, $\text{Fe}_3\text{Mo}_3\text{N}$ and $\text{Co}_3\text{Mo}_3\text{N}$ have been observed. Just the characteristic peaks of MoN and CoN have been found in XRD spectra of the passivated $\text{Co}_x\text{Mo}_y\text{N}/\gamma\text{-Al}_2\text{O}_3$ catalyst. These results could be suggested that the molybdenum and nickel, or iron, or cobalt nitrides highly disperse or may be generated in amorphous state on the surface of $\gamma\text{-Al}_2\text{O}_3$, when the loadings of MoO_3 and NiO, or Fe_2O_3 , or Co_2O_3 are 10 and 22.1, or 11.8, or 9.8 wt% respectively. A comparable study has been reported in the works of Y. Chu *et al*⁷, who confirmed that using XRD, molybdenum and nickel nitrides can be formed for high metal loadings intentionally.

The TPR-MS profiles for the passivated $\text{Co}_x\text{Mo}_y\text{N}/\gamma\text{-Al}_2\text{O}_3$, $\text{Fe}_x\text{Mo}_y\text{N}/\gamma\text{-Al}_2\text{O}_3$ and $\text{Ni}_x\text{Mo}_y\text{N}/\gamma\text{-Al}_2\text{O}_3$ catalysts are shown in **Figure 2**. It can be seen that there are two

Figure 1 XRD patterns of (a) $\gamma\text{-Al}_2\text{O}_3$, (b) $\text{Co}_x\text{Mo}_y\text{O}/\gamma\text{-Al}_2\text{O}_3$, (c) $\text{Fe}_x\text{Mo}_y\text{O}/\gamma\text{-Al}_2\text{O}_3$, (d) $\text{Ni}_x\text{Mo}_y\text{O}/\gamma\text{-Al}_2\text{O}_3$, (e) $\text{Co}_x\text{Mo}_y\text{N}/\gamma\text{-Al}_2\text{O}_3$, (f) $\text{Fe}_x\text{Mo}_y\text{N}/\gamma\text{-Al}_2\text{O}_3$, (g) $\text{Ni}_x\text{Mo}_y\text{N}/\gamma\text{-Al}_2\text{O}_3$

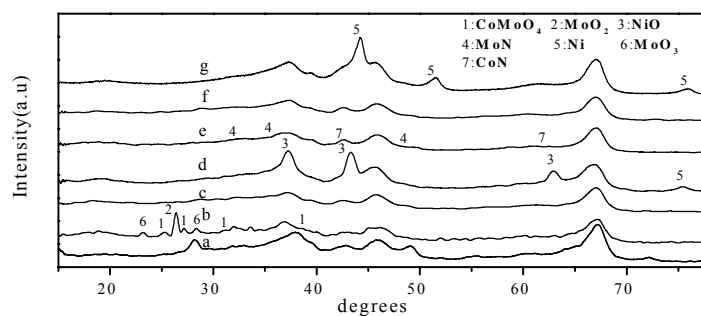


Figure 2 TPR-MS profiles of passivated samples

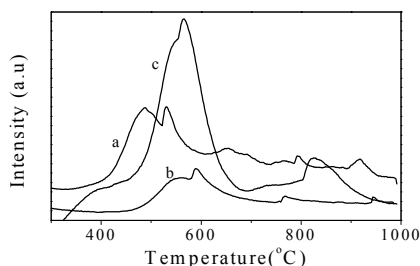
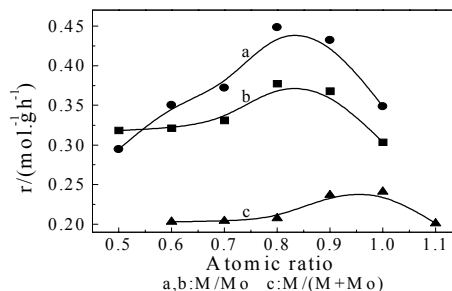


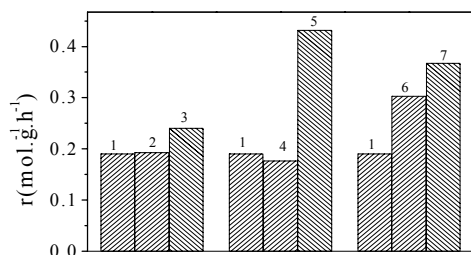
Figure 3 Ammonia decomposition activity as a function of atomic ratio for three nitrides



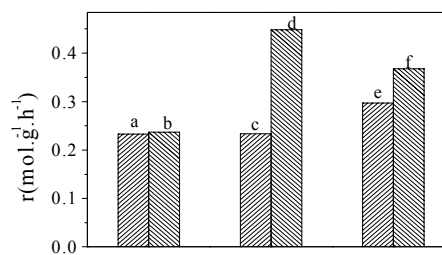
nitrogen desorption peaks at temperatures of 400-700 °C, and 727-1000 °C respectively. Z. B. Wei *et al*⁸ reported that for the fresh Mo_2N , the N_2 desorption at 600 °C in TPR correspond to the liberation of N_2 during the transformation of $\gamma\text{-Mo}_2\text{N}$ to $\beta\text{-Mo}_2\text{N}$ and around 880°C in TPR is due to the partial decomposition or complete reduction of $\beta\text{-Mo}_2\text{N}$ to Mo. And they thought that the NH_x absorbed species could be removed during the passivation treatment. Therefore, the peaks at temperature of 400-700°C should be ascribed to the structural change of nitrides and the peaks at temperature of 727-1000°C to the complete reduction of formed nitrides to metal, which also indicates that there are some nitride species formed in the period of temperature programmed ammonia reaction on the surface of catalyst.

Figure 3 shows that the effect of the presence of second metal Co, Ni and Fe on the activity of ammonia decomposition for $\text{MoN}/\gamma\text{-Al}_2\text{O}_3$ in the range of atomic ratio 0.5-1.1. With the increase of atomic ratios of Co, or Ni, or Fe to Mo, the activity of $\text{MoN}/\gamma\text{-Al}_2\text{O}_3$ increases gradually, and when the atomic ratios are equal to about 0.8, the activities reach the highest values. However, the promotions of the presence of Co, Ni and Fe on the $\text{MoN}/\gamma\text{-Al}_2\text{O}_3$ have remarked difference. The presence of cobalt shows significant promotion on the activity, and the presence of iron just shows a slight promotion.

Figure 4 visibly shows the synergic action between Fe, or Co, or Ni and Mo in the case of their best atomic ratios with the comparison of the ammonia decomposition

Figure 4 The comparison of ammonia decomposition activity between monometallic

- 1: Mo_xN/γ-Al₂O₃ (10%MoO₃); 2: Fe_xN/γ-Al₂O₃ (11.8%Fe₂O₃);
 3: Fe_xMo_yN/γ-Al₂O₃ (10%MoO₃·11.8%Fe₂O₃);
 4: Co_xN/γ-Al₂O₃ (9.8%Co₂O₃);
 5: Co_xMo_yN/γ-Al₂O₃ (10%MoO₃·9.8%Co₂O₃);
 6: Ni_xN/γ-Al₂O₃ (22.1%NiO);
 7: Ni_xMo_yN/γ-Al₂O₃ (10%MoO₃·22.1%NiO).

Figure 5 The comparison of ammonia decomposition activity between nitrides and

- a: Fe_xMo_yO/γ-Al₂O₃ (10%MoO₃·11.8%Fe₂O₃);
 b: Fe_xMo_yN/γ-Al₂O₃ (10%MoO₃·11.8%Fe₂O₃);
 c: Co_xMo_yO/γ-Al₂O₃ (10%MoO₃·9.8%Co₂O₃);
 d: Co_xMo_yN/γ-Al₂O₃ (10%MoO₃·9.8%Co₂O₃);
 e: Ni_xMo_yO/γ-Al₂O₃ (10%MoO₃·22.1%NiO);
 f: Ni_xMo_yN/γ-Al₂O₃ (10%MoO₃·22.1%NiO).

activity of monometallic nitrides and bimetallic nitrides. This result indicates that bimetallic nitrides are more active catalysts than monometallic nitrides for ammonia decomposition, particularly Co_xMo_yN/γ-Al₂O₃ catalyst. This result might be interpreted as the decrease of nitrogen adsorption energy on Mo in the presence of Co⁹. Also Co (or Ni, Fe)-Mo binary sites might have more active than Mo-Mo sites for ammonia decomposition.

Figure 5 shows the activities of the nitrides and their corresponding precursor oxides for ammonia decomposition. For Co_xMo_yN/γ-Al₂O₃ and Ni_xMo_yN/γ-Al₂O₃, their activities are significantly higher than those of their precursor oxides, which suggested that bimetallic oxides can be nitrated or reduced into active form, but this is a slow process. However, for Fe_xMo_yN/γ-Al₂O₃, this process may be easier because their activities seem to be identical.

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