

RKCL5155

**PREPARATION AND EVALUATION OF AMMONIA  
DECOMPOSITION CATALYSTS BY HIGH-THROUGHPUT  
TECHNIQUE**

**Hongchao Liu<sup>a, b</sup>, Hua Wang<sup>a</sup>, Jiangnan Shen<sup>a, b</sup>, Ying Sun<sup>a, b</sup>  
and Zhongmin Liu<sup>a\*</sup>**

<sup>a</sup> Laboratory of Applied Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China;

<sup>b</sup> Graduate School of the Chinese Academy of Sciences, Beijing 100049, China

*Received May 10, 2007, in revised form September 10, 2007, accepted September 14, 2007*

**Abstract**

The high-throughput technique has been successfully employed to investigate systematically NH<sub>3</sub> decomposition catalysts for CO<sub>x</sub>-free hydrogen production. Supported  $\gamma$ -Mo<sub>2</sub>N catalysts not only could be prepared and evaluated by the high-throughput experiment, but are also active for NH<sub>3</sub> decomposition like supported Ni and Co catalysts. Additionally, the preparation process and support play important roles on the catalytic performance of supported  $\gamma$ -Mo<sub>2</sub>N catalysts.

*Keywords:* Metal nitride, ammonia decomposition, high-throughput

**INTRODUCTION**

Recently, more attentions have been paid to NH<sub>3</sub> decomposition due to its outstanding benefits on CO<sub>x</sub>-free hydrogen production as compared with that from carbonaceous materials [1]. Many catalysts such as Ru-based, Ni-based and even metal nitride catalysts have been studied individually for NH<sub>3</sub>

---

\* Corresponding author. E-mail: liuzm@dicp.ac.cn

decomposition and reviewed in the literature [2]. However, the method of preparation and evaluation of the catalysts one by one, especially the metal nitride, is time-consuming due to rigorous preparation conditions.

For the high-throughput technique has been proven that it could accelerate the screening and testing of catalysts and increase the probability of discovering new catalysts or optimizing existing ones. It is a promising methodology in heterogeneous catalysis [3]. We have developed a high-throughput screening system by the incorporation of a multistream reactor, and a multistream mass spectrometer screening (MSMSS) system to test and characterize catalysts [4, 5]. Clearly, it is interesting to employ this technique in the screening of  $\text{NH}_3$  decomposition catalysts for  $\text{CO}_x$ -free hydrogen production.

In this study, the preparation and screening of  $\text{NH}_3$  decomposition catalysts have been performed by using the home-made high-throughput system. The effects of the preparation process and the support have also been investigated on the performance of the catalysts.

## EXPERIMENTAL

### Catalyst preparation

The supported metal catalysts were prepared by impregnating supports (40~60 mesh) with the precursor solution prepared with a computer-controlled Varian sample preparation system. Following impregnation, the samples were dried overnight at room temperature and then calcined at 773 K for 3 h. For multiple impregnation, the above operation was repeated several times.

The home-made MSMSS system was employed to prepare and test the nitrated samples. All of the 33 fresh samples (about 100 mg for each one) were loaded into the respective tube reactor in a home-made multi-stream reactor. Subsequently, the samples were nitrated in a  $\text{H}_2/\text{N}_2$  mixture flow ( $\text{H}_2/\text{N}_2$  ratio: 5:1, SV: 10000 mL/min·g-cat) first the temperature was increased from room temperature to 623 K with a heating rate of 8 K/min, then at 0.5 K/min to 773 K, and 2 K/min to 923 K, respectively, finally maintained at 923 K for 150 min. After nitrification, all the samples were tested in-situ.

### Catalyst characterization

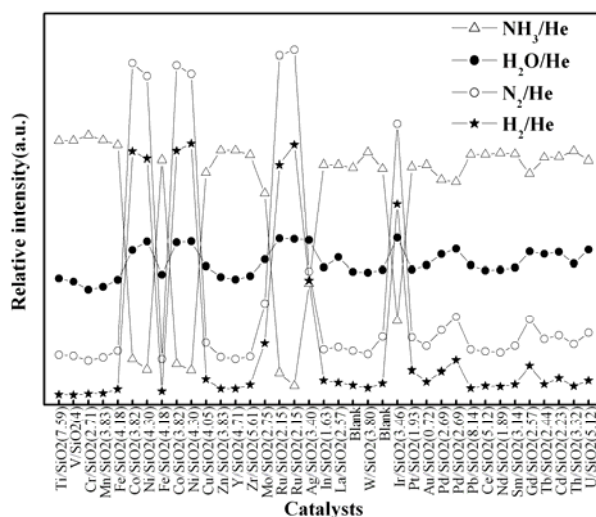
Powder X-ray diffraction (XRD) patterns of the samples were recorded using a D/max-rb type X-ray diffractometer (Cu  $\text{K}\alpha$  radiation) in the  $2\theta$  range of 10-80°. The chemical compositions were determined with a Philips Magix X spectrometer.

### Catalyst testing

Catalytic testing was carried out in a multistream reactor under pure  $\text{NH}_3$  (flow rate: 60 mL/min) and He was (flow rate: 20 mL/min) used as reference gas. Prior to the reaction, the supported metal catalysts were reduced under pure  $\text{NH}_3$ , and the freshly nitrated catalysts as well were purged with a flow of He. The effluent gases were detected with a mass spectrometer (Hiden Analytical). To obtain information with regard to the activity of catalysts, selected mass ions representing the effluent gas were detected during the test process, in which the  $m/e$  mass number were: 2 ( $\text{H}_2$ ), 4 (He), 16 ( $\text{NH}_3$ ), 18 ( $\text{H}_2\text{O}$ ) and 28 ( $\text{N}_2$ ), respectively. The time for data collection of the effluent gases for each sample tube was 9 s.

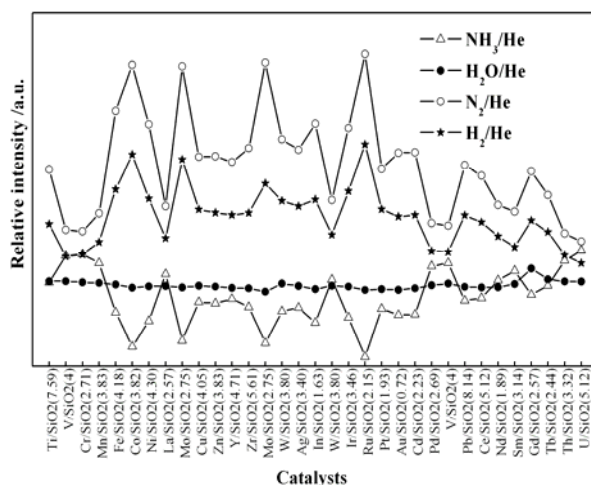
To validate the results of the high-throughput experiment, a fixed-bed continuous flow quartz reactor was employed to evaluate catalytic activity. Analysis of the effluent was performed with an on-line gas chromatograph (Varian CP-3800) equipped with a Poropak N column and a thermal conductivity detector.

## RESULTS AND DISCUSSION



**Fig. 1.** Relative intensity of the reactants and products of ammonia decomposition over transition metal catalysts supported on  $\text{SiO}_2$  at 843 K. [For supported catalysts, the number in bracket refers to the metal loading]

Figure 1 shows the activity of  $\text{NH}_3$  decomposition over different transition metals catalysts supported on silica. The relative intensities of  $\text{NH}_3$ ,  $\text{H}_2$  and  $\text{N}_2$  over the sample tubes such as  $\text{Co/SiO}_2(3.82)$  are nearly identical to that of their duplicates, respectively, and different from that of the other sample tubes and blank tubes, indicating the high reproducibility and no “crosstalk” between the neighboring tubes. The  $\text{Ru/SiO}_2$  catalysts are the most active as seen in Fig. 1. We have found that even then loaded on different supports, the Ru-based catalysts still exhibit lower initial reaction and higher performance than the nonprecious metal catalysts. However, the high price renders their industrial application quite questionable. However, it is interesting to see that supported Ni and Co catalysts as nonprecious metal catalysts, which are cheaper than the Ru-based catalysts, show higher performance in Fig. 1.



**Fig. 2.** Relative intensity of reactants and products of ammonia decomposition over nitrated transition metal catalyst supported on  $\text{SiO}_2$  at 923 K. [For supported catalysts, the number in bracket refers to the metal loading]

Figure 2 shows the activity of samples treated with temperature-programmed nitrification under a  $\text{H}_2/\text{N}_2$  mixture flow. At 923 K, high relative intensities of  $\text{NH}_3$ ,  $\text{H}_2$  and  $\text{N}_2$  over the supported Ru could be obtained which are similar to that in Fig. 1. One can see that the almost inert Fe catalyst in Fig. 1 shows higher catalytic performance for  $\text{NH}_3$  decomposition after nitrification. The apparent activation energy of  $\text{NH}_3$  decomposition over iron nitrides is nearly two-times smaller in comparison with clean iron [6]. Itoh *et al.* [7] also assumed iron nitride to be the active intermediate formed when  $\text{NH}_3$  decomposed over Fe-(Ce, Zr) $\text{O}_2$  composite powder. Therefore, the enhanced performance of iron catalysts might be attributed to the formation of iron nitrides. On the other hand, changes can be observed in the relative intensity of  $\text{NH}_3$ ,  $\text{H}_2$  and  $\text{N}_2$  over

supported Mo catalysts between the unnitrided sample (in Fig. 1) and nitrated sample (in Fig. 2). MoN<sub>x</sub> could be synthesized from MoO<sub>3</sub> and it is effective in catalyzing NH<sub>3</sub> decomposition reaction [8]. To identify whether it was nitrated, the supported Mo catalyst after nitridation was characterized by the XRD method. Figure 3 shows the XRD patterns of MoN<sub>x</sub>/SiO<sub>2</sub>. Peaks at 37°, 43.2°, 63.1°, 75°, which are assigned to the {111}, {200}, {220}, {311} reflections of  $\gamma$ -Mo<sub>2</sub>N (JCPDS, 25-1366), could be observed, indicating the formation of  $\gamma$ -Mo<sub>2</sub>N/SiO<sub>2</sub> from MoO<sub>3</sub>/SiO<sub>2</sub>. Therefore, the enhanced performance of the supported Mo catalyst nitrified under H<sub>2</sub>/N<sub>2</sub> mixture flow should be attributed to the formation of  $\gamma$ -Mo<sub>2</sub>N.

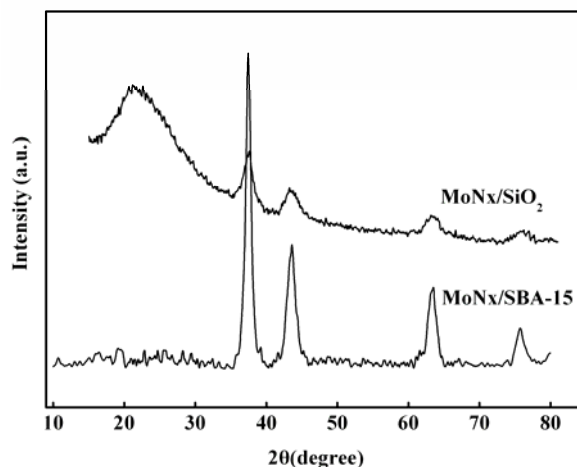


Fig. 3. XRD patterns of MoN<sub>x</sub>/SiO<sub>2</sub> and MoN<sub>x</sub>/SBA-15 after reaction

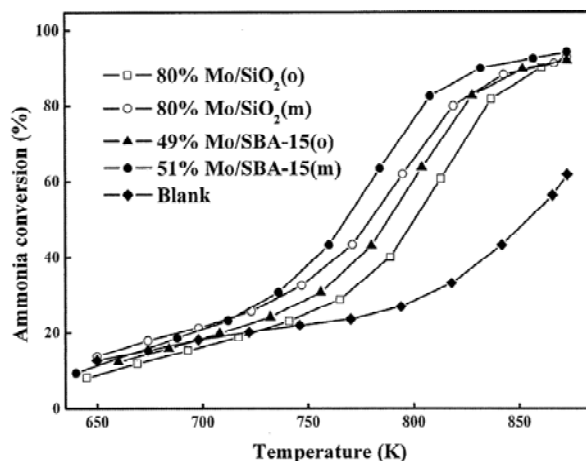
Nitrides such as vanadium nitride and titanium nitrides as NH<sub>3</sub> decomposition catalysts have also been reported [2]. However, hardly any changes of the activity of the SiO<sub>2</sub>-supported Ti, V and W catalysts could be observed after treatment when comparing the data in Figs 1 and 2. Previous investigation [9] shows the formation of vanadium nitride, as well as tungsten nitride, which requires higher final synthesis temperatures than molybdenum under an ammonia atmosphere. Therefore, we deduce that the supported Ti, V and W were hardly nitrated under the selected conditions by this high-throughput technique.

To clarify the effect of the preparation process and the support on the catalytic performance, a series of MoN<sub>x</sub> catalysts with SBA-15 and SiO<sub>2</sub> as supports were prepared and tested by the high-throughput technique for NH<sub>3</sub> decomposition. To distinguish the results of high-throughput experiment, NH<sub>3</sub> conversion were calculated from the following equation:

$$\text{Conversion} = 100 \times \frac{I_0 - I}{I_0}$$

where  $I_0$  and  $I$  represent the relative MS signal of  $\text{NH}_3$  before and after reactions, respectively.

The XRD pattern of one  $\text{MoN}_x/\text{SBA-15}$  prepared with the high-throughput experiment is shown in Fig. 3. Obvious characteristic peaks of  $\gamma\text{-Mo}_2\text{N}$  could be observed. To distinguish the precursors prepared by different methods, the catalysts were labeled as  $\text{MoN}_x/\text{SBA-15(o)}$  and  $\text{MoN}_x/\text{SBA-15(m)}$ , in which the symbol “o” and “m” represent the one-step impregnation and multiple impregnation, respectively. Figure 4 shows partial results of high-throughput experiments. Obviously, the  $\text{NH}_3$  conversion over  $\text{MoN}_x/\text{SBA-15(m)}$  is higher than that over  $\text{MoN}_x/\text{SBA-15(o)}$  when the reaction temperature is increased from 700 to 850 K. Similar result could be obtained on  $\text{SiO}_2$ -supported molybdenum nitride catalysts. The results indicate that the multiple impregnation is superior to one-step impregnation in the preparation of precursors for supported molybdenum nitride in  $\text{NH}_3$  decomposition reaction.



**Fig. 4.** Comparison of ammonia conversions over  $\text{Mo}_2\text{N}/\text{SiO}_2$  and  $\text{Mo}_2\text{N}/\text{SBA-15}$  catalysts by the high-throughput method. [“o” and “m” in parentheses represent one-step impregnation and multiple impregnation, respectively]

Higher  $\text{NH}_3$  conversions over the  $\text{MoN}_x/\text{SBA-15}$  could be observed than that over  $\text{MoN}_x/\text{SiO}_2$  under identical reaction conditions in Fig. 4, indicating that the effect of the support structure couldn't be neglected although SBA-15 and  $\text{SiO}_2$  are both siliceous materials. With regard to SBA-15, the high surface area allows for a higher dispersion of the active component than for

conventional amorphous silica, and the presence of the uniform pore-size distribution allows, in principle, for a better control on the particle size of the active component and thereby also on the catalytic properties. Therefore, we conclude that SBA-15 is a more suitable than SiO<sub>2</sub> as a support of molybdenum nitride catalysts in the ammonia decomposition reaction.

Ammonia decomposition reactions over MoN<sub>x</sub>/SBA-15 and MoN<sub>x</sub>/SiO<sub>2</sub> with the same weight loading synthesized by the same procedure have also been performed in a fixed-bed continuous flow reactor. More than 80% ammonia conversion could be achieved over the MoN<sub>x</sub>/SBA-15 at 823 K with a GHSV<sub>NH<sub>3</sub></sub> of 3600 mL/h·g-cat, which is higher than that for MoN<sub>x</sub>/SiO<sub>2</sub>. The result is similar to that obtained by the high-throughput technique, indicating that the high-throughput technique is suitable for preparing and testing metal catalysts for NH<sub>3</sub> decomposition.

## CONCLUSIONS

The high-throughput technique is an effective and reliable method, has been successfully performed for a primary screening of supported catalysts for NH<sub>3</sub> decomposition. Supported Ni, Co and  $\gamma$ -Mo<sub>2</sub>N catalysts might be promising substitutes of Ru-based catalysts in the NH<sub>3</sub> decomposition reaction. The preparation process of the precursors and support of supported  $\gamma$ -Mo<sub>2</sub>N catalysts play a decisive role in the catalytic performance for NH<sub>3</sub> decomposition. Moreover, it is worth pointing out that the preparation and testing of supported  $\gamma$ -Mo<sub>2</sub>N catalysts by high-throughput techniques provide a new route to study these catalysts of noble metal character in many reactions involving hydrogen.

## REFERENCES

1. R. Metkemeijer, P. Achard: *Int. J. Hydrogen Energy*, **19**, 535 (1994).
2. S.F. Yin, B.Q. Xu, X.P. Zhou, C.T. Au: *Appl. Catal. A*, **277**, 1 (2004).
3. W.F. Maier: *Angew. Chem. Int. Ed.*, **38**, 1216 (1999).
4. H. Wang, Z.M. Liu, J.H. Shen: *J. Comb. Chem.*, **5**, 802 (2003).
5. H. Wang, Z.M. Liu, J.H. Shen, H.C. Liu: *Catal. Commun.*, **5**, 55 (2004).
6. W. Arabczyk, J. Zamblyny: *Catal. Lett.*, **60**, 167 (1999).
7. M. Itoh, M. Masuda, K. Machida: *Mater. Trans.*, **43**, 2763-2767 (2002).
8. R.S. Wise, E.J. Markel: *J. Catal.*, **145**, 335 (1994).
9. J.B. Claridge, A.P.E. York, A.J. Brungs, M.L.H. Green: *Chem. Mater.*, **12** 132 (2000).