



Influence of alkali metal amides on the catalytic activity of manganese nitride for ammonia decomposition



Fei Chang^{a,b}, Jianping Guo^{a,*}, Guotao Wu^a, Peikun Wang^{a,b}, Pei Yu^{a,b}, Ping Chen^{a,c,d,*}

^a Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

^b University of Chinese Academy of Sciences, Beijing 100049, China

^c State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

^d Collaborative Innovation Center of Chemistry for Energy Materials, Dalian 116023, China

ARTICLE INFO

Article history:

Received 31 March 2016

Received in revised form 19 August 2016

Accepted 9 September 2016

Available online 15 September 2016

Keywords:

Alkali metal amide

Manganese nitride

Electronic promotion

Ammonia decomposition

ABSTRACT

Strong promoting effect of alkali metal amides, i.e., LiNH_2 , NaNH_2 and KNH_2 , on the catalytic activity of manganese nitride (MnN) for ammonia decomposition has been demonstrated, which is evidenced by ca. 100 K drop in onset temperature and by ca. 50–60 kJ mol^{-1} reduction in apparent activation energy as compared with the neat MnN . The order of promotion capability of alkali metal amides can be ranked as $\text{LiNH}_2 > \text{KNH}_2 \geq \text{NaNH}_2$, either in term of NH_3 conversion rate or turnover frequency (TOF), which is distinctly different from that of conventional alkali metal oxides or hydroxides, i.e., $\text{K} > \text{Na} > \text{Li}$. This phenomenon suggests that the promoting mechanism of alkalis depends on their chemical forms. When alkalis are in the form of amide or imide, they may function as co-catalysts by participating in the catalytic circle directly rather than by executing electronic promotion influence on transition metals.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

With large annual production, high hydrogen content (17.7 wt%), high energy density (3 kWh kg^{-1}), facile storage and transportation, ammonia is an ideal energy carrier that may play important roles in the forthcoming hydrogen economy [1,2]. Decomposition of ammonia to CO_x -free ($x = 1, 2$) H_2 can be catalyzed by a number of transition metals, alloys, metal carbides and nitrides [3–5], among which Ru-based catalysts are the most active while their performances are affected by the nature of the supports and additives [3,6–11]. However, the high cost and limited supply of Ru hinder its practical application. Hence, there is a need to develop highly efficient and non-noble metal alternatives for catalyzing ammonia decomposition.

Owing to the noble metal-like catalytic properties, transition metal nitrides have been evaluated for many reactions including hydrodenitrogenation (HDN), NO decomposition, ammonia synthesis and decomposition [12]. VN, Mo_2N and Fe_3N with large surface area or specific morphologies were tested in NH_3 decomposition [13–15]. The ternary nitrides (Co-Mo-N, Ni-Mo-N) combining elements from both the left and right sides of the volcano curve pos-

sess an optimal N binding energy and exhibit impressive ammonia decomposition activities [16–18]. Except for the early work of Lotz [19], however, little attention has been given to manganese nitride due to its poor intrinsic activity for ammonia decomposition.

Alkali metal oxides or hydroxides are indispensable electronic promoters of transition metal catalysts. However, their promoting mechanisms are still under debate. For both ammonia synthesis and decomposition, it has been reported that the promoting effect of alkali metal oxide or hydroxide is correlated with their electronegativities, that is, the higher the electronegativity of the alkali, the lower is the promoting effect, i.e., in the sequence of $\text{Cs} > \text{K} > \text{Na} > \text{Li}$ [20,21]. Among them, lithium is nearly non-promotive. Recently we found that when lithium is in the form of imide (Li_2NH), it can synergize with manganese nitride (MnN) and lead to a comparable activity as that of the highly active Ru/CNTs catalyst [22]. A two-step pathway was proposed for the interpretation of catalysis of the $\text{MnN-Li}_2\text{NH}$ composite, in which Li_2NH reacts with MnN to form a relatively stable ternary nitride intermediate (Li_7MnN_4) and H_2 , and then the ammoniation of Li_7MnN_4 to Li_2NH , MnN and N_2 [23]. Li_2NH plays a role as a co-catalyst which is substantially different from the “electron-donating” effect of those of alkali metal oxides or hydroxides in the conventional catalysts. Besides Li, Na or K only has its amide form, namely NaNH_2 or KNH_2 . A recent report also showed that NaNH_2 exhibited catalytic effect on NH_3 decomposition when tested in a stainless steel reactor [24]. In this context, it would be interesting to figure out if the amides of Na or K may

* Corresponding authors at: Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China.

E-mail addresses: guojianping@dicp.ac.cn (J. Guo), pchen@dicp.ac.cn (P. Chen).

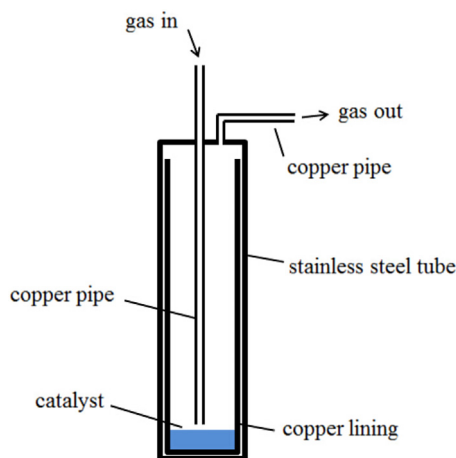


Fig. 1. Sketch map of the Cu lining tank reactor.

have similar function as Li_2NH on manganese nitride for ammonia decomposition.

In this study, therefore, the influences of NaNH_2 and KNH_2 on the catalytic performance of MnN in ammonia decomposition were investigated and the catalytic activities of NaNH_2 - and KNH_2 - MnN were compared with that of the Li_2NH - MnN composite. We found that both NaNH_2 and KNH_2 have positive effects on the catalytic activity of MnN , but are inferior to that of Li_2NH . The order of promoting capability of alkali amides/imide can be ranked as $\text{Li} > \text{K} \geq \text{Na}$, which is different from the order of conventional alkali oxides or hydroxides. The interaction of MnN and alkali metal amides were characterized by using temperature-programmed reaction (TPR) and X-ray diffraction (XRD). Those experimental data indicate that alkali metal amides have different functioning mechanisms from oxides or hydroxides.

2. Experimental

2.1. Catalyst preparation

LiNH_2 (Aldrich, 95%), NaNH_2 (Aldrich, 98%), MnCl_2 (Alfa, 97%) and potassium metal (Aldrich, 98%) were used as received. All sample handling was performed in an argon-filled glove box. KNH_2 was prepared by reacting potassium metal with ammonia at room temperature for ca. two days. The solid white powder product was collected and characterized to be KNH_2 by XRD (X-ray diffraction) measurements. MnN was prepared according to the previous report [22]. MnCl_2 and LiNH_2 with a molar ratio of 1:2 were ball-milled on a Retsch planetary ball mill (PM 400) for 3 h at a rotate velocity of 150/min. Then the black product was heated to 573 K and held for 3 h under a pure NH_3 flow. After that, the solid was washed by tetrahydrofuran (THF) solution to remove LiCl byproduct. MnN-LiNH_2 , MnN-NaNH_2 and MnN-KNH_2 catalysts were prepared by ball-milling MnN and the corresponding alkali metal amide in a molar ratio of 1:1 at 150 rounds per minute for 3 h.

2.2. Catalyst test

Ammonia decomposition activity tests were performed in a self-made Cu lining tank reactor as shown in Fig. 1. The catalyst samples (0.2 g) were placed in the bottom of the Cu lining and tested under a flow of pure NH_3 (45 ml min^{-1}) at ambient pressure. The activity tests were performed in the temperature range of 583–760 K. Under those reaction conditions the external and internal mass diffusion limitations can be excluded. Each data point shown in Fig. 2 was recorded after 1 h of time on stream at the corresponding temper-

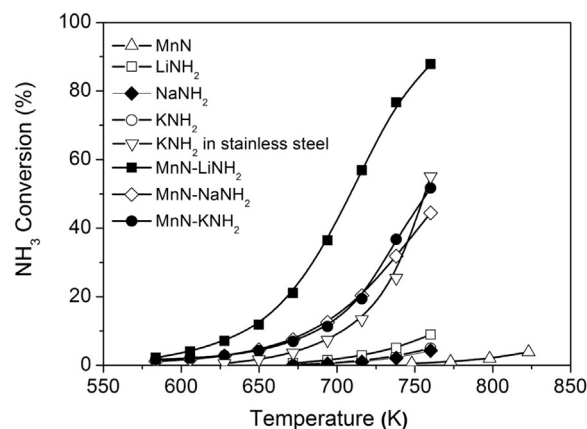


Fig. 2. Temperature dependences of the activities of different catalysts for NH_3 decomposition. MnN catalyst was tested in a quartz reactor under $\text{WHSV} = 40000 \text{ ml}_{\text{NH}_3} \text{ g}^{-1} \text{ cat} \text{ h}^{-1}$. All the other catalysts were tested in the Cu lining tank reactor with a precursor loading 0.2 g and NH_3 flow rate = 45 ml min^{-1} ($\text{WHSV} = 13500 \text{ ml}_{\text{NH}_3} \text{ g}^{-1} \text{ cat} \text{ h}^{-1}$). The ammonia decomposition activity of neat KNH_2 in a stainless steel reactor is also shown here.

ature. During this period, the activity of tested sample is relatively stable with an error of $\pm 4\%$. Apparent activation energy values (E_a) were obtained from the Arrhenius plots, in which the ammonia conversions are far from thermodynamic equilibrium values.

The effluent gases were analyzed by a gas chromatograph equipped with a TCD and a Porapak N column, using hydrogen as the carrier gas. Ammonia conversion is defined as: $\text{Conversion}_{\text{NH}_3} = \left(1 - \frac{C_{\text{out}}}{C_{\text{in}}}\right) \times 100\%$. C_{out} is the ammonia concentration at the reactor outlet. C_{in} is the ammonia concentration at the reactor inlet.

The turnover frequency (TOF) was also obtained here for the purpose of comparison of different catalysts. The calculation procedure is shown as follows,

$$\text{TOF}_{\text{H}_2} = \frac{P \times F}{R \times T} \times \text{Conversion}_{\text{NH}_3} \times \frac{3}{2}$$

P is ambient pressure; F is ammonia flow rate; R is the gas constant; T is the temperature; N_{Mn} is the total number of Mn atoms in the catalysts determined by ICP-OES method. All the values adopted in the equation should convert to the International System of Units.

2.3. Catalyst characterization

Powder X-ray diffraction (XRD) patterns were recorded on a PANalytical X'pert diffractometer with $\text{Cu-K}\alpha$ radiation ($\lambda = 0.154 \text{ nm}$) at a setting of 40 kV and 40 mA. The sample cell is covered with KAPTON film to avoid air and moisture contamination. The contents of Mn and alkali metals in the catalyst were determined by inductively coupled plasma optical emission spectrometer (ICP-OES, optima 7300DV, Perkin-Elmer, USA) and shown in Table 1. The temperature-programmed reaction (TPR) and temperature-programmed decomposition (TPD) have been widely applied in the characterization of chemical reactions and catalyst properties. In this work, we use these techniques to investigate the interaction of MnN and alkali metal amides. The TPR and TPD were carried out on a home-made system combining the reactor and the mass spectrometer (Hiden HPR20) to record the signals of N_2 ($m/z = 28$), H_2 ($m/z = 2$) and NH_3 ($m/z = 17$). The samples were heated from room temperature to the desired temperatures at a ramping rate of 5 K min^{-1} in the Argon flow (flow rate = 40 ml min^{-1}).

Download English Version:

<https://daneshyari.com/en/article/6455306>

Download Persian Version:

<https://daneshyari.com/article/6455306>

[Daneshyari.com](https://daneshyari.com)