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### 1. Introduction

The on-site generation of hydrogen for fuel cells is of great important for environmental protection consideration.<sup>1</sup> The direct generation of clean and cheap hydrogen motivates the investigation on catalytic ammonia decomposition because ammonia has a high hydrogen storage density, low price,  $CO_x$ -free, complete production technology and transportation technology and other advantages. On the other hand, the catalytic removal of ammonia from gasification product gas or direct ammonia fuel cells, are highlighted as well.<sup>2,3</sup>

Recently, many catalysts for ammonia decomposition have been investigated, and the effects of active metals (Ru, Rh, Pt, Pd, Ni, Fe, Co and Mo) and support materials (carbon nanotubes, activated carbon, Al<sub>2</sub>O<sub>3</sub>, MgO, ZrO<sub>2</sub> and TiO<sub>2</sub>) on the catalysis of ammonia decomposition were studied.<sup>4–9</sup> Although the precious metal catalysts have high activity for

## Homogeneous precipitation method preparation of modified red mud supported Ni mesoporous catalysts for ammonia decomposition

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Red mud modified by an acid digestion and alkali reprecipitation approach was employed as support for the preparation of Ni/MRM catalysts using the homogeneous precipitation method. The textural and structural properties of the as-received red mud (RM), the modified red mud (MRM) and the as-prepared Ni/MRM catalysts were characterized by X-ray diffraction (XRD), energy dispersive X-ray fluorescence (EDXRF), thermogravimetry-differential scanning calorimetry analysis (TG-DSC), Fourier transform infrared spectra (FT-IR), transmission electron microscopy (TEM) combined with energy-dispersive X-ray spectroscopy (EDX) and N<sub>2</sub> sorption techniques. The analysis results revealed a mesoporous nanocatalyst system with high surface area and uniform pore-size distribution. The results of the catalytic activity measurements showed that these mesoporous nanostructured Ni/MRM catalysts were very active for ammonia decomposition. The catalyst with 15% Ni loading and calcined at 600 °C exhibited the highest catalytic activity. Due to its unique properties and the feature of resource utilization of industrial solid waste, MRM holds great promise for developing catalysts and catalyst supports for applications in various catalytic reactions including catalytic ammonia decomposition.

ammonia decomposition, the high cost and limited availability discourage their extensive applications. Much attention has been recently been paid to base metal as catalysis, especially Ni-based catalysts, for the purpose to find an alternative catalytic component to reduce using or even replace the noble metal.<sup>9–11</sup> Our recent studies<sup>10</sup> have demonstrated that the high surface area Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> solid solutions supported Ni catalysts display high activity for ammonia decomposition to hydrogen. Wang *et al.*<sup>11</sup> investigated the role of support (Al<sub>2</sub>O<sub>3</sub>, MgO and TiO<sub>2</sub>) in the high-performance Ni-based catalytic system for ammonia decomposition.

Red mud, an aluminum industry waste, is a serious pollution hazardous material due to its high alkalinity in case of disposal. In general, red mud is a very fine material in terms of particle size distribution, having an average particle size <10  $\mu$ m. It is primarily composed of iron, aluminum, titanium, silicon, calcium oxides and hydroxides. The treatment and resource utilization of red mud has received widespread attention. Due to its stability, high surface area, sintering resistance and resistance to poisoning, red mud has been employed as catalyst and catalyst support for various catalytic reactions, such as hydrogenation,<sup>12–16</sup> hydrodechlorination<sup>17–19</sup> and exhaust gas clean-up.<sup>20–23</sup> Ng *et al.*<sup>24</sup> have employed red mud supported Ru as catalyst for ammonia decomposition and proved that it possesses high activity.



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In this work, we proposed an application of modified red mud (MRM) as support for Ni catalysts in catalytic ammonia decomposition. In view of the strong basicity and structural complexity of red mud, dilute acid digestion and alkali reprecipitation (same as sol-gel method) were applied to the red mud sample for modifying the surface and crystal structure, similar to the reported approach of Sushil and Batra.<sup>23</sup> The MRM sample was employed as support for the preparation of Ni/MRM catalysts by homogeneous precipitation method. The textural and structural properties of the red mud and the as-prepared Ni/MRM catalysts were characterized by means of XRD, EDXRF, TG-DSC, FT-IR, N<sub>2</sub> sorption and TEM-EDX. The effect of the Ni loading amount and calcination temperature on the catalytic ammonia decomposition activities of the mesoporous Ni/MRM catalysts were investigated in detail. As a result, the NH<sub>3</sub> conversion of 97.9% with the  $\rm H_2$  formation rate of 32.8 mmol  $\rm min^{-1}~g_{cat}^{-1}$  was achieved at 700 °C over the Ni catalyst supported on the mesoporous/ high-surface-area MRM.

### 2. Experimental section

#### 2.1 Catalysts' preparation

The red mud (RM) sample was collected from a downstream slurry pond in Henan Zhongmei Aluminum Corporation, China (the main chemical composition is showed in Table 1). Furthermore red mud exhibits strong alkaline property (pH = 10.26), due to the sodium oxide.<sup>25</sup> The sample was dried, ground and sieved to a size of <150  $\mu$ m.

In a typical process of red mud modification, 25 g of red mud sample was taken and 100 ml distilled water was added to it. After stirring for 5 min, 150 ml of 6 M HCl solution was added. The sample was digested at 85 °C on a water-bath heater for 2 h. The digested sample was subsequently prepared by sol–gel method, as described below. It was precipitated by adding aqueous ammonia and simultaneous stirring until pH  $\approx$  8, and kept for 30 min. The solution and the resulting precipitate was aged at 70 °C for 30 min, sonicated for 10 min, washed several times with warm distilled water until pH  $\approx$  7, and then washed again with anhydrous ethanol. Finally, the precipitate was separated by filtration, dried for 12 h in air at 110 °C, but not calcined. The as-prepared sample was modified red mud, and denoted as MRM.

The catalysts for  $NH_3$  decomposition were prepared by homogeneous precipitation method. At room temperature, the calculated amount of  $Ni(NO_3)_2 \cdot 6H_2O$  and an excess of urea (the mole ratio of Ni and urea was 1:4) were dissolved in 200 ml of distilled water and then mixed with 6 g of MRM under vigorous stirring. The mixture reacted at 95 °C on a Heating Magnetic Stirrer for 10 h. Subsequently, the solution and the resulting precipitate was washed several times with distilled water until pH  $\approx$  7, washed again with anhydrous ethanol, dried in the oven at 110 °C for 12 h, then milled and calcined at 600 °C for 2 h. The content of Ni was 0, 3, 6, 9, 12, 15, 18 wt.%, and the corresponding catalysts were denoted as *x*%-Ni/MRM (*x* = 0, 3, 6, 9, 12, 15 and 18). In order to make clear the influence of the calcination temperature on the catalyst property, a series of Ni/MRM catalysts calcined at different temperature were prepared in the similar manner.

#### 2.2 Characterization

X-ray diffraction (XRD) analysis was performed on a Bruker-AXS D8 Advance diffractometer, with  $CuK_{\alpha}$  radiation at 40 kV and 25 mA in a scanning range of 10–80° (2 $\theta$ ). The diffraction peaks of the crystalline phase were compared with those of standard compounds reported in the JCPDS Date File. The chemical composition of samples were carried out by means of energy dispersive X-ray fluorescence (EDXRF) spectrometer (Panalitical Magix, PW2403). Thermogravimetry-differential scanning calorimetry analysis (TG-DSC) was done on a Setaram SETSYS Evolution 24 thermogravimetric analyzer. The sample was heated with a rate of 15 °C min<sup>-1</sup> from 20 °C to 1000 °C in pure argon. Fourier transform infrared spectra (FT-IR) were measured on a Bruker V70 spectrometer, with the KBr pellet technique, and the ranges of spectrograms were  $4000-400 \text{ cm}^{-1}$ . N2 adsorption-desorption isotherms were collected at liquid nitrogen temperature using a Quantachrome AsiQM0000-3 sorption analyzer. Before carrying out the measurement, each sample was degassed at 180 °C for more than 6 h. The specific surface areas  $(S_{BET})$  of the samples were calculated following the multi-point BET (Brunauer-Emmett-Teller) procedure. The pore size distributions were determined from the adsorption branch of the isotherms using the DFT method. Transmission electron microscopy (TEM) combined with energy-dispersive X-ray spectroscopy (EDX) analysis was performed on a JEOL JEM-2200FS microscope, operating at 200 kV. The samples were dispersed in ethanol and treated with ultrasound for 5 min, and then deposited on a copper grid coated with preformed holey carbon film.

#### 2.3 Catalytic testing

Ammonia decomposition experiments were carried out in a continuous-flow fixed-bed microreactor. And the reactor tube was a quartz tube with an inner diameter of 6 mm, loaded with about 0.1 g of powder catalyst deposited between two

Table 1	The main	chemical	composition	of RM	, MRM an	d 600 °C	<ul> <li>calcined</li> </ul>	15%-Ni/	MRM cataly	st
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	Main composition (wt.%)									
Samples	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	$TiO_2$	K <sub>2</sub> O	Na <sub>2</sub> O	CaO	MgO	NiO	
RM	23.25	16.94	15.05	4.27	1.82	3.72	16.94	1.93	0.062	
MRM	29.97	21.9	19.4	5.48	1.77	0.12	1.93	0.73	< 0.001	
15%-Ni/MRM	26.55	19.41	17.23	4.87	1.56	0.1	1.78	0.69	19.64	

quartz wool plugs. Before the measurement, the prepared catalyst sample was reduced *in situ* in a  $H_2$  flow for 2 h and then purged with a flow of pure Ar. The pure  $NH_3$  was used as the reactant at a flow rate of 50 mL min<sup>-1</sup> at atmospheric pressure. The conversion was measured at steady state after 15 min. The products were analyzed online by a SP-6800A6 gas chromatograph equipped with a thermal conductivity detector and Poropak Q column, using  $N_2$  as the carrier gas. The  $H_2$  formation rate was translated from the  $H_2$  content in the outer gas, and the catalytic activity was described as the conversion of ammonia.

### 3. Results and discussion

Fig. 1 shows the XRD patterns of RM and Ni/MRM catalysts with different Ni loading amounts calcined at 600 °C. It can be seen clearly from Fig. 1 that RM is a complex mixture of phases mainly comprised of hydrogarnet (3CaO·Al<sub>2</sub>O<sub>3</sub>·SiO<sub>2</sub>·4H<sub>2</sub>O), cancrinite (Na<sub>6</sub>CaAl<sub>6</sub>Si<sub>6</sub>(CO<sub>3</sub>)O<sub>24</sub>·2H<sub>2</sub>O), hematite (Fe<sub>2</sub>O<sub>3</sub>), goethite (FeOOH), corundum ( $Al_2O_3$ ), gibbsite ( $\gamma$ -Al(OH)<sub>3</sub>), diaspore (AlO(OH)), perovskite (CaTiO<sub>3</sub>), quartz (SiO<sub>2</sub>), rutile (TiO<sub>2</sub>) and calcite (CaCO<sub>3</sub>). Meanwhile, the main phases in MRM-600 are hematite (Fe<sub>2</sub>O<sub>3</sub>), aluminum oxide ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) and quartz (SiO<sub>2</sub>). After modified and calcined at 600 °C, complex group of compounds in RM, such as hydrogarnet and cancrinite, are decomposed. And, most Na and Ca have been removed. When the Ni content is below 12%, no reflections characteristic of NiO structure presented, which may be due to the high dispersion of the Ni species with too small particle sizes on the surface of the support to be identified by the conventional X-ray diffraction method. When the Ni species content increased to 12%, the weak diffraction peaks attributed to NiO crystal phase appeared at 37.7, 43.3 and 62.4° (2 $\theta$ ), indicating the



Fig. 1 XRD patterns of RM (1, hydrogarnet ( $3CaO \cdot Al_2O_3 \cdot SiO_2 \cdot 4H_2O$ ); 2, cancrinite ( $Na_6CaAl_6Si_6(CO_3)O_{24} \cdot 2H_2O$ ); 3, hematite ( $Fe_2O_3$ ); 4, goethite (FeOOH); 5, corundum ( $Al_2O_3$ ); 6, gibbsite ( $Al(OH)_3$ ); 7, diaspore (AlO(OH)); 8, perovskite ( $CaTiO_3$ ); 9, quartz ( $SiO_2$ ); 10, rutile ( $TiO_2$ ); 11, calcite ( $CaCO_3$ )) and Ni/MRM catalysts with different Ni loading amounts calcined at 600 °C (1, hematite ( $Fe_2O_3$ ); 2, aluminum oxide ( $\gamma$ - $Al_2O_3$ ); 3, quartz ( $SiO_2$ ); 4, bunsenite (NiO)).

excess of Ni species and the growth of the NiO nanoparticles in the Ni/MRM systems. The average size of NiO particles in the 12%-Ni/MRM catalyst calcined at 600 °C, calculated from the NiO (2 2 0) reflection peak ( $2\theta = 62.4^{\circ}$ ) by the Scherrer formula, is 14 nm. While the average size of NiO particles in the 15 and 18%-Ni/MRM catalysts calcined at 600 °C, calculated from the NiO (2 0 0) reflection peak ( $2\theta = 43.3^{\circ}$ ) by the Scherrer formula, are 17 and 23 nm, respectively.

The 15%-Ni/MRM sample was taken as being representative for the investigation of the thermal stability of the as-prepared Ni/MRM catalysts. Fig. 2 shows the XRD patterns of 15%-Ni/MRM catalysts calcined at different temperature (500, 600 and 700 °C). From Fig. 2, we can see that goethite (FeOOH) is not completely transformed into oxide in the samples of 15%-Ni/MRM catalyst calcined at 500 °C. This indicated that only when the calcination temperature reached 600 °C the samples can accomplish crystal phase transition. While, with the increase of the precalcination temperature of the Ni/MRM catalysts from 500 to 700 °C, a progressive increase in the relative intensity of the lines of hematite, aluminum oxide ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) and quartz (SiO<sub>2</sub>) phase is seen, indicating an increase of the degree of crystallinity and the growth of particle size by the thermal treatment.

Table 1 shows the main chemical composition of RM, MRM and 600 °C-calcined 15%-Ni/MRM catalyst. From Table 1, we can see that the content of  $Al_2O_3$ ,  $SiO_2$ ,  $Fe_2O_3$ ,  $TiO_2$  and  $K_2O$ has changed little, and the inert components (Na<sub>2</sub>O and CaO) were mainly removed. As for NiO, its content in RM itself is very low, as well as that in MRM. When supported Ni species with the theoretical content of 15 wt.% (calculated as Ni), we got the practical content of 19.64 wt.% (calculated as NiO), which is equivalent to the theoretical value.

The TG-DSC results of RM and the uncalcined 15%-Ni/MRM catalyst are shown in Fig. 3. The TG-DSC curves of RM show a continuous weight loss of 13% from 20 to 1000 °C (Fig. 3a). The weight loss of 1% from 20 to 233 °C can be attributed to



Fig. 2 XRD patterns of 15%-Ni/MRM catalysts calcined at different temperature: 1, hematite (Fe<sub>2</sub>O<sub>3</sub>); 2, aluminum oxide ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>); 3, quartz (SiO<sub>2</sub>); 4, bunsenite (NiO); 5, goethite (FeOOH).

the physical water content of RM by taking DSC curve into account which produced an endothermic peak at 84.4 °C. Furthermore the weight loss of 2.8% from 233 to 335 °C is due to the decomposition of gibbsite,<sup>26-28</sup> partial boehmite (formed from the slight decomposition of gibbsite)<sup>28</sup> and partial goethite<sup>27,28</sup> that was deduced from the interpretation of the endothermic peak at 289.8 °C in DSC. Another endothermic peak is observed at 552.6 °C in DSC. This endothermic peak at these temperatures from 335 to 645 °C with the total mass loss of 5.6%, refers to the decomposition of boehmite (formed from the slight decomposition of gibbsite),<sup>26,27</sup> diaspore<sup>26</sup> and goethite. An endothermic peak starting at about 645 °C and ending at 783 °C is seen at 742 °C in DSC, resulted from the decomposition of calcite.<sup>26,28</sup> And this calcite decomposition caused 3% of the mass loss. After 783 °C, the endothermic peak occuring at 898.3 °C in DSC is related to sodium aluminum carbonate silicate decomposition in the red mud.<sup>26</sup> Fig. 3b shows the TG-DSC curves of the uncalcined 15%-Ni/MRM catalyst, which have a continuous weight loss of 22.7% from 20 to 1000 °C. The weight loss of 8.7% from 20 to 209 °C can be attributed to the physical water and the decomposition of partial Ni(OH)<sub>2</sub> by taking the DSC curve into account which produced an endothermic peak at 91.4 °C. Two weak endothermic peaks are observed at 228.2 and 256.3 °C in DSC. The endothermic peaks at these temperatures from 209 to 332 °C together with the mass loss of 6.6%, refer to the decomposition of gibbsite, partial boehmite (formed from the slight decomposition of gibbsite) and partial goethite. The endothermic peak starting at about 332 °C and ending at 612 °C seen at 559.2 °C in the DSC resulted from the decomposition of boehmite (formed from the slight decomposition of gibbsite), diaspore and goethite. What's more, the decomposition of goethite to hematite and the decomposition of gibbsite to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> are believed to occur (consistent with the XRD analysis results in Fig. 1). Finally, it can be observed that the mass loss of the uncalcined 15%-Ni/MRM catalyst has almost completed at 600 °C (consistent with the XRD analysis results in Fig. 2).

The FT-IR spectra of RM and 600 °C-calcined 15%-Ni/MRM catalyst are shown in Fig. 4. The broad peak at the region of

3650-3200 cm<sup>-1</sup> corresponds to OH vibrations and appears as a result of hydration due to the presence of H<sub>2</sub>O in RM, as well as of higher intensities in 15%-Ni/MRM at 3451 cm<sup>-1</sup>.<sup>29</sup> The peak at 1425  $\text{cm}^{-1}$  represents the existence of CaCO<sub>3</sub> in RM,<sup>26</sup> which disappears owing to its reaction with HCl after acid treatment. The stretching vibrations of Fe-O bands of hematite structure are detected in RM at the peaks at 1630, 540 and 476  $\text{cm}^{-1}$ ,<sup>26</sup> and show higher intensities at 1630  $\text{cm}^{-1}$ , equal at 559 and 486 cm<sup>-1</sup> in 15%-Ni/MRM catalyst. What's more, for 15%-Ni/MRM catalyst, it is a remarkable fact that compared with standard FT-IR spectra of hematite, the intensity of the peak at 486 cm<sup>-1</sup> is much higher than that of the peak at 559 cm<sup>-1</sup>, which may be because the peak at 486 cm<sup>-1</sup> not only represents hematite but also represents NiO. Vibration relating to goethite can be observed in RM at 756  $\text{cm}^{-1}$ ,<sup>23</sup> and disappears in 15%-Ni/MRM. The peak at 1003 cm<sup>-1</sup> in RM is for the stretching vibration of Si-O band<sup>29</sup> and of lower intensities in 15%-Ni/MRM at 1015 cm<sup>-1</sup>. The Al-O bands of the corundum structure at 683 and 621 cm<sup>-1</sup> in the spectrum of RM disappear after modification.<sup>26,29</sup> And the stretching vibration relating to y-Al<sub>2</sub>O<sub>3</sub> can be observed in 15%-Ni/MRM sample at the peak of 719 cm<sup>-1</sup>. This may be due to the fact that the Al in RM is partially solubilized after acid treatment, and translates into gibbsite after alkaline reprecipitation, subsequently translates into  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> after calcination (consistent with the TG-DSC results in Fig. 3b). These results are consistent with the XRD analysis results of RM and 600 °C-calcined 15%-Ni/MRM catalyst.

Fig. 5 presents the  $N_2$  adsorption-desorption isotherms and the corresponding pore size distribution curves of RM and Ni/MRM catalysts with different Ni loading amounts calcined at 600 °C. Their textural properties are provided in Table 2. From Fig. 5 and Table 2, we can see that the as-received red mud has a very small surface area, substantially non-porous structure. However, the surface area and pore volume of 600 °C-calcined MRM and Ni/MRM catalysts are all enlarged noticeably compared with that of RM. The isotherms of all the prepared samples are of classical type IV, characteristic of mesoporous materials according to the IUPAC. The



Fig. 3 TG-DSC curves of (a) RM and (b) the uncalcined 15%-Ni/MRM catalyst.





Fig. 5 (Left)  $N_2$  adsorption-desorption isotherms and (right) the corresponding pore size distribution curves of RM and Ni/MRM catalysts with different Ni loading amounts calcined at 600 °C.

well-defined hysteresis loops with a steep desorption branch and less steep adsorption branch belong to the H2-type, indicating that the effective radii of the mesoporous bodies are heterogeneously distributed and the effective radii of the narrow entrances are all of equal size.<sup>30</sup> The H2 type of the hysteresis loop is typical for wormhole-like mesostructures and hierarchical scaffold-like mesoporous structures formed by surfactantassisted nanoparticle assembly.<sup>30</sup> The pore size distribution curves of 600 °C-calcined MRM and Ni/MRM catalysts with different Ni contents are determined by the DFT method from the adsorption branch of the isotherms, exhibit a narrow peak centered at 3.8–7.5 nm (Fig. 5), indicating the good homogeneity of the pores. All the samples possess high surface areas of about 200 m<sup>2</sup> g<sup>-1</sup> (Table 2). With the increase of Ni content from 3 to 18%, the pore volume increased from 0.34 to 0.77 cm<sup>3</sup> g<sup>-1</sup>. This illustrates that the homogeneous precipitation method has a positive impact on the textural properties of the prepared catalysts.

Fig. 6 depicts the N<sub>2</sub> adsorption–desorption isotherms and the corresponding pore size distributions of the 15%-Ni/MRM catalysts calcined at different temperature. The textual properties of the samples are also listed in Table 2. The pore size distributions of the 15%-Ni/MRM catalysts calcined at different temperature are also narrow (Fig. 6). With the increase of the calcination temperature, the surface areas of these catalysts decreased from 259 to 180 m<sup>2</sup> g<sup>-1</sup> (due to the particle sintering, Table 2). Interestingly, a high surface area of 180 m<sup>2</sup> g<sup>-1</sup> can still be obtained after calcination at 700 °C for 2 h, indicating the high thermal stability of these modified red mud supported Ni catalysts.

Fig. 7 shows the TEM-EDX images of the 600 °C-calcined 15%-Ni/MRM catalyst. The composition of this sample is confirmed by the EDX spectrum (as shown in Fig. 7b), which reveals the presence of Fe, Al, Si, O and Ni on the surface of the 600 °C-calcined 15%-Ni/MRM catalyst (Cu peaks from the TEM grid). And the EDX Ni element map (Fig. 7d) demonstrates the high dispersion of Ni species in the catalyst. The HRTEM image (Fig. 7e) demonstrates that the 15%-Ni/MRM catalyst possesses a disordered wormhole-like mesopore structure (illustrated in combination with the H2 type of the hysteresis loop in Fig. 5), formed by the agglomeration of the nanoparticles. The accessible pores are connected randomly, lacking discernible long-range order in the pore arrangement among the small particles, being in good agreement with the N<sub>2</sub> adsorption-desorption isotherms. In addition, we observe

Fable 2         The physical properties and catalytic activities of the investigated catalysts										
Samples	Calcination temperature (°C)	Surface area <sup><i>a</i></sup> $(m^2 g^{-1})$	$ \begin{pmatrix} V_{\rm tot} \\ (\rm cm^3 g^{-1}) \end{pmatrix} $	${D_{ m DFT-ads}}^b$ (nm)	Conversion <sup>c</sup> (%)	$H_2 \text{ production}^c$ (mmol min <sup>-1</sup> $g_{cat}^{-1}$ )	$\begin{array}{c} E_{\rm a} \\ (\rm kJ \ mol^{-1}) \end{array}$			
RM	110	8	0.08	14.6	_	_				
MRM	110	225	0.39	5.0	—		—			
MRM-600	600	190	0.39	4.8	63.4	21.2	170.7			
3%-Ni/MRM	600	199	0.34	3.8	69.3	23.2	116.7			
6%-Ni/MRM	600	205	0.49	5.7	72.0	24.1	96.4			
9%-Ni/MRM	600	221	0.61	7.5	75.9	25.4	91.4			
12%-Ni/MRM	600	214	0.67	7.5	93.2	31.2	77.1			
15%-Ni/MRM	600	219	0.76	7.5	97.9	32.8	70.3			
18%-Ni/MRM	600	217	0.77	7.5	82.0	27.5	83.2			
15%-Ni/MRM	500	259	0.81	7.5	78.8	26.4	82.3			
15%-Ni/MRM	700	180	0.66	7.5	51.5	17.2	92.6			

<sup>*a*</sup> Multi-point BET surface area. <sup>*b*</sup> Maximum of DFT pore diameter as determined from the adsorption branch. <sup>*c*</sup> The data were measured at 700  $^{\circ}$ C under pure NH<sub>3</sub> flow of 50 ml min<sup>-1</sup>.



Fig. 6 (Left)  $N_2$  adsorption-desorption isotherms and (right) the corresponding pore size distribution curves of 15%-Ni/MRM catalysts calcined at different temperature. The absorbed volume was shifted by 200 and 400 units for the curves of data sets 15%-Ni/MRM-600 and 15%-Ni/MRM-700, and the dV/dD value was shifted by 0.15 and 0.3 units for the curves of data sets 15%-Ni/MRM-600 and 15%-Ni/MRM-700, respectively.

some flocculent structure in the low-resolution TEM images (Fig. 7a). From the HRTEM image (Fig. 7e), we can see that the flocculent structure is assembled from the nanoparticles.

It is likely that a part of NiO nanoparticles assemble into the flocculent structure on the surface of the support during the loading process.

The catalytic activities of the prepared Ni/MRM catalysts for  $NH_3$  decomposition as a function of reaction temperature are presented in Fig. 8 and 9. The results show a similar behavior that the ammonia conversions increased with the increase of the catalytic reaction temperature measured in the catalyst bed for all the catalysts, indicating faster decomposition at higher temperature. The data of ammonia conversion and  $H_2$  production are shown in Table 2.

Fig. 8 shows the catalytic activities of the Ni/MRM catalysts with different Ni content and calcined at 600 °C. The catalytic activity of pure 600 °C-calcined MRM support is also included in the same figure for comparison purpose. It is noted from Fig. 8 that the activity of MRM-600 is low (63.4% of ammonia was decomposed at 700 °C), while the activities of all the Ni/MRM catalysts are higher than that of pure MRM. The pure MRM support also shows some catalytic activity, which is due to the support's large surface area and pore volume, and its main components (Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>) play an important role for ammonia decomposition. After supported Ni species, the activity of the catalyst increased



Fig. 7 TEM-EDX images of 600 °C-calcined 15%-Ni/MRM catalyst: (a) TEM image, (b) EDX spectrum related to (a), (c) BF TEM image, (d) EDX Ni element map related to (c), (e) HRTEM image.

obviously (97.9% NH<sub>3</sub> decomposition for the most active catalyst). This highlights that there is a synergistic effect between Ni species and the MRM support, which strongly affects the catalytic activity in ammonia decomposition. In comparison with the reported results of red mud support Ru catalysts for ammonia decomposition,<sup>24</sup> the high surface area and porosity should respond for the high activity of the Ni/MRM catalysts. This is in agreement with the reported results that the catalytic decomposition of ammonia is sensitive to the textural and structural property of the catalyst.<sup>10,31-33</sup> The catalytic activities of Ni/MRM catalysts enhanced with the increase of Ni loadings from 3 to 15%, and the 15%-Ni/MRM catalyst exhibited the highest catalytic activity (97.9% NH<sub>3</sub> conversion and 32.8 mmol min<sup>-1</sup>  $g_{cat}^{-1}$  H<sub>2</sub> production at reaction temperature of 700 °C). This catalytic activity is comparable to the Ni/MCM-41 (TIE) catalyst,<sup>32</sup> which showed 98.8% NH<sub>3</sub> conversion and 33.1 mmol min<sup>-1</sup> g<sub>cat</sub><sup>-1</sup> H<sub>2</sub> production at reaction temperature of 700 °C. At the same time, when the Ni loadings increased from 0 to 9%, the catalytic activities enhanced slightly. However, once the Ni loadings reached 12%, the catalytic activities soared to 93.2% NH3 conversion at reaction temperature of 700 °C. A further increase of the Ni content (18%) resulted in the significant decrease of the catalytic activity. This indicate that the finely dispersed Ni species should be responsible for the activity, whereas the excess of Ni species and the growth of the NiO nanoparticles when the high loading maybe have a negative effect on the catalytic activity of ammonia decomposition, supported by the XRD results (Fig. 1).

Fig. 9 displays the catalytic performance for ammonia decomposition of 15%-Ni/MRM catalysts calcined at different temperature. It is seen that the catalytic activities of the 15%-Ni/MRM catalysts increased with the increased precalcination temperature from 500 to 600 °C. However, when the precalcination temperature increased to 700 °C, the catalytic activities became particularly low (even lower than that of the pure MRM support). This indicates that the high calcination temperature will result in the growth and agglomeration



Fig. 8 The activities of the Ni/MRM catalysts calcined at 600 °C with different Ni loading.



Fig. 9 The activities of 15%-Ni/MRM catalysts calcined at different temperature.

of the catalyst, further reducing the surface area and total pore volume, and then decreasing the catalyst's activity. When the reaction temperature is below 450 °C, the catalytic activities of the catalysts calcined at 500-700 °C are close to each other. When the reaction temperature is increased further, the catalyst calcined at 600 °C shows higher activity than that of the 500 and 700 °C-calcined samples. The 600 °Ccalcined 15%-Ni/MRM catalyst, which has the high surface area of 219 m<sup>2</sup> g<sup>-1</sup> and the nano-scale particle size, exhibits the highest catalytic activity for ammonia decomposition. It is believed that the high activity of these Ni/MRM catalysts correspond to their high surface area and mesoporous structure. The mesoporous frameworks provides a large surface to volume ratio, and hence more active sites are available for ammonia decomposition, which is beneficial for achieving enhanced catalytic activity. The TG-DSC data have indicated that after 600 °C calcination, the 15%-Ni/MRM catalyst has reached the thermal balance. Hence, the calcination temperature of 600 °C is suitable.

The apparent activation energies  $(E_a)$  were obtained from the Arrhenius relationship between the rate constant (k)and the temperature (T), which can be described by the equation:<sup>31</sup>  $\ln(k) = -E_a/RT$  + constant, and the results are listed in Table 2. It is seen that the MRM support had the highest activation energy (170.7 kJ mol<sup>-1</sup>). After supported the active species Ni (3%), the activation energy decreased to 116.7 kJ mol<sup>-1</sup>, and correspondingly the ammonia conversion increased from 63.4% to 69.3% at 700 °C. By increasing the Ni contents, the catalyst of 15%-Ni/MRM showed the highest activity and the lowest activation energy (70.3 kJ mol<sup>-1</sup>) in the present work. This activation energy is comparable to that of the Ni/CeO<sub>2</sub> catalysts,<sup>10</sup> and much lower than most of the published Ni-based catalysts.<sup>10,32</sup>

### 4. Conclusions

Mesoporous nanostructured Ni/MRM catalysts with high surface areas and narrow mesopore size distributions have been successfully prepared by the homogeneous precipitation method. The resulting Ni/MRM catalysts are found to be active in catalytic ammonia decomposition, and the catalytic activity comparable to that of the previously reported Ni-based catalysts systems. The content of Ni and the precalcination temperature can affect the catalytic properties of the catalysts remarkably. The 600 °C-calcined 15%-Ni/MRM catalyst has the highest activity. The synergistic effect between Ni and nanostructural MRM support, the highly dispersed Ni species, and high surface area of the catalysts were responsible for the high catalytic activity and hydrogen production. This investigation demonstrates the feasibility of utilizing the waste from the aluminum industry for the decomposition of ammonia to hydrogen.

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### References

- 1 A. S. Chellappa, C. M. Fischer and W. J. Thomson, *Appl. Catal.*, *A*, 2002, 227, 231.
- 2 J. Hongrapipat, W.-L. Saw and S. Pang, *Biomass Conversion* and *Biorefinery*, 2012, 2, 327.
- 3 F. Schüth, R. Palkovits, R. Schlögl and D. Su, *Energy Environ. Sci.*, 2012, 5, 6278.
- 4 S. F. Yin, Q. H. Zhang, B. Q. Xu, W. X. Zhu, C. F. Ng and C. T. Au, *J. Catal.*, 2004, 224, 384.
- 5 J. Taguchi, T. Nakato and T. Okuhara, *Chem. Lett.*, 1999, 4, 277.
- 6 D. C. Huang, C. H. Jiang, F. J. Liu, Y. C. Cheng, Y. C. Chen and K. L. Hsueh, *Int. J. Hydrogen Energy*, 2013, 38, 3233.
- 7 L. Wang, Y. Zhao, C. Y. Liu, W. M. Gong and H. C. Guo, *Chem. Commun.*, 2013, 49, 3787.
- 8 X. Z. Duan, G. Qian, X. G. Zhou, D. Chen and W. K. Yuan, *Chem. Eng. J.*, 2012, 207–208, 103.

- 9 X. Z. Duan, G. Qian, Y. Liu, J. Ji, X. G. Zhou, D. Chen and W. K. Yuan, *Fuel Process. Technol.*, 2013, 108, 112.
- 10 Q. F. Deng, H. Zhang, X. X. Hou, T. Z. Ren and Z. Y. Yuan, *Int. J. Hydrogen Energy*, 2012, 37, 15901.
- 11 X. G. Wang, Y. Wei, J. Zhang, H. Xu and W. Li, *Acta Pet. Sin.*, *Pet. Process. Sect.*, 2006, 22, 33.
- 12 S. Wang, H. M. Ang and M. O. Tade, *Chemosphere*, 2008, 72, 1621.
- 13 A. M. Mastral, C. Mayoral, M. T. Izquierdo and C. Pardos, *Fuel Process. Technol.*, 1993, 36, 177.
- 14 J. Llano, R. Rosal, H. Sastre and F. Diez, Fuel, 1994, 73, 688.
- 15 J. Álvarez, S. Ordóñez, R. Rosal and H. Sastre, *Appl. Catal.*, A, 1999, 180, 399.
- 16 I. H. Metecan, T. Karayildirim, J. Yanik, M. Saglam and M. Yuksel, *Oil Shale*, 2003, 20, 69.
- 17 S. Ordóñez and H. Sastre, Appl. Catal., B, 2001, 29, 263.
- 18 S. Ordóñez and H. Sastre, Catal. Today, 2002, 73, 325.
- 19 J. Halász, M. Hodos, I. Hannus, G. Tasi and I. Kiricsi, *Colloids Surf.*, A, 2005, 265, 171.
- 20 J. F. Lamonier, G. Leclerco, M. Dufour and L. Leclercq, Recents Prog. Genie Procedes, 1995, 43, 31.
- 21 J. R. Paredes, S. Ordonez, A. Vega and F. V. Diez, *Appl. Catal.*, *B*, 2004, 47, 37.
- 22 J. F. Lamonier, F. Wyralski, G. Leclercq and A. Aboukais, Can. J. Chem. Eng., 2005, 83, 737.
- 23 S. Sushil and V. S. Batra, J. Hazard. Mater., 2012, 203–204, 264.
- 24 P. F. Ng, L. Li, S. Wang, Z. Zhu, G. Lu and Z. Yan, *Environ. Sci. Technol.*, 2007, 41, 3758.
- 25 V. M. Sglavo, R. Campostrini, S. Maurina, G. Carturan, M. Monagheddu, G. Budroni and G. Cocco, *J. Eur. Ceram. Soc.*, 2000, 20, 235.
- 26 A. Alp and M. Goral, J. Therm. Anal. Calorim., 2003, 73, 201.
- 27 A. Atasoy, J. Therm. Anal. Calorim., 2005, 81, 357.
- 28 M. L. C. P. Antunes, C. P. Costa de Jesus, P. K. Kiyohara, A. C. V. Coelho and R. L. Frost, *Ind. Eng. Chem. Res.*, 2012, 51, 775.
- 29 A. Gök, M. Omastová and J. Prokeš, *Eur. Polym. J.*, 2007, 43, 2471.
- 30 H. G. EI-Shobaky and M. M. Mokhtar, Appl. Surf. Sci., 2007, 253, 9407.
- 31 J. Zhang, H. Y. Xu and W. Z. Li, *Appl. Catal., A*, 2005, 296, 257.
- 32 X. K. Li, W. J. Ji, J. Zhao, S. J. Wang and C. T. Au, J. Catal., 2005, 236, 181.
- 33 J. Zhang, H. Y. Xu, X. L. Jin, Q. J. Ge and W. Z. Li, Appl. Catal., A, 2005, 290, 87.