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# Mesoporous modified-red-mud supported Ni catalysts for ammonia decomposition to hydrogen

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## ABSTRACT

Mesoporous modified-red-mud (MRM) was obtained via the modification of as-received red mud (RM) by the acid digestion and alkali reprecipitation approach, which was further employed as the support for preparation of Ni/MRM catalysts by the impregnation method. The textural and structural properties of the MRM and as-prepared Ni/MRM catalysts were fully characterized by X-ray diffraction (XRD), thermogravimetry-differential thermal gravity analysis (TG-DTG), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and Fourier transform infrared spectra (FT-IR) techniques. The catalytic behavior of the prepared Ni/MRM catalysts for ammonia decomposition was investigated, indicating excellent catalytic activity, comparable to the previously reported metal oxide supported Ni catalysts. This study demonstrates the feasibility of utilizing the waste from the aluminum industry for the decomposition of ammonia to hydrogen.

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## 1. Introduction

Red mud is a by-product of the Bayer process in aluminum industry. It poses a serious pollution hazard due to its high alkalinity in case of disposal. The amount of red mud generated (per ton of alumina produced) varies from 0.3 to 2.5 tons [1]. Generally, red mud is a very fine material in terms of its uniform particle size distribution, showing an average

particle size of <10 μm. It is primarily composed of iron, aluminum, titanium, silicon, calcium oxides and hydroxides such as hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>), goethite (FeOOH), magnetite (Fe<sub>3</sub>O<sub>4</sub>), boehmite (AlO(OH)), gibbsite (Al(OH)<sub>3</sub>), rutile (TiO<sub>2</sub>), anatase (TiO<sub>2</sub>), quartz (SiO<sub>2</sub>), calcite (CaCO<sub>3</sub>), perovskite (CaTiO<sub>3</sub>), etc. Therefore, the treatment and resource utilization of red mud has received widespread attention.

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Nowadays red mud has been developed for various applications, which include building and structural materials [2–4], adsorbents for water and gas treatment [5–10] as well as catalysts for specific reactions, e.g. hydrogenation [11–17], hydrodechlorination [18–20], exhaust gas clean-up [21–24] and catalytic ammonia decomposition [25].

Fuel cells as an attractive power source, generate electricity from hydrogen through an electrochemical process, which is quiet and durable with only water and heat as the byproducts. They are environmental-friendly, highly efficient and recyclable. Therefore, the generation of clean and cheap hydrogen for fuel cells motivates the investigation on catalytic ammonia decomposition, because ammonia has numerous advantages such as the high hydrogen storage density, complete production and transportation technologies, low price, CO<sub>x</sub>-free nature. On the other hand, the catalytic removal of ammonia from gasification product gas or direct ammonia fuel cells, are highlighted as well [26,27].

The effects of active metals (Ru, Rh, Pt, Pd, Ni and Fe) and support materials (carbon nanotubes (CNTs), activated carbon (AC), Al<sub>2</sub>O<sub>3</sub>, MgO, ZrO<sub>2</sub> and TiO<sub>2</sub>) on the catalysis of ammonia decomposition have been extensively studied, which demonstrated that the Ru catalyst using CNTs as the support exhibited the highest conversion of NH<sub>3</sub> [28]. Recently, red mud has been employed as catalyst support due to its strong stability, high surface area, sintering resistance and resistance to poisoning. Moreover, it is much more cost-effective in comparison with Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and CNTs, which required complicated preparation procedures. For example, Ng et al. [25] employed red mud supported Ru catalyst for catalytic ammonia decomposition, which show high catalytic activity. However, due to the limited availability of noble metals, seeking alternative catalysts with low cost and fair performance is one of the current focuses. Ni-based catalysts have thus attracted much attention. Our recent studies [29] have revealed that the high surface area Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> solid solution supported Ni catalysts display high activity for ammonia decomposition to hydrogen. Wang et al. [30] 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.

Herein, 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 (the 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 Pratt and Christoverson [17]. Noticeably unlike the previous approaches, we did not seek complete extraction of the active ingredients, such as iron and aluminum, only expecting the various components left by the packaged and embedded status with each other under a little moderate reaction condition. The MRM sample was employed as the support for the preparation of Ni/MRM catalysts. The textural and structural properties of the RM, MRM and the as-prepared Ni/MRM catalysts were characterized by means of XRD, TG-DTG, N<sub>2</sub> sorption, SEM, TEM and FT-IR. The effect of the Ni loading amount and calcination temperature on the catalytic ammonia decomposition

activities of the mesoporous Ni/MRM catalysts were investigated detailedly.

## 2. Materials and methods

### 2.1. Modification of red mud

The red mud (RM) sample was collected from a downstream slurry pond in Henan Zhongmei Aluminum Corporation, China (major compositions (wt.%): Fe<sub>2</sub>O<sub>3</sub> 15.05%; Al<sub>2</sub>O<sub>3</sub> 23.25%; SiO<sub>2</sub> 16.94%; CaO 16.94%; TiO<sub>2</sub> 4.27%; Na<sub>2</sub>O 3.72%; MgO 1.93%). And red mud exhibits strong alkaline property (pH = 10.26), due to the sodium oxide [31]. The sample was dried, ground and sieved to a size of <150 μm.

In a typical process of modified red mud, 25 g of red mud sample were added into 100 ml of distilled water. After stirring for 5 min, 150 ml of 6 M HCl solution were 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 ≈ 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 ≈ 7, and then washed again with anhydrous ethanol. Treating the sample with low surface tension of anhydrous ethanol can maintain the organizational structure of the colloid to some extent, and then improve the BET specific surface area and pore size of the sample. On the other hand, washing with anhydrous ethanol was advantageous to remove chlorine ion. Finally, the precipitate was separated by filtration, dried 12 h in air at 110 °C, but not calcined. The as-prepared sample was modified red mud, and denoted as MRM.

### 2.2. Preparation of Ni/MRM catalysts

The catalysts for NH<sub>3</sub> decomposition were prepared by impregnation method, as described below. At room temperature, the calculated amount of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O was dissolved in 3.0 ml of anhydrous ethanol and then mixed with 1.0 g of MRM. The mixture was sonicated for 10 min and evaporated at 110 °C for 2 h. Then the sample was grinded to powder and calcined at different temperatures (400, 500 and 600 °C) for 2 h to obtain the tested catalyst, which was designated as x wt.-% Ni/MRM (x = 0, 3, 6, 9, 12 and 15).

### 2.3. Characterization

X-ray diffraction (XRD) analysis was performed on a Bruker-AXS D8 Advance diffractometer, with CuK<sub>α</sub> radiation at 40 kV and 25 mA in a scanning range of 10–80° (2θ). The diffraction peaks of the crystalline phase were compared with those of standard compounds reported in the JCPDS Date File. Thermogravimetry-differential thermal gravity analysis (TG-DTG) was done on a NETZSCH STA449C Simultaneous Thermal Analyzer. N<sub>2</sub> adsorption–desorption isotherms were collected at liquid nitrogen temperature using a Quantachrome AsiQM0000-3 sorption analyzer. Before carrying out the measurement, each sample was

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