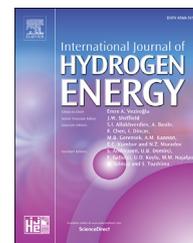




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Ni nanoparticles supported on mica for efficient decomposition of ammonia to CO_x-free hydrogen

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ABSTRACT

A wet impregnation method is used to synthesize Ni nanocatalysts supported on naturally abundant mica nanosheets for decomposition of ammonia to CO_x-free hydrogen. The prepared catalysts are characterized by XRD, SEM, TEM, N₂ sorption, TG, XPS, H₂-TPR and NH₃/H₂-TPD techniques. The catalytic tests exhibit that the Ni/mica catalysts are highly active for ammonia decomposition. The two-dimensional structure of mica favors mass transportation, which can remarkably promote the catalytic process. The NH₃/H₂-TPD curves of Ni/mica show no desorption signals of NH₃ and H₂, indicating the presence of weak desorption energy barrier. The content of Ni in the catalysts is related to the crystallite size of Ni species, affecting their catalytic properties. As demonstrated in this study, the Ni/mica catalyst with 15% Ni loading amount exhibits the highest catalytic activity and long-term stability. At a high space velocity of 30000 cm³ g_{cat}⁻¹ h⁻¹, 97.2% ammonia conversion is achieved over the 15%Ni/mica catalyst at 650 °C, indicating the Ni/mica is a promising catalyst for ammonia decomposition.

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Introduction

Hydrogen (H₂) has recently drawn much attention because its potential use as a clean fuel. Practically, storage of H₂ has always been a great challenge for its applications. Over the last several decades, great efforts have been devoted to H₂ storage materials searching and developing. Ammonia, containing high H₂ content (17.6 wt%) and large energy density (3000 Wh/kg), is regarded as a suitable carrier for H₂ storage [1–3]. Importantly, H₂ generated from ammonia has no CO which is

negative to the proton exchange membrane fuel cells (PEMFC) [4,5]. Hydrogen produced from hydrocarbons by steam reforming containing a large amount of CO cannot be directly used for PEMFC systems because the membrane electrode assemblies (MEAs) within the stack cannot tolerate such high CO levels [6,7]. Only H₂ containing CO less than a few ppm can enter the stack and react in the anode electrocatalyst layer of the MEAs. Thus, catalytic abatement of CO is necessary before practical use of the hydrogen derived from hydrocarbons [8,9]. Alternatively, catalytic decomposition of NH₃ to H₂ is one of the most promising ways to produce pure H₂. Up to now,

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many noble metals, such as Ru, Ir, Pd and Pt-Ni, have been found to be highly active for NH_3 decomposition [10–14]. However, low availability and high price of these noble metal catalysts hinder them in-use widely. Many studies are focused on the non-noble metal catalysts (Fe, Co, Ni, MoC, MnN_x , etc.) [15–20]. Among them, Ni catalyst is believed to be one of the most promising candidates for ammonia decomposition, due to its high catalytic activity, low price, and long-term stability [15,21,22].

In order to improve the catalytic performance of Ni-based catalysts, a lot of work was done by depositing Ni onto supports such as carbon nanotubes [21], layered double hydroxides [4,22], zeolites [23] and metal oxides [24–27]. After Ni was supported, some of its properties including reducibility, particle size and distribution, textural properties and electronic structure were obviously changed, which made great influence on the catalytic performance. It was reported that the layered double hydroxides-derived $\text{Ni}_x(\text{Mg}_y\text{Al}_z\text{O}_n)$ catalysts exhibited enhanced catalytic activity for ammonia decomposition due to the hydrogen spillover effect, that is, accelerating the reaction cycles over the active Ni species [4]. Sato et al. prepared Ni/Mg-Al hydrotalcite-like compounds with different Mg/Al ratios for ammonia decomposition. Ni_MgAl(6:1) exhibited significantly high NH_3 decomposition activity due to the presence of a large number of exposed Ni^0 and high basicity of the Ni_MgAl(6:1) catalyst [22]. Furthermore, many different kinds of rare earth metal oxides were used in the preparation of high-activity Ni-based catalysts. Okura et al. [24] investigated the catalytic performance of Ni catalysts supported on five different rare-earth oxides (Y_2O_3 , CeO_2 , La_2O_3 , Sm_2O_3 and Gd_2O_3) for ammonia decomposition. The Ni/ Y_2O_3 catalysts exhibited the best catalytic activity owing to the fact that Y_2O_3 could reduce the hydrogen atoms adsorbed on the Ni surface. Deng et al. [26] synthesized robust mesoporous Ni/ $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ for ammonia decomposition. The mesoporous structure of catalyst favored mass transportation and could supply more active sites during the catalytic reaction. However, the exploitation of a new support with both low cost and layered structure/porous structure is still a great challenge.

In recent years, a lot of natural minerals or industrial wastes (such as red mud, fly ash and attapulgite clay) were utilized as supports or active species of environmental-friendly catalysts for various applications including waste water treatment, CO oxidation and ammonia decomposition, exhibiting pretty high catalytic activity and stability in comparison to commercial catalysts [28–33]. Mica, a natural layered mineral possessing high thermal stability and large porosity, could be used as a promising catalyst support. Importantly, the two-dimensional structure of mica could prevent the aggregation of the metal nanoparticles, and thus, enhancing their catalytic properties [33]. Indeed, the catalyst nanoparticles supported on the mica were found to be active in various reactions, such as methyl orange photocatalytic degradation [33], water oxidation [34], and ethylene oligomerization [35].

Herein, a series of Ni catalysts supported on mica nanosheets were prepared by a simple wet impregnation method. The reducibility, Ni particle size and distribution, and desorption processes of NH_3 and H_2 , were all examined to signify the affecting factors of Ni/mica catalysts. The prepared

catalysts with two-dimensional structure exhibited high catalytic activity and long-term stability for ammonia decomposition. Since mica is natural abundant and much low-cost, the prepared catalysts are quite promising and could be widely used in various catalytic reactions including ammonia decomposition.

Experimental

Catalysts preparation

The mica (purity $\geq 99.0\%$, 200 mesh) was obtained from the Beijing HWRK Chem Co., and denoted as MS. Its chemical formula was represented as $\text{K}_{0.75}\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$. $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was supplied by the Tianjin Guangfu Fine Chemical Corp. All chemicals were used as received without further purification.

The Ni/mica catalysts were synthesized by a wet impregnation method. Typically, the calculated amount of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved into 50 ml of distilled water. Afterwards, 2 g of MS was immersed into the above solution and stirred for 2 h. Then, the mixture was evaporated at 100°C , dried at 110°C for 12 h, and followed by calcination at 700°C for 4 h with a heating rate of $5^\circ\text{C}/\text{min}$. The obtained sample was denoted as $x\%\text{Ni}/\text{MS}$, where $x\%$ represented the mass percent of Ni ($x = 0, 1, 5, 10, 15, 20$ and 30). To further investigate the influence of calcination temperature, the 15% Ni/MS samples were calcined at 800 and 900°C for 4 h with a heating rate of $5^\circ\text{C}/\text{min}$.

Characterization

X-ray diffraction (XRD) patterns were measured on a Bruker D8 Focus diffractometer (Cu $K\alpha$ radiation) at 40 kV and 40 mA, with a scanning rate of $12^\circ/\text{min}$. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images were recorded on a Jeol JSF-7500L microscope at 5 kV and a Jeol JEM-2800 microscope at 200 kV, respectively. Thermogravimetric analysis (TGA) was tested on a TA SDT Q600 instrument in pure air (100 mL/min) with a heating rate of $10^\circ\text{C}/\text{min}$ from room temperature to 900°C using Al_2O_3 as the reference. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Scientific ESCALAB 250Xi spectrometer. All the spectra were corrected by the containment carbon (C 1s) at 284.8 eV.

H_2 temperature-programmed reduction (H_2 -TPR) experiments were conducted on a Quantachrome ChemBET 3000 analyzer. Before the test, 50 mg sample was degassed at 200°C in helium for 2 h. After cooling down to room temperature, the sample was reduced by H_2/Ar mixed gas (20 ml/min) with a heating rate of $10^\circ\text{C}/\text{min}$. For comparison, 7.5 mg NiO was taken for H_2 -TPR experiment. Ammonia and hydrogen temperature-programmed desorption (NH_3/H_2 -TPD) tests were also carried out on a Quantachrome ChemBET 3000 analyzer. During the tests, 200 mg reduced Ni/mica was desorbed at 600°C for 1 h, and subsequently cooled down to 60°C . 5% NH_3/Ar or 10% H_2/Ar was then fed to catalyst for 0.5 h at 60°C and further swept to baseline by He. The desorbing signal was measured by a thermal conductivity detector (TCD).

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