



Short communication

Liquid phase hydrogenation of adiponitrile over directly reduced Ni/SiO₂ catalyst

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ABSTRACT

Liquid phase hydrogenation of adiponitrile (ADN) to 6-aminocapronitrile (ACN) and hexamethylenediamine (HMD) was investigated on Ni/SiO₂ catalysts prepared under different conditions. In this reaction, the highly reactive imine intermediate forms condensation byproducts by reacting with the primary amine products (ACN and HMD). A highly dispersed Ni/SiO₂ catalyst prepared by the direct reduction of Ni(NO₃)₂/SiO₂ was found to suppress the condensation reactions by promoting the hydrogenation of adsorbed imine, and it gave excellent hydrogenation activity and primary amine selectivity. Addition of NaOH increased the primary amine selectivity to 79% at the ADN conversion of 86%.

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1. Introduction

The selective hydrogenation of adiponitrile (ADN) to 6-aminocapronitrile (ACN) is the key step in the butadiene hydrocyanation route for the manufacture of caprolactam [1–4]. It is catalyzed by Raney Ni catalysts [5,6] prepared by removing the aluminum from binary Al–Ni alloys using an aqueous alkaline solution. This catalyst preparation process consumes a lot of energy and causes environmental pollution. It is also well known that Raney type catalysts have low mechanical strength, which leads to much catalyst consumption and they are pyrophoric and cannot be exposed to air. Due to these drawbacks, many attempts have been made to replace Raney Ni by a supported Ni catalyst where the main challenge is to achieve a satisfactory ACN selectivity at high ADN conversion [7,8].

A general reaction scheme for the hydrogenation of ADN is given in Fig. 1 [9–11]. ADN is selectively hydrogenated to ACN and then to hexamethylenediamine (HMD) which is used for producing Nylon-6,6. During the sequential hydrogenation, a highly reactive imine intermediate is formed, which has a strong tendency towards intermolecular condensation with the primary amine products (ACN and HMD) and intramolecular cyclization to undesired condensation byproducts and hexamethyleneimine (HMI). The formation of the primary amines has to compete with the side reactions. From the chemistry, it can be seen

that improving the hydrogenation activity of the catalyst would be an effective way to suppress the byproducts.

In this work, a highly dispersed Ni/SiO₂ catalyst prepared by the direct reduction of a Ni(NO₃)₂ precursor [12] was used to promote the hydrogenation of the imine intermediate, thus increasing both the catalytic activity and primary amine selectivity. The influence of the addition of NaOH was also studied.

2. Experimental

2.1. Catalyst preparation

The preparation of the supported metal catalyst by incipient wetness impregnation comprised three steps: impregnation, calcination and reduction. In this work the Ni/SiO₂ catalyst prepared by the direct reduction (DR) of Ni(NO₃)₂/SiO₂ in H₂ was denoted as Ni_{DR}/SiO₂. For comparison, another catalyst prepared by calcination and reduction (CR) was denoted as Ni_{CR}/SiO₂. They were prepared as follows. The loading amount of nickel was 20 wt.%.

Ni_{DR}/SiO₂: First, SiO₂ (Alfa Aesar) was soaked in an aqueous solution of Ni(NO₃)₂ (98%, Alfa Aesar) at room temperature. Then, the mixture was treated by ultrasonic waves for 2 h and dried at 80 °C for 12 h. Finally, the catalyst precursor was reduced in H₂ flow at 450 °C for 8 h.

Ni_{CR}/SiO₂: The impregnated and dried Ni(NO₃)₂/SiO₂ was calcined at 450 °C for 4 h and then reduced in H₂ flow. The other steps were the same as those for Ni_{DR}/SiO₂. Before reduction, the calcined (C) catalyst was denoted as Ni_C/SiO₂.

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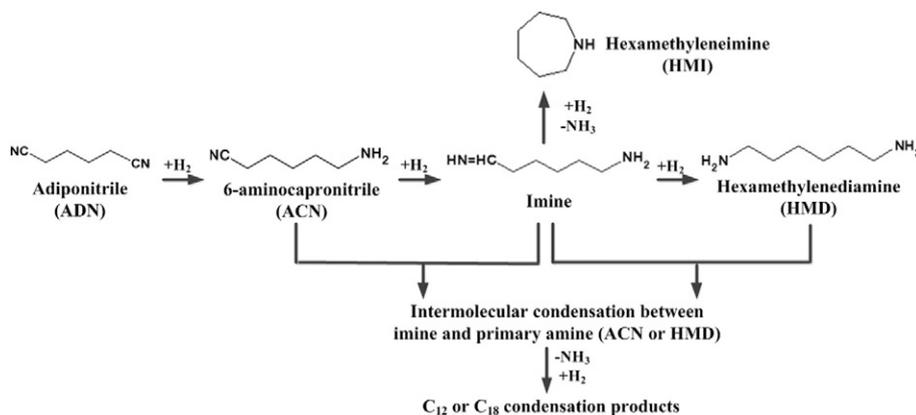


Fig. 1. Mechanism of ADN hydrogenation.

2.2. Catalyst characterization

The specific surface area and pore structure of the support and two catalysts were determined by N₂ adsorption with a Quadrasorb SI instrument. The crystalline phase of the catalysts was characterized by a Bruker Advance D8 X-ray diffractometer with a Cu K α radiation source. The H₂ uptake of the catalysts was determined by H₂ chemisorption on a Quantachrome ChemBET Pulsar TPR/TPD instrument. The active Ni area was calculated assuming H/Ni_{surface} = 1 and a surface area of 6.5 × 10⁻²⁰ m² per Ni atom [13]. A JEM-2010 transmission electron microscope (TEM, JEOL Ltd., Tokyo, Japan) were employed to examine the Ni particle size of the catalysts.

2.3. Catalytic reaction

The hydrogenation of ADN was carried out in a stainless steel autoclave equipped with a temperature control system and magnetic stirrer. Typically, 5 g ADN (98%, Alfa Aesar), 80 mL of methanol (>99.5%, Beijing Chemical Works), 5 g pre-reduced catalyst and 0.1 g NaOH (>96.0%, Beijing Chemical Works) were added into the reactor. The hydrogenation conditions were: 80 °C, 3 MPa, 500 rpm. The products were sampled on-line and were analyzed by a gas chromatograph (GC 7890F, Techcomp Instrument Company) equipped with a flame ionization detector and a KB-624 capillary column (30 m × 0.32 mm × 1.8 μm, Kromat). The condensation byproducts were secondary and tertiary amines with a high molecular weight which were not eluted in the GC. Dimethyl phthalate was used as the internal standard to determine the content of ADN, ACN and HMD. The conversion of ADN and the selectivity to ACN and HMD were calculated as:

$$\text{ADN conversion} = \frac{\text{moles of converted ADN}}{\text{moles of ADN feedstock}} \times 100\%. \quad (1)$$

$$\text{ACN selectivity} = \frac{\text{moles of ACN}}{\text{moles of converted ADN}} \times 100\%. \quad (2)$$

$$\text{HMD selectivity} = \frac{\text{moles of HMD}}{\text{moles of converted ADN}} \times 100\%. \quad (3)$$

3. Results and discussion

3.1. Catalyst characterization

Table 1 summarized the physical properties of SiO₂ and two catalysts. The SiO₂ had a specific surface area of 245 m²/g and a pore volume of 0.9 cm³/g, which decreased after the introduction of Ni.

The XRD patterns of the catalysts are shown in Fig. 2. Ni_{CR}/SiO₂ and Ni_{DR}/SiO₂ gave very sharp peaks, which indicated large NiO and Ni crystallites. Louis et al. [14] investigated the Ni/SiO₂ catalyst and found out the existence of nickel phyllosilicates, which were located at the surface of silica and acted as the anchoring sites for the NiO and Ni particles. Calcination led to the decomposition of the nickel phyllosilicates and the migration of NiO, which resulted in large Ni particles after reduction. In the case of Ni_{DR}/SiO₂, NiO was reduced to Ni before the decomposition of the anchoring sites. The broader diffraction peaks of the Ni phase indicated smaller Ni crystallite sizes [15]. In this moderate reduction process, the Ni species were not completely reduced to the metallic state and some NiO reflexes were present in the XRD pattern of Ni_{DR}/SiO₂. However, the H₂ uptake by Ni_{DR}/SiO₂ (76.2 μmol/g) was five times that of Ni_{CR}/SiO₂ (15.4 μmol/g), corresponding to the active nickel areas of 6.0 and 1.2 m²/g (Table 1). The Ni_{DR}/SiO₂ catalyst exhibited excellent H₂ chemisorption ability due to its superior Ni dispersion.

The TEM images of the two catalysts are presented in Fig. 3. The sizes of most of the Ni particles on Ni_{DR}/SiO₂ were around 10 nm, while those on Ni_{CR}/SiO₂ were much larger, which was in accordance with the XRD and H₂ uptake results.

3.2. Catalytic hydrogenation of ADN

Fig. 1 showed that ADN was selectively hydrogenated to ACN and then to HMD. The change in the concentration of ACN with time showed the presence of a consecutive reaction mechanism and the maximum ACN yield occurred at a particular reaction time [11]. Since both ACN and HMD are useful products, their selectivity should be a target used to evaluate the catalytic performance.

Table 2 shows the results from the hydrogenation of ADN over Ni_{DR}/SiO₂ and Ni_{CR}/SiO₂. As seen in Group 3 and 4, Ni_{DR}/SiO₂ exhibited superior hydrogenation activity with 86% ADN conversion in 80 min compared to Ni_{CR}/SiO₂ with 82% ADN conversion after a reaction time of 360 min. The selectivity to the primary amine products (ACN and HMD) over Ni_{DR}/SiO₂ was also higher than that over Ni_{CR}/SiO₂ because of less condensation byproduct formation. HMI was formed on both catalysts, but its selectivity over Ni_{DR}/SiO₂ was higher than that over Ni_{CR}/SiO₂, which was different from the selectivity to the condensation byproducts.

Table 1

Surface area, pore structure and metallic Ni surface area of SiO₂, Ni_{CR}/SiO₂ and Ni_{DR}/SiO₂.

Sample	S _{BET} /m ² g ⁻¹	Pore volume /cm ³ g ⁻¹	Pore size /nm	Surface area of Ni /m ² g ⁻¹
SiO ₂	245	0.9	17.8	
Ni _{CR} /SiO ₂	188	0.7	17.7	1.2
Ni _{DR} /SiO ₂	203	0.7	17.4	6.0

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