Catalysis Communications 73 (2016) 80–83

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Liquid phase hydrogenation of adiponitrile over directly reduced Ni/SiO_2 catalyst

Zekun Jia [a], Bin Zhen [a,b], Minghan Han [a,*], Chengqiang Wang [a]

[a] Department of Chemical Engineering, Tsinghua University, Beijing 100084, China
[b] College of Chemistry and Chemical Engineering, Tianjin University of Technology, Tianjin 300384, China

ARTICLE INFO

Article history:
Received 28 August 2015
Received in revised form 13 October 2015
Accepted 14 October 2015
Available online xxxx

Keywords:
Adiponitrile hydrogenation
Ni/SiO_2
6-Aminocapronitrile
Hexamethylenediamine

ABSTRACT

Liquid phase hydrogenation of adiponitrile (ADN) to 6-aminocapronitrile (ACN) and hexamethylenediamine (HMD) was investigated on Ni/SiO_2 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/SiO_2 catalyst prepared by the direct reduction of $Ni(NO_3)_2/SiO_2$ 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%.

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/SiO_2 catalyst prepared by the direct reduction of a $Ni(NO_3)_2$ 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/SiO_2 catalyst prepared by the direct reduction (DR) of $Ni(NO_3)_2/SiO_2$ in H_2 was denoted as Ni_{DR}/SiO_2. For comparison, another catalyst prepared by calcination and reduction (CR) was denoted as Ni_{CR}/SiO_2. They were prepared as follows. The loading amount of nickel was 20 wt.%.

Ni_{DR}/SiO_2: First, SiO_2 (Alfa Aesar) was soaked in an aqueous solution of $Ni(NO_3)_2$ (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 H_2 flow at 450 °C for 8 h.

Ni_{CR}/SiO_2: The impregnated and dried $Ni(NO_3)_2/SiO_2$ was calcined at 450 °C for 4 h and then reduced in H_2 flow. The other steps were the same as those for Ni_{DR}/SiO_2. Before reduction, the calcined (C) catalyst was denoted as Ni_C/SiO_2.

* Corresponding author.
E-mail address: hanmh@tsinghua.edu.cn (M. Han).

http://dx.doi.org/10.1016/j.catcom.2015.10.021
1566-7367/

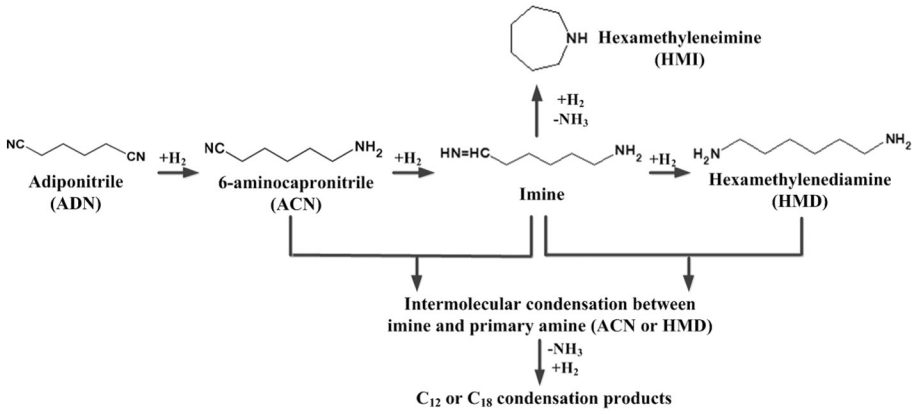


Fig. 1. Mechanism of ADN hydrogenation.

2.2. Catalyst characterization

The specific surface area and pore structure of the support and two catalysts were determined by N_2 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 Kα radiation source. The H_2 uptake of the catalysts was determined by H_2 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} m^2 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 online 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 SiO_2 and two catalysts. The SiO_2 had a specific surface area of 245 m^2/g and a pore volume of 0.9 cm^3/g, which decreased after the introduction of Ni.

The XRD patterns of the catalysts are shown in Fig. 2. Ni_C/SiO_2 and Ni_{CR}/SiO_2 gave very sharp peaks, which indicated large NiO and Ni crystallites. Louis et al. [14] investigated the Ni/SiO_2 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}/SiO_2, 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}/SiO_2. However, the H_2 uptake by Ni_{DR}/SiO_2 (76.2 μmol/g) was five times that of Ni_{CR}/SiO_2 (15.4 μmol/g), corresponding to the active nickel areas of 6.0 and 1.2 m^2/g (Table 1). The Ni_{DR}/SiO_2 catalyst exhibited excellent H_2 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}/SiO_2 were around 10 nm, while those on Ni_{CR}/SiO_2 were much larger, which was in accordance with the XRD and H_2 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}/SiO_2 and Ni_{CR}/SiO_2. As seen in Group 3 and 4, Ni_{DR}/SiO_2 exhibited superior hydrogenation activity with 86% ADN conversion in 80 min compared to Ni_{CR}/SiO_2 with 82% ADN conversion after a reaction time of 360 min. The selectivity to the primary amine products (ACN and HMD) over Ni_{DR}/SiO_2 was also higher than that over Ni_{CR}/SiO_2 because of less condensation byproduct formation. HMI was formed on both catalysts, but its selectivity over Ni_{DR}/SiO_2 was higher than that over Ni_{CR}/SiO_2, which was different from the selectivity to the condensation byproducts.

Table 1
Surface area, pore structure and metallic Ni surface area of SiO_2, Ni_{CR}/SiO_2 and Ni_{DR}/SiO_2.

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

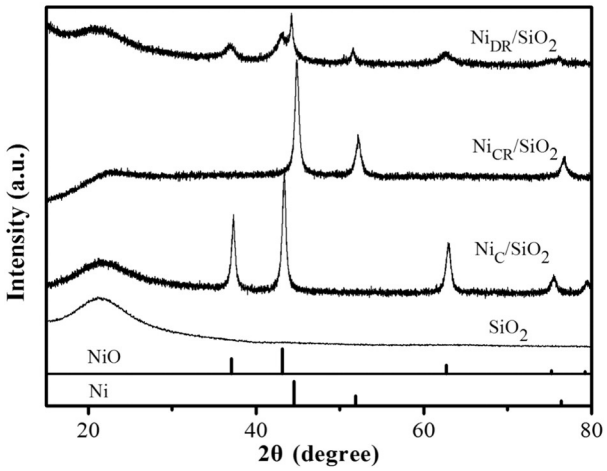
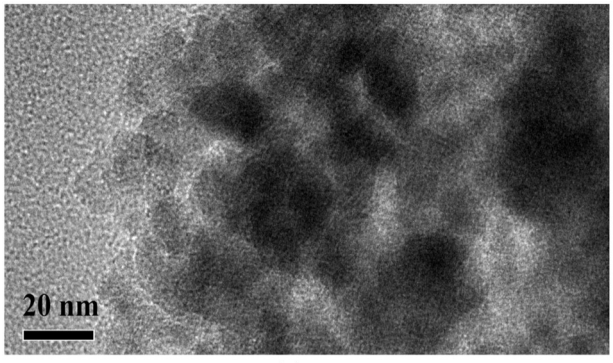
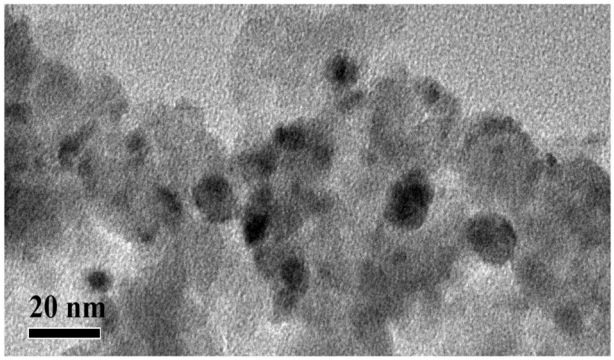


Fig. 2. XRD pattern of SiO_2, Ni_C/SiO_2, Ni_{CR}/SiO_2 and Ni_{DR}/SiO_2.

It has been demonstrated that the condensation reactions occur on the catalyst surface and not homogeneously in the liquid phase [16,17]. To minimize these, much work has been done on modifying the catalysts, such as decreasing catalyst acidity by doping with K or using alkaline MgO support [8,13,18,19]. Although these methods achieved good primary amine selectivity, it was at the cost of decreasing the catalytic activity. In this work, the Ni_{DR}/SiO_2 catalyst that exhibited a superior catalytic performance to Ni_{CR}/SiO_2 indicated that good hydrogenation activity and a high primary amine selectivity were not incompatible. The imine adsorbed on the catalyst surface reacted by either consecutive hydrogenation to primary amines or by condensation reactions with the primary amines formed. These are two parallel reactions. The highly dispersed Ni particles and excellent H_2 uptake ability of Ni_{DR}/SiO_2 promoted the hydrogenation to inhibit the condensation reactions at the same time. On the other hand, since Ni_{DR}/SiO_2 has a superior H_2 adsorption activity versus Ni_{CR}/SiO_2, it adsorbed more electron-rich imines. The adsorbed imino C atom was subject to a nucleophilic attack by an amino N atom, resulting in the formation of a secondary imine which was further hydrogenated to HMI [11,13]. Consequently, the selectivity to HMI over Ni_{DR}/SiO_2 was higher than that over Ni_{CR}/SiO_2.



(a)



(b)

Fig. 3. TEM images of (a) Ni_{CR}/SiO_2 and (b) Ni_{DR}/SiO_2.

Table 2
Catalytic performance of Ni_{CR}/SiO_2 and Ni_{DR}/SiO_2 catalysts.

Group[a]	Time /min	Conversion /%	Selectivity/%			
			ACN	HMD	HMI[b]	Condensation byproducts[c]
1	360	55	41	1	8	50
2	100	85	55	12	21	12
3	360	82	50	4	9	37
4	80	86	66	13	18	3

[a] Group 1 catalyzed by Ni_{CR}/SiO_2 without NaOH addition. Group 2 catalyzed by Ni_{DR}/SiO_2 without NaOH addition. Group 3 catalyzed by Ni_{CR}/SiO_2 with 0.1 g NaOH addition. Group 4 catalyzed by Ni_{DR}/SiO_2 with 0.1 g NaOH addition.
[b] Calibration factor for HMI and the internal standard was set at 1.
[c] Calculated based on that the selectivity to all components was 100%.

The effect of NaOH on the hydrogenation activity and product selectivity was also investigated. NaOH is a general and effective additive used in ADN hydrogenation catalyzed by Raney Ni in a solvent such as methanol [20,21]. As seen in Table 2, the addition of NaOH improved the catalytic activity and the primary amine selectivity of both catalysts. Since amines are more strongly adsorbed on the catalyst surface than nitriles, they retard the hydrogenation of nitriles [22]. NaOH benefited the desorption of amines, which not only promoted nitrile hydrogenation but also inhibited the condensation reactions between the amines and imines. Therefore, when NaOH was introduced, the ADN conversion over Ni_{CR}/SiO_2 increased from 55% to 82% in the same reaction time. The facile desorption of the primary amines helped decrease the selectivity to the condensation byproducts from 50% to 37% over Ni_{CR}/SiO_2 and from 12% to 3% over Ni_{DR}/SiO_2.

4. Conclusion

The liquid phase hydrogenation of ADN was investigated on Ni_{CR}/SiO_2 and Ni_{DR}/SiO_2 catalysts and the conclusions were:

(1) Ni_{DR}/SiO_2 exhibited superior hydrogenation activity to Ni_{CR}/SiO_2, which was due to its higher Ni dispersion and therefore smaller Ni particles.
(2) In the reaction, the imine intermediate reacted by three parallel reactions: hydrogenation, intramolecular cyclization and intermolecular condensation. The highly reactive Ni_{DR}/SiO_2 promoted the hydrogenation of adsorbed imines, thus inhibiting the condensation reactions and increasing the selectivity to primary amines.
(3) The formation of HMI was promoted on Ni_{DR}/SiO_2 by the strong adsorption between the Ni particles and electron rich imines.
(4) The addition of NaOH increased the hydrogenation activity and primary amine selectivity. The use of the combination of Ni_{DR}/SiO_2 and NaOH increased the primary amine selectivity to 79% at the ADN conversion of 86%.

References

[1] G. Dahlhoff, J.P.M. Niederer, W.F. Hoelderich, Catal. Rev. Sci. Eng. 43 (2001) 381–441.
[2] C.A. Tolman, R.J. Mckinney, W.C. Seidel, J.D. Druliner, W.R. Stevens, Adv. Catal. 33 (1985) 1–46.
[3] J. Brunelle, A. Seigneurin, L. Sever, US Patent 6479658, 2002.
[4] P. Leconte, US Patent 20120095212, 2012.
[5] S.B. Ziemecki, US Patent 5151543, 1992.
[6] V. Boschat, J.P. Brunelle, B. Darrier, B. Chevaljer, J.L. Bobet, US Patent 6521779B1, 2003.
[7] S.B. Ziemecki, A.S. Ionkin, US Patent 6080884, 2000.

[8] H. Liao, S. Liu, F. Hao, P. Liu, K. You, D. Liu, H. Luo, React. Kinet. Mech. Catal. 109 (2013) 475–488.
[9] B. Chen, U. Dingerdissen, J.G.E. Krauter, H.G.J. Lansink Rotgerink, K. Mobus, D.J. Ostgard, P. Panster, T.H. Riermeier, S. Seebald, T. Tacke, H. Trauthwein, Appl. Catal. A Gen. 280 (2005) 17–46.
[10] D. Tichit, R. Durand, A. Rolland, B. Coq, J. Lopez, P. Marion, J. Catal. 211 (2002) 511–520.
[11] B.W. Hoffer, J.A. Moulijn, Appl. Catal. A Gen. 352 (2009) 193–201.
[12] M. Montes, C. Penneman de Bosscheyde, B.K. Hodnett, F. Delannay, P. Grange, B. Delmon, Appl. Catal. 12 (1984) 309–330.
[13] H. Li, Y. Xu, H. Li, J.F. Deng, Appl. Catal. A Gen. 216 (2001) 51–58.
[14] C. Louis, Z.X. Cheng, M. Che, J. Phys. Chem. 97 (1993) 5703–5712.
[15] Y. Nakagawa, H. Nakazawa, H. Watanabe, K. Tomishige, ChemCatChem 4 (2012) 1791–1797.
[16] J.L. Dallons, A. van Gysel, G. Janne, Catalysis of Organic Reactions, Marcel Dekker, New York, 1992.
[17] J. Volf, J. Pašek, Stud. Surf. Sci. Catal. 27 (1986) 105–144.
[18] H. Chen, M. Xue, J. Shen, Catal. Lett. 135 (2010) 246–255.
[19] M. Serra, P. Salagre, Y. Cesteros, F. Medina, J.E. Sueiras, Appl. Catal. A Gen. 272 (2004) 353–362.
[20] W. Schnurr, R. Fischer, P. Bassler, W Harder, US patent 5512697, 1996.
[21] M.S. Kathryn, US Patent 5296628, 1994.
[22] Y. Huang, W.M.H. Sachtler, Appl. Catal. A Gen. 182 (1991) 365–378.