



Microcalorimetric adsorption and infrared spectroscopic studies of supported nickel catalysts for the hydrogenation of diisopropylimine to diisopropylamine

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ABSTRACT

Diisopropylimine (DIPI) was used as a probe molecule to investigate the hydrogenation of C=N on the Ni/Al₂O₃, Ni/LaAlO and Ni/LaOx catalysts. Microcalorimetric adsorption and infrared spectroscopy were applied to determine the surface bond strengths and structures of the reactant and product. It was found that the acidic support favored the adsorption and activation of DIPI and H₂ on Ni, leading to the increased activity (TOF) for the hydrogenation of DIPI, while the basic support promoted the dehydrogenation of the amine product on Ni, being unfavorable for the hydrogenation of DIPI. In particular, the conversion of DIPI was significantly increased when isopropanol (IPA) was used as a solvent, due to the hydrogen transfer reaction (HTR) between IPA and DIPI, which was further evidenced by the infrared spectrum of co-adsorbed IPA and DIPI.

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1. Introduction

Imines are important organic chemicals that can be used to synthesize substances for antiseptics, analgesia, anticancer and anti-inflammation [1–6]. They are also crucial organic intermediates used in the organic synthesis, pharmaceutical chemistry and fine chemistry [7,8]. Amines can be produced from the catalytic hydrogenation of imines, in which chiral amines can be synthesized on chiral catalysts [9–11]. The condensation of aldehydes/ketones with amines or ammonia produces imines which can then be hydrogenated into important amines (especially secondary amines) [12,13]. For example, the condensation of glucose with methylamine produces N-methylglucosimine which is then hydrogenated into N-methylglucosamine (MGA) that is an intermediate for the production of a series of green surfactants N-alkyl-N-methylglucamide (AGA) [14–19]. In this process, the synthesis of MGA is usually performed in a batch reactor, in which the condensation and hydrogenation reactions occur simultaneously [20,21]. However, fixed-bed reactors are usually taken as being more efficient than batch reactors [22]. Another important example is the synthesis of rubber antioxidants through the imine intermediates. For instance, 4-aminodiphenylamine reacts with acetone and methyl isobutyl ketone (MIBK), respectively, to the

corresponding imines which are then hydrogenated into 4-isopropylaminodiphenylamine (4010NA) and N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (4020) [23–27].

Above reactions usually involve in two sequential steps, i. e., the condensation for the production of imines, and the hydrogenation of imines to amines. Usually, the two reactions are performed in one pot, and thus it is difficult to study the reaction mechanism of each step and to achieve the optimal conditions for the two reactions simultaneously. Considering this situation, we intentionally separated the two steps and studied them separately, by using probe molecules. Specifically, we synthesized diisopropylimine (DIPI) by the condensation of acetone with isopropylamine. In this work, DIPI was used as a probe molecule to investigate the hydrogenation of C=N double bond in order to obtain some information about the reaction mechanism and the essential factors that affect the performance of such reactions.

In this work, catalysts Ni/Al₂O₃, Ni/LaAlO and Ni/LaOx were prepared and used for the hydrogenation of DIPI. These catalysts possessed differently dispersed Ni nano particles and different surface acidic and basic properties [28,29], and thus exhibited different activities for the hydrogenation of DIPI. In addition, microcalorimetric adsorption and infrared spectroscopy were used to study the surface bond strengths and structures of the reactant and product on the catalysts, trying to deepen the understanding of the hydrogenation of C=N double bonds.

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2. Experimental

2.1. Preparation of catalysts

The catalysts Ni/Al₂O₃ and Ni/LaOx containing about 60 wt% Ni were prepared by the co-precipitation method. The 60%Ni/LaAlO was prepared by the sequential precipitation [22]. In the latter case, NiAlOx was first precipitated, followed by the precipitation of NiLaOx, with the Ni/Al₂O₃/LaOx ratio of 60/24/16. The procedure is described in detail in Supplementary Data (SD).

2.2. Preparation of diisopropylimine

Diisopropylimine (DIPI) was synthesized by the condensation of acetone with isopropylamine. The procedure is described in detail in SD.



2.3. Characterization of catalysts

The phases of supports and supported nickel were determined by X-ray diffraction (XRD). X-ray fluorescence spectrometer (XRF) was used to measure the chemical compositions of catalysts. Transmission electron microscopy (TEM) was performed to observe the nano particles of supported Ni. The reduction behavior of catalysts was studied by temperature-programmed reduction (TPR). The surface areas and pore sizes were measured using the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively. The procedures are described in detail in SD.

H₂ and O₂ adsorptions were carried out in a home-made volumetric adsorption system. The procedure is described in detail in SD. The reduction degree, dispersion, average particle size, and active surface area of the sample were calculated by the amounts of H₂ and O₂ adsorbed and the loading of nickel [30].

Microcalorimetric adsorptions of H₂, CO, NH₃, CO₂, DIPI, diisopropylamine (DIPA) and isopropanol (IPA) were performed using a Tian–Calvet type C-80 microcalorimeter connected to a glass vacuum system. The surface structures of adsorbed species (DIPI, DIPA and IPA) were recorded by Fourier transformed infrared spectroscopy (FTIR). The specific procedures are described in detail in SD.

2.4. Catalytic tests

The specific procedure is also described in detail in SD. In brief, the hydrogenation of DIPI was performed in a stainless steel fixed-bed reactor. Pure DIPI or its solution (20 wt% DIPI) was pumped into the reactor and flowed downward with H₂ through the packed catalyst bed. The products were collected and analyzed by gas chromatography. The turnover frequency (TOF) was calculated by dividing the number of molecules converted per second by the number of active nickel atoms determined by H₂ adsorption.

3. Results and discussion

3.1. Textural and structural properties of catalysts

Fig. S1 in SD shows the N₂ adsorption-desorption isotherms (A) and pore size distributions (B) for the catalysts Ni/Al₂O₃, Ni/LaAlO

and Ni/LaOx. The catalysts exhibited the type IV adsorption isotherms with H3 hysteresis loops, characteristic of mesopores.

Table 1 lists the composition, surface areas and pore parameters of the reduced catalysts. The loading of Ni analyzed by XRF was close to 60%, which was the value desired for all the catalysts. The surface areas were measured to be 279, 224 and 26 m²/g for the Ni/Al₂O₃, Ni/LaAlO and Ni/LaOx with the average pore sizes of about 8.7, 7.8 and 19.6 nm, respectively.

The number of surface Ni atoms can be titrated by the adsorption of H₂ [31,32]. The data from H₂-O₂ titration are also given in Table 1. The uptakes of H₂ were measured to be 709, 948 and 350 μmol/g, respectively, for the Ni/Al₂O₃, Ni/LaAlO and Ni/LaOx. The reducibilities (the percentages of Ni reduced) were estimated to be about 76, 85 and 109%, respectively, for the Ni/Al₂O₃, Ni/LaAlO and Ni/LaOx according to the uptakes of O₂. Apparently, nickel in Al₂O₃ was difficult to reduce [33,34] while the addition of LaOx promoted the reduction of nickel in the catalysts. The reducibility was higher than 100% for the Ni/LaOx, indicating some degrees of reduction of LaOx to the lower valent states. The dispersions of Ni, average sizes of Ni particles and active surface areas of Ni can also be estimated according to the uptakes of H₂ and O₂. It is seen from Table 1 that the dispersion of Ni was low (7.3%) and the Ni particles were large (13.8 nm) in the Ni/LaOx, while the dispersion of Ni was much higher (23.8%) and the Ni particles were much smaller (4.2 nm) in the Ni/Al₂O₃ than in the Ni/LaOx. In particular, the Ni/LaAlO exhibited the even higher dispersion of Ni (26.2%) and smaller Ni particles (3.9 nm) than the Ni/Al₂O₃. The active surface Ni area of Ni/LaAlO (74.2 m²/g) was also significantly higher than that of Ni/Al₂O₃ (55.5 m²/g). The active surface Ni area of the Ni/LaOx was low (27.4 m²/g), owing to the low dispersion of Ni in this catalyst. It should be mentioned that the active Ni surface area measured by the H₂-O₂ titration for the Ni/LaOx was even higher than its BET area. Such seemingly contradictory data might be caused by the partial reduction of LaOx. In fact, it was reported that metallic Ni could be alloyed with reduced La to form the hydrogen storage materials [35]. Thus, the adsorption of H must occur not only on Ni but also on the reduced La in the Ni/LaOx catalyst, leading to the overestimation of H uptake on Ni.

Fig. S2 in SD shows the XRD patterns of catalysts reduced in H₂ at 723 K. Metallic Ni particles were determined in the catalysts. According to Scherrer equation, the sizes of Ni particles in the Ni/Al₂O₃, Ni/LaAlO and Ni/LaOx were estimated to be about 4.0, 3.6 and 10.9 nm, respectively, in consistence with the results of H₂-O₂ titration.

Fig. S3 in SD shows the TPR profiles for the Ni/Al₂O₃, Ni/LaAlO and Ni/LaOx. The main reduction peak of Ni/LaOx was lower than that of Ni/Al₂O₃, indicating the presence of LaOx weakened the interactions of Ni²⁺ with Al₂O₃, leading to the higher reducibility of nickel in the Ni/LaAlO than in the Ni/Al₂O₃.

Fig. S4 in SD shows the TEM images for the catalysts reduced in H₂ at 723 K. The average sizes of Ni particles in the Ni/Al₂O₃, Ni/

Table 1
Composition, surface area and pore parameters of the Ni/Al₂O₃ Ni/LaAlO and Ni/LaOx reduced at 723 K in H₂.

Catalyst	Ni/Al ₂ O ₃	Ni/LaAlO	Ni/LaOx
Loading (wt%)	56.5%	55.2%	59.9%
S _{BET} (m ² /g)	279	224	26
Pore size (nm)	8.7	7.8	19.6
V _{pore} (cm ³ g)	0.78	0.59	0.14
H ₂ uptake (μmol/g)	709	948	350
O ₂ uptake (μmol/g)	2975	3619	4789
Reducibility (%)	67.7	82.4	109
Dispersion (%)	23.8	26.2	7.3
D _{Ni} (nm)	4.2	3.9	13.8
S _{Ni} (m ² /g)	55.5	74.2	27.4

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