

Liquid-phase hydrogenation of *o*-chloronitrobenzene over supported nickel catalysts

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Abstract

The effect of supports (SiO_2 , ZrO_2 , TiO_2 and Al_2O_3) on the performance of nickel catalysts for the hydrogenation of *o*-chloronitrobenzene was investigated. It was found that the supports strongly influenced the catalytic performance of the catalysts, and Ni/TiO_2 showed the best catalytic performance. Over Ni/TiO_2 , 99.9% conversion of *o*-chloronitrobenzene and 99.5% selectivity of *o*-chloroaniline were obtained at 1.5 MPa and 363 K. The good performance of Ni/TiO_2 was perhaps attributed to the strong polarization of $\text{N}=\text{O}$ band induced by oxygen vacancies of TiO_x which was produced by a high temperature reduction, and the $\text{N}=\text{O}$ band polarized was attacked easily by hydrogen dissociatively adsorbed on the nickel particles.

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1. Introduction

Aromatic haloamines are important intermediates in industry for the synthesis of many fine chemicals, such as dyes, drugs, herbicides and pesticides. The main methods to these haloamines are the reduction of the corresponding nitrocompounds, either with metal–acid or with hydrogen over a metal catalyst. The process using the latter is growing, mainly due to its lower impact on environment because no acid effluents are produced.

Many catalysts have been studied for the hydrogenation of nitro-substituted aromatic halo-compounds, including polymer-stabilized colloidal noble metal clusters [1–5], supported noble metal catalysts [6–10], raney nickel [11] and amorphous alloy [12,13]. Because the nitro compound contains an aromatic halogen, the reduction of the nitro group without dehalogenation presents a particularly difficult problem. The noble metal catalysts showed a good catalytic performance even under mild reaction conditions, especially Pt-based catalysts; however, their rather rare resource restricts their application. As to raney nickel, there exist

some drawbacks in the industrial practice, for example, the severe corrosion and the pollution resulted from its preparation process and the safety problem during its storage and application; additionally, in order to inhibit dehalogenation, some toxic promoters such as bases were used, and so the extra processing steps to remove them were adopted. Supported nickel catalysts have been widely used in many hydrogenation reactions [14–16] owing to their high reactivity, easy availability and lower price. However, few literatures about hydrogenation of halonitroaromatic compounds over them have been reported so far.

The aim of the present work is to investigate the effects of supports (ZrO_2 , SiO_2 , TiO_2 and $\gamma\text{-Al}_2\text{O}_3$) on the hydrogenation of *o*-chloronitrobenzene (*o*-CNB) to *o*-chloroaniline (*o*-CAN) over supported nickel catalysts, and to find a promising one.

2. Experimental

2.1. Catalyst preparation

Nickel-based catalysts were prepared by incipient impregnation. The supports, including ZrO_2 (monoclinic

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phase), SiO₂, TiO₂ (anatase phase) and γ -Al₂O₃, were impregnated with an aqueous solution of Ni(NO₃)₂, and then placed at room temperature for 12 h. After drying at 383 K for 4 h and air calcination at 773 K for 4 h, the sample was reduced at 723 K in a flowing hydrogen–argon mixture with a volume ratio of 1:9 for 2 h, and the catalyst were obtained. ZrO₂, SiO₂, TiO₂ and γ -Al₂O₃ supported nickel catalysts were labeled as Ni/ZrO₂, Ni/SiO₂, Ni/TiO₂ and Ni/ γ -Al₂O₃, respectively. For all catalysts, the content of nickel was set to 15 wt%.

2.2. Activity test

The liquid phase hydrogenation of *o*-chloronitrobenzene was carried out in a 250 mL stainless steel autoclave reactor, which was charged with *o*-chloronitrobenzene (5.0 g) and the catalyst (0.5 g) in 100 mL ethanol solvent. At first, air was flushed out of the reactor with nitrogen at room temperature, and then hydrogen was fed into the reactor. After replacing nitrogen with hydrogen, the reactor was heated to 363 K and increased to 1.5 MPa, and then the hydrogenation reaction started with stirring at 1000 rpm. During the run, a series of samples were withdrawn periodically and analyzed by a gas chromatograph equipped with a flame ionization detector (FID) and an OV-101 capillary column. The products were identified by an Agilent GC6890-MS5973.

2.3. Catalyst characterization

X-ray diffraction (XRD) patterns were obtained with RIGAKU D/MAX-2500 diffractometer with Cu K α radiation (40 kV, 100 mA). The average nickel crystallite size was estimated from XRD line-broadening by employing Scherrer equation.

Temperature programmed reduction (TPR) was carried out in a tubular quartz reactor, where 50 mg catalyst was loaded in the thermostatic zone. The reduction was con-

ducted in a flow of H₂–N₂ mixture (volume ratio, 10:90) at a heating rate of 10 K/min. The consumption of hydrogen was detected using a thermal conduction detector (TCD).

The morphology of the catalysts after reduction was studied by transmission electron microscopy (TEM, JEOL JEM100-CX-II).

BET specific surface area and pore volume were measured with a SORPTOMATIC 1900 surface analysis apparatus by N₂ volumetric adsorption method at 77 K. Hydrogen chemisorption was performed in a Thermal Finiggin TPDRO1100 instrument. After reduction at 723 K for 2 h, the hydrogen on the nickel surface was removed with 20 ml/min of He (99.999%) for 30 min. The catalyst sample was subsequently cooled to 298 K under He stream, and then He stream was switched to N₂. After the TCD was stable under N₂ stream, H₂ pulses (100 μ l/pulse) were injected until the effluent area of consecutive pulses was constant. The dispersion of Ni was calculated assuming a stoichiometry of one hydrogen molecule adsorbed on per two surface nickel atoms [17], and it was given by $D = N_i/N_t = H/Ni$. The specific surface area, pore structure and nickel dispersion of catalysts with different supports are listed in Table 1.

3. Results and discussion

Table 2 presents the hydrogenation of *o*-CNB over the different nickel catalysts. There was a remarkable difference of specific activity over different catalysts. Although Ni/TiO₂ had the less nickel dispersion as listed in Table 1, its TOF was larger about 174 and 25 times than that on Ni/SiO₂ and Ni/ZrO₂, respectively. Ni/ γ -Al₂O₃ showed very much low catalytic performance. The conversion of *o*-CNB over Ni/SiO₂ reached 19.2% at 30 min, however, it increased slowly along with the reaction, and only was 60.8% at 660 min. The conversion of *o*-CNB over Ni/TiO₂ and Ni/ZrO₂ exceeded 99.0% after reaction for

Table 1
Specific surface area, pore structure and nickel dispersion of catalysts with different supports

Catalyst	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore radius (\AA)	H ₂ amount of chemisorption (μ mol/g cat)	H/Ni
Ni/SiO ₂	111.4	0.063	11.4	15.2	0.01
Ni/TiO ₂	90.5	0.050	11.1	0.5	0.0004
Ni/ZrO ₂	16.4	0.009	11.0	3.4	0.003
Ni/ γ -Al ₂ O ₃	187.1	0.107	11.4	–	–

Table 2
Catalytic performance of nickel based catalysts with different supports for hydrogenation of *o*-chloronitrobenzene

Catalysts	Reaction time (min)	Turnover frequency ^a (s ⁻¹)	<i>o</i> -CNB conversion (mol%)	<i>o</i> -CAN selectivity (mol)%
Ni/ γ -Al ₂ O ₃	30		0.6	100
	120		1.2	100
Ni/SiO ₂	30	0.2	19.3	93.7
	660		60.8	96.4
Ni/ZrO ₂	30	1.4	26.4	89.1
	240		99.6	98.1
Ni/TiO ₂	30	34.9	99.1	99.2
	60		99.9	99.6

^a Specific activity per Ni surface atom (s⁻¹) for hydrogenation of *o*-CNB over Ni catalysts at first 30 min.

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