



Catalysis, Kinetics and Reaction Engineering

Preparation of Ni/bentonite catalyst and its applications in the catalytic hydrogenation of nitrobenzene to aniline[☆]

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ABSTRACT

Ni supported on bentonite was prepared by the impregnation method with different nickel contents, applied to the hydrogenation of nitrobenzene to aniline in a fixed-bed reactor, and it was characterized by X-ray diffraction (XRD), H₂-temperature programmed reduction (H₂-TPR), and X-ray photoelectron spectrometry (XPS). The results showed that Ni/bentonite catalyst with 20 wt% nickel content provided a higher conversion of nitrobenzene and selectivity of aniline compared to other catalysts. NiO was the precursor of the active component of the catalyst, and the small crystallite size as well as the highly dispersed NiO on the Ni/bentonite-20 catalyst, contributed to the catalytic performance. The hydrogenation of nitrobenzene was carried out at 300 °C with a H₂ gaseous hourly space velocity of 4800 ml·(g cat)⁻¹·h⁻¹ and a nitrobenzene liquid hourly space velocity of 4.8 ml·(g cat)⁻¹·h⁻¹ over Ni/bentonite-20. A 95.7% nitrobenzene conversion and 98.8% aniline selectivity were obtained. While the nitrobenzene liquid hourly space velocity was 4.8 ml·(g cat)⁻¹·h⁻¹, the yield of aniline was more than 95.0% during a 10-hour reaction.

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1. Introduction

Aniline is an aromatic compound which contains an amino group that provides a unique reactivity. This unique reactivity makes aniline an important intermediate for producing polyurethanes, dyes, explosives, pharmaceuticals, and agriculture chemicals [1,2]. Catalytic hydrogenation is a promising way to produce aniline because it is easier to control, much safer and has little impact on the environment. Aniline, as previously described, is mainly produced by the catalytic hydrogenation of nitrobenzene over a variety of supported metal catalysts, such as Pd supported on polymer [3], Cu–Cr–Mo/SiO₂ [4], Ni/SBA-15 [5] and Pd/C [6], either in the vapour or liquid phase. Generally, noble metal catalysts are used for the hydrogenation of nitrobenzene liquid phase to produce aniline [6], and commercially, the reaction is carried out in the vapour phase over copper-based catalysts [7]. On the other hand, both the Bechamp reduction and sulphide reduction in the conventional non-catalytic process generate large amounts of waste [8]. Major problems, such as the cost of the catalyst and the impact caused by the reaction on the environment, remain unsolved, and the

development of greener, cheaper, more effective, and conveniently-handled catalysts for this hydrogenation process is still highly desirable.

Bentonite, with a layer structure containing a larger amount of mesoporous, is a good catalyst support due to its strong metal support interaction and low cost, and its numerous applications in the catalytic field have been reported [9–12]. Based on our previous studies of nitrobenzene catalytic hydrogenation to aniline in a gas–liquid–solid system [13–15], and with the goal of developing a sustainable catalytic process with high efficiency, Ni/bentonite catalysts with different nickel loading amounts were prepared, characterized, and applied for the hydrogenation of nitrobenzene in the gas phase in a fixed-bed reactor.

2. Experimental

2.1. Preparation of Ni/bentonite catalysts

Ni(NO₃)₂·6H₂O and bentonite were weighed in the mass ratios of *m*(Ni)/*m*(bentonite)=0.05, i.e. 0.5 g Ni and 10.0 g bentonite, and each was dissolved in 100 ml of deionized water. The bentonite suspension was heated to 70 °C with a 200 r·min⁻¹ agitation for 0.5 h, which ensured the full swelling of bentonite. Then, the Ni(NO₃)₂ solution was dropped into the bentonite suspension with a 200 r·min⁻¹ agitation at 70 °C for 4 h, to obtain a slurry. The slurry was dried at 100 °C for 12 h and then calcined at 400 °C for 4 h. The obtained catalyst with a Ni loading amount of 5 wt% was marked as Ni/bentonite-5. The same procedure was followed to prepare Ni/bentonite catalysts with 10 wt%, 15 wt%, 20 wt%, and

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25 wt% Ni loading amounts, and the obtained catalysts were marked as Ni/bentonite-10, Ni/bentonite-15, Ni/bentonite-20, and Ni/bentonite-25, respectively.

2.2. Characterization of catalysts

X-ray diffraction (XRD) was conducted with a Bruker D8 Advance X-ray diffractometer, using Cu K α radiation ($\lambda = 0.154$ nm). The average size of the NiO crystallite was estimated from the (200) plane of NiO at $2\theta = 43.3^\circ$ using the Scherrer equation. The NiO crystallite sizes, $d(\text{NiO})$, were converted to the corresponding Ni crystallite sizes after reduction, $d(\text{Ni})$, using the relative molar volumes of metallic Ni and NiO [16], as show in Eq. (1).

$$d(\text{Ni}^0) = 0.84d(\text{NiO}) \quad (1)$$

The H₂ temperature programmed reduction (H₂-TPR) experiment was conducted on a TP-5000 multi-function adsorption instrument (Tianjin Xianquan Industry and Trade Development Co.). The X-ray photoelectron spectra of the catalysts were measured by a Thermo ESCA LAB 250X multifunction imaging electron spectrometer (Thermo Fisher Scientific Co., Ltd.) using an Al K α ray as the X-ray source. The weight fraction of Ni in the samples was precisely determined by ICP-OES using a Perkin Elmer Optima 5300 CV after dissolution of the samples using nitric acid. H₂ temperature programmed desorption (H₂-TPD) was taken on a TP-5080 multi-function adsorption instrument (Tianjin Xianquan Industry and Trade Development Co. Ltd.). About 0.10 g Ni/bentonite sample was added into a quartz reactor, flushed at 150 °C for 2 h in Ar to remove the physically adsorbed molecules. After that, the sample was cooled to 50 °C, and H₂ was introduced at 30 ml·min⁻¹ for 0.5 h for dynamic absorption measurements of H₂. Subsequent static adsorption tests were performed at 0.2 MPa for 1.5 h to insure saturation adsorption of H₂. After that, gas desorption experiments were carried out in 30 ml·min⁻¹ He (99.999%) in a range of 50–800 °C with a ramp rate of 10 °C·min⁻¹. The amount of gas desorbed was monitored by a thermal conductivity detector (TCD) held at 45 °C.

The specific surface area, particle size and dispersion of the metallic Ni were calculated based on the chemisorbed H₂ using Eqs. (2)–(4) [17].

Ni metal specific surface area (SA_{Ni}):

$$SA_{\text{Ni}} = \frac{V_1 \times SF \times N_A}{W_s \times V_m \times R_{\text{Ni}}} \times RA. \quad (2)$$

Ni dispersion $D(\%)$:

$$D = \frac{V_1 \times SF \times FW_{\text{Ni}}}{W_s \times R_{\text{Ni}} \times V_m} \times 100. \quad (3)$$

Ni crystallite size $d(\text{Ni}^0)$:

$$d(\text{Ni}^0) = \frac{6 \times 10^3}{SA_{\text{Ni}} \times P_{\text{Ni}}} \quad (4)$$

where, V_1 was the volume (ml) of H₂ chemisorbed at standard temperature and pressure (STP) conditions to form a monolayer, W_s was the weight of the sample (g), V_m was the molar volume of H₂ (22414 ml·mol⁻¹), SF was the stoichiometric factor (Ni:H molar ratio during chemisorption), which is taken as 1, N_A was the Avogadro constant (6.023×10^{23}), RA was the atomic cross-sectional area of Ni (0.0649 nm²), R_{Ni} was the weight fraction of Ni in the sample as determined by ICP, FW_{Ni} was the molecular weight of Ni (58.71 g·mol⁻¹), and P_{Ni} was the density of Ni metal (8.9 g·cm⁻³).

2.3. Catalytic hydrogenation of nitrobenzene to aniline

Gas phase catalytic hydrogenation of nitrobenzene to aniline over the Ni/bentonite catalyst was conducted in a fixed-bed reactor that consisted of a quartz reaction tube with an inner diameter of 8 mm and a tube length of 285 mm. Approximately 0.5 g of catalyst was added to the quartz tube and was reduced at 400 °C for 1.0 h accompanied by H₂ (99.999%) flow at a rate of 30 ml·min⁻¹. After the catalyst was reduced and cooled to 300 °C, nitrobenzene was pumped and vaporized at 300 °C through a vaporizer, and the catalytic hydrogenation of nitrobenzene to aniline was conducted at 300 °C with a nitrobenzene liquid hourly space velocity (LHSV) between 2.4–7.2 ml·(g cat)⁻¹·h⁻¹. The products were collected at the outlet using a test tube cooled by ice water, and were analysed by an Agilent 4890D gas chromatograph. The conversion of nitrobenzene, and the selectivity and yield of aniline were quantitatively analysed using the peak-area internal standard method with methylbenzene as the internal standard.

$$\text{Nitrobenzene conversion : } X = \frac{m_{\text{NBO}} - m_{\text{NB}}}{m_{\text{NBO}}} \times 100\% \quad (5)$$

$$\text{Aniline selectivity : } S = \frac{m_{\text{NB1}}}{m_{\text{NBO}} - m_{\text{NB}}} \times 100\% \quad (6)$$

$$\text{Aniline yield : } Y = X \times S \times 100\% \quad (7)$$

where m_{NBO} , m_{NB} , and m_{NB1} are the total mass of nitrobenzene consumed in the reaction, the remaining mass of nitrobenzene in the product, and the mass of nitrobenzene consumed to produce equivalent aniline in the product, respectively.

3. Results and Discussion

3.1. Physical and chemical properties of Ni/bentonite catalysts

Fig. 1 shows the XRD patterns of bentonite and Ni/bentonite catalysts with different nickel contents before H₂ reduction. The patterns showed obvious diffraction peaks at $2\theta = 19.9^\circ$ and 35.0° , which corresponded to the (101) and (107) planes of montmorillonite (JCPDS card NO. 29-1499). The diffraction peaks at $2\theta = 20.9^\circ$, and 26.6° corresponded to the (101) and (107) planes of SiO₂ (JCPDS card NO. 46-1045). These findings indicated that the support was a typical bentonite [18]. The diffraction peaks at $2\theta = 37.2^\circ$, 43.3° , and 62.9° corresponded to the (111), (200) and (220) planes of cubic NiO (JCPDS card NO. 47-1049), respectively, which indicated that NiO was formed after the nickel loading catalysts were calcined at 400 °C for

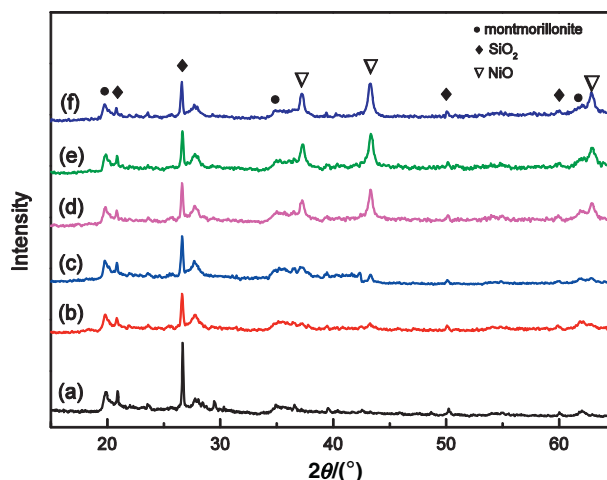


Fig. 1. XRD patterns of bentonite (a) and Ni/bentonite catalysts with 5 wt% (b), 10 wt% (c), 15 wt% (d), 20 wt% (e), and 25 wt% (f) nickel content before H₂ reduction.

4 h. However, the diffraction peaks of NiO were very weak in the 5 wt% and 10 wt% Ni/bentonite catalysts due to lesser amounts of Ni on bentonite.

On the basis of the data of line broadening at half the maximum intensity (full width at half-maximum, FWHM) and the Bragg angle (θ), the Scherrer equation [19] was used to calculate the mean crystallite size of the NiO. The corresponding crystallite size metallic Ni was calculated by Eq. (1). Furthermore, the specific surface area SA_{Ni} , crystallite size and dispersion of metallic Ni were calculated based on chemisorbed H_2 using Eqs. (2)–(4) and the results are listed in Table 1.

In Table 1, the average crystallite size of NiO on Ni/bentonite-15, Ni/bentonite-20, and Ni/bentonite-25 calculated by the Scherrer equation was 23.6, 18.5, and 21.0 nm, respectively. The corresponding Ni crystallite size calculated by Eq. (1) was 19.8, 15.5, and 17.6 nm, respectively. As comparison, the corresponding Ni crystallite sizes calculated based on chemisorbed H_2 using Eq. (4) was 15.2, 7.7, and 11.6 nm, respectively. Therefore, the metallic Ni crystallite size calculated by both Eqs. (1) and (4) were accordant and the metallic Ni crystallite size on Ni/bentonite-20 was smaller than the other two catalysts. Furthermore, the metallic Ni dispersion in the Ni/bentonite-20 catalyst was higher than that of the Ni/bentonite-15 and Ni/bentonite-25 catalysts. In general, metallic Ni was the active site in the nitrobenzene hydrogenation process [20], and the catalytic activity can be correlated with the dispersion and crystallite size of metallic Ni [21]. It has been suggested that a homogeneous dispersion of NiO on the support would lead to a rich exposition of metallic Ni on the surface of bentonite, leading to more catalytic sites and a higher catalytic activity for the target reaction. Therefore, Ni/bentonite-20 should have a better catalytic performance on the nitrobenzene hydrogenation process for the higher dispersion and smaller crystallite size of metallic Ni.

3.2. Effect of nickel contents on the catalytic hydrogenation of nitrobenzene to aniline

Fig. 2 presents the results of the catalytic hydrogenation of nitrobenzene to aniline over the Ni/bentonite catalysts with different nickel contents, which also shows bentonite as a comparison. When using bentonite as catalyst, aniline was not detected in the product. With the increase of the additive nickel contents, the conversion of nitrobenzene increased from 75.4% to 95.7% and then decreased to 93.8%; the selectivity of aniline increased from 91.4% to 98.8% and then decreased to 97.7%. The conversion of nitrobenzene and the selectivity of aniline both reached maximum values when the nickel content was 20 wt%, which were 95.7% and 98.8%, respectively. The main by-product confirmed by GC–MS was hydrazobenzene; however, the hydrazobenzene selectivity in the products was only 2% to 5%, which was very small and can be ignored in the subsequent discussion.

According to the XRD patterns, the crystallite size of NiO (200) on the Ni/bentonite-20 catalyst calculated by the Scherrer equation was 18.5 nm, which was smaller than the crystallite size of NiO in the other catalysts. The catalytic activity was relevant to the crystallite size of Ni obtained from NiO after the reduction process. The calculated crystallite size and dispersion of metallic Ni are listed in Table 1, and

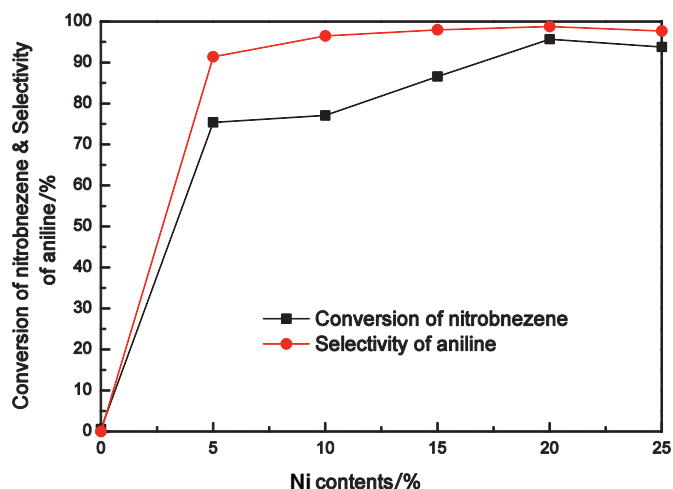


Fig. 2. Effect of different nickel contents on the catalytic hydrogenation of nitrobenzene to aniline over Ni/bentonite catalysts. Reaction conditions: $T = 300\text{ }^{\circ}\text{C}$, $LHSV = 4.8\text{ ml} \cdot (\text{g cat})^{-1} \cdot \text{h}^{-1}$, $GHSV = 4800\text{ ml} \cdot (\text{g cat})^{-1} \cdot \text{h}^{-1}$.

the conversion of nitrobenzene and the selectivity of aniline were in accordance with these calculated data. Ni/bentonite-20 catalyst with a smaller crystallite size and higher dispersion of metallic Ni exhibited a good catalytic performance, providing 95.7% conversion of nitrobenzene and 98.8% selectivity of aniline. Furthermore, the selectivity of aniline might be correlated to the support. The dispersion and crystallite size of metallic Ni impacted the selectivity of aniline relatively. As seen in Fig. 2, the selectivity of aniline with different Ni/bentonite catalysts ranged from 96.5% to 98.8% when the nickel content was more than 10 wt%. This small fluctuation was probably caused by the dispersion and crystallite size of metallic Ni.

3.3. H_2 -TPR analysis of catalysts

Ni species is the main centre of catalytic activity for the hydrogenation process of nitrobenzene and the reducibility of NiO species loaded on the support is highly affected by the metal-support interaction [22]. A H_2 temperature programmed reduction (H_2 -TPR) analysis was made to evaluate the reducibility of the NiO species, the amount of Ni on the reduction of Ni species, and the interaction between Ni and bentonite. The results are shown in Fig. 3 and Table 2. Generally, Ni^{2+} is reduced to Ni^0 without going through intermediate oxides; therefore, H_2 consumption peaks appearing at different temperatures should be assigned to different species [23]. From Fig. 3, only two Gaussian fitting peaks (peak α and β) were found in the H_2 -TPR profiles of the Ni/bentonite-5 sample within the temperature range of 100–650 $^{\circ}\text{C}$, and three Gaussian fitting peaks (peak α , β , and γ) are shown in Fig. 3 within the temperature range of 100–650 $^{\circ}\text{C}$ for the other catalysts. Peak α , which occurred in the temperature range of 413.2–436.2 $^{\circ}\text{C}$ (presented in Table 1), corresponded to the bulk NiO located on the external surface of the bentonite with a weak interaction with the

Table 1

The crystallite size, Ni metal surface area, and the metallic Ni dispersion in the Ni/bentonite catalysts

Catalysts	Ni loading ^① /%	H_2 adsorbed amount ^② /mmol $\cdot$ g ^{−1}	$d(\text{NiO})$ ^③ /nm	Nickel crystallite size/nm		$SA_{Ni}/\text{m}^2 \cdot \text{g}^{-1}$	Metallic Ni dispersion/%
				XRD ^④	H_2 -TPD		
Ni/bentonite-15	7.49	0.085	23.6	19.8	15.2	44.3	6.7
Ni/bentonite-20	10.06	0.225	18.5	15.5	7.7	87.4	13.3
Ni/bentonite-25	11.81	0.176	21.0	17.6	11.6	58.2	8.8

① Determined by ICP before H_2 reduction.

② Determined by H_2 -TPD.

③ Calculated by the Scherrer equation.

④ From $d(\text{NiO})$ using Eq. (1).

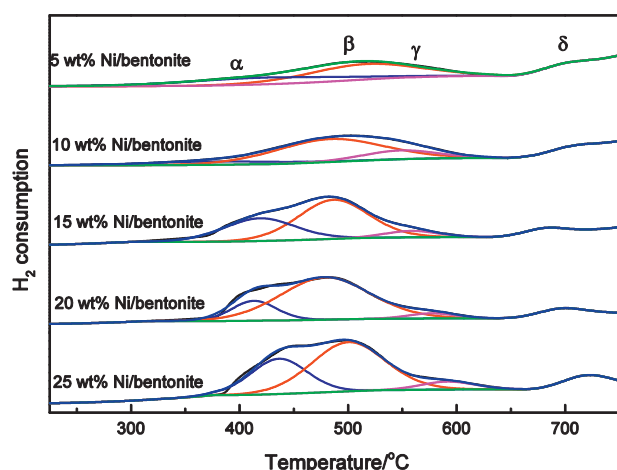


Fig. 3. H_2 -TPR profiles of the Ni/bentonite catalysts with 5 wt%, 10 wt%, 15 wt%, 20 wt%, and 25 wt% nickel content.

bentonite [24], while peak β , which occurred within the temperature range of 478.9–515.5 °C, was caused by the reduction of NiO nanoparticles confined within the mesoporous and thus had a relatively strong interaction with the bentonite [24–26]. From Fig. 3, with the increase of the loading amount of nickel from 5 wt% to 25 wt%, the amount of Ni species also increased, which was in accordance with other publications [27,28]. As shown in Table 2, the total reduced peak area increased with the Ni loading amount of the catalyst from 5 wt% to 25 wt%, indicating the increase of the amount of nickel oxide. For the Ni/bentonite-20 catalyst, the reduction peaks of α and β were centred at 412.1 °C and 477.5 °C, respectively, which were lower than that of Ni/bentonite-5 (442.9 °C, 521.2 °C), Ni/bentonite-10 (451.3 °C, 500.1 °C), Ni/bentonite-15 (418.1 °C, 486.4 °C), and Ni/bentonite-25 (441.6 °C, 506.5 °C), indicating the much higher dispersion of NiO on the surface of bentonite for the Ni/bentonite-20 catalyst [29]. The lower reducing temperature was beneficial, which can avoid the formation of Ni crystal grains during the hydrogenation process, and more Ni species can be exposed on the surface of the support, which can increase the reducibility of the catalyst. Out of all the Ni/bentonite catalysts, the lowest reduction temperatures of peak α and peak β were observed when the nickel content was 20 wt%, suggesting that this catalyst exhibited an optimum reducing behaviour. Peak γ , presented in Fig. 3 when the nickel content was more than 10 wt% and centred the temperature range of 558.1–591.7 °C, can be ascribed to smaller dispersed NiO particles, which had an intermediate interaction with the bentonite support [26]. Peak δ , which occurred in all Ni/bentonite catalyst samples at approximately 700 °C, was relatively weak and can be attributed to the reduction of nickel aluminate or nickel silicate [25,26].

The reduction temperatures of peak α and peak β in the Ni/bentonite-20 catalyst were centred at 413.2 °C and 478.9 °C, respectively, and were lower than the corresponding reduction temperatures in

the other catalysts. This indicates the high dispersion of NiO on the surface of bentonite [29], which may increase the catalytic activity of Ni/bentonite in the hydrogenation of nitrobenzene. Combined with the XRD results, both the smaller crystallite size of NiO and high dispersion of NiO on bentonite attributed to the optimal conversion of nitrobenzene and selectivity of aniline.

3.4. XPS analysis

X-ray photoelectron spectroscopy (XPS) was utilized to study the oxidation states of the elements on the surfaces of the bentonite and Ni/bentonite-20 catalysts; the results are shown in Fig. 4. The binding energies of approximately 854.4 eV (Ni 2p_{3/2}) and 873.6 eV (Ni 2p_{1/2}) can be ascribed to Ni²⁺ in NiO [30,31], and the binding energy of approximately 856.5 eV was caused by nickel aluminate [28,32,33]. The binding energies of approximately 861.8 eV and 880.0 eV corresponded to the strong shake-up process of Ni 2p_{3/2} and Ni 2p_{1/2}, respectively, in NiO [31,33,34]. The O 1s peaks in Fig. 4 can be fitted to three sub-peaks centred at 532.2 eV, 531.2 eV, and 529.6 eV, which corresponded to the three types of O on SiO₂ [35], Al₂O₃ [36], and NiO [34,37], respectively. Compared to bentonite, there were decreases of 0.2 eV and 0.4 eV in the binding energies of Gaussian fitting peaks centred at 532.2 eV and 531.2 eV and attributed to the O in SiO₂ and Al₂O₃, respectively, in the Ni/bentonite-20 catalyst, which indicated that there was a strong interaction between the metal and bentonite after the metals were loaded into the support [38].

3.5. Catalytic hydrogenation of nitrobenzene to aniline on Ni/bentonite catalysts

3.5.1. Effect of reduction temperature

Reduction temperature is an important parameter, and the effects of the reduction temperature on the nitrobenzene hydrogenation to aniline were studied from 350 to 550 °C. The results are shown in Fig. 5.

According to Fig. 5, when the reduction temperatures were 350, 400, 450, 500, and 550 °C, the nitrobenzene conversions were 87.5%, 95.7%, 96.4%, 96.2%, and 94.6%, respectively. The conversion of nitrobenzene first increased with the increase of reduction temperature; then, it remained stable, and the change in the selectivity of aniline was within 3% as the reduction temperatures changed, indicating that the reduction temperature had slight impacts on the aniline selectivity. Metallic Ni was the active site in the nitrobenzene hydrogenation reaction [19], and the crystallite size of metallic Ni was related to the crystallite size of NiO after the reduction process, which suggesting that enough metallic Ni active sites were obtained for nitrobenzene hydrogenation after reduction at 400 °C. Therefore, 400 °C was chosen as the optimal reduction temperature for this hydrogenation process.

3.5.2. Effect of nitrobenzene space velocity

The Ni/bentonite-20 catalyst was utilized in aniline synthesis from nitrobenzene with various nitrobenzene liquid space velocities (LHSV) from 2.4–7.2 ml·(g cat)^{−1}·h^{−1}, to investigate the effects of LHSV on the synthetic process. The results are presented in Fig. 6. With the increase of LHSV from 2.4 to 7.2 ml·(g cat)^{−1}·h^{−1}, the conversion of nitrobenzene decreased from 99.9% to 57.2%, and the selectivity of aniline decreased from 99.2% to 88.2%. The increase of LHSV probably shortened the contact time between the surface of the catalyst and the nitrobenzene/H₂ mixing gases, thus leading to insufficient contact between the nitrobenzene/H₂ gases. Although the conversion of nitrobenzene and the selectivity of aniline decreased, 2.4 ml·(g cat)^{−1}·h^{−1} was chosen as the optimal space velocity for the high conversion of nitrobenzene and selectivity of aniline. 4.8 ml·(g cat)^{−1}·h^{−1} was chosen for the other reactions to provide a comparison of the data.

Table 2

Temperatures and area distributions of reduction peaks of Ni/bentonite catalysts with different nickel contents^①

Catalyst	Centred temperature of Ni species reduction/°C			Peak area distribution			Total area distribution
	α	β	γ	α	β	γ	
Ni/B-5	442.9	521.2	–	1730	6043	–	7773
Ni/B-10	451.3	500.1	557.9	4245	6139	1659	12043
Ni/B-15	418.1	486.4	558.4	5827	10175	1225	17227
Ni/B-20	412.1	477.5	578.4	2984	14482	721	18187
Ni/B-25	441.6	506.5	586.3	11912	10309	1896	24117

^① The results were measured from H_2 -TPR profiles and the area distributions were calculated by integration of the area under the peaks.

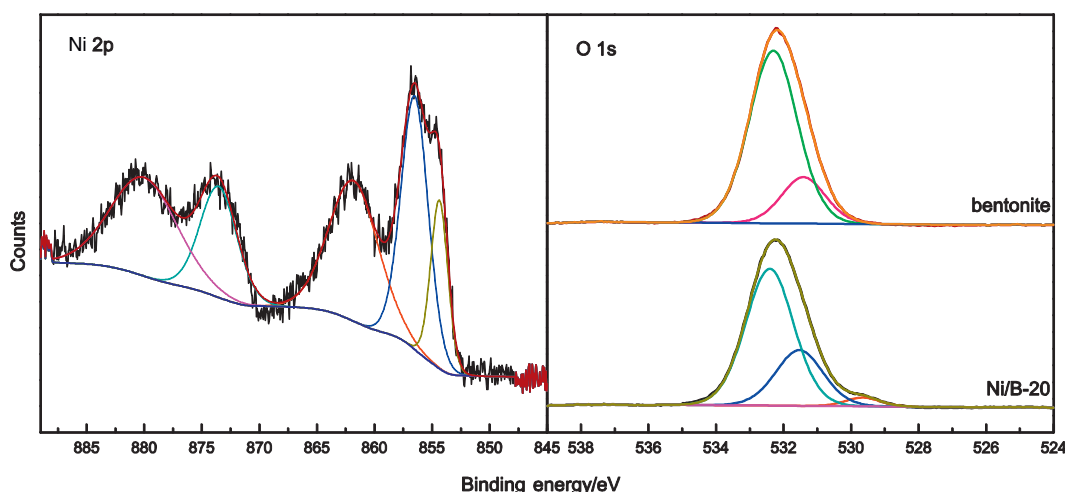


Fig. 4. XPS spectra of Ni 2p and O 1s regions for bentonite and Ni/bentonite-20 catalyst.

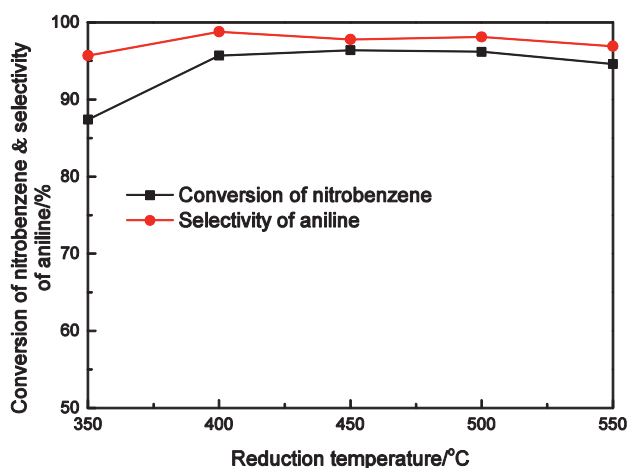


Fig. 5. Effect of the reduction temperature on the conversion of nitrobenzene and selectivity of aniline over Ni/bentonite-20. Reaction conditions: $T = 300\text{ }^{\circ}\text{C}$, $\text{LHSV} = 4.8\text{ ml}\cdot(\text{g cat})^{-1}\cdot\text{h}^{-1}$, $\text{GHSV} = 4800\text{ ml}\cdot(\text{g cat})^{-1}\cdot\text{h}^{-1}$.

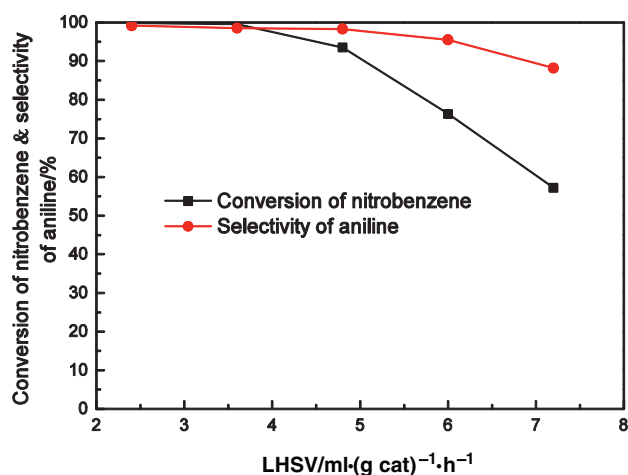


Fig. 6. Effect of nitrobenzene liquid space velocity (LHSV) on the catalytic hydrogenation of nitrobenzene to aniline over Ni/bentonite-20. Reaction conditions: $T = 300\text{ }^{\circ}\text{C}$, $\text{LHSV} = 2.4\text{--}7.2\text{ ml}\cdot(\text{g cat})^{-1}\cdot\text{h}^{-1}$, $\text{GHSV} = 4800\text{ ml}\cdot(\text{g cat})^{-1}\cdot\text{h}^{-1}$.

3.5.3. Effect of H_2 space velocity

The Ni/bentonite-20 catalyst was utilized in aniline synthesis from nitrobenzene with various H_2 gaseous space velocities (GHSV) from $1200\text{--}6000\text{ ml}\cdot(\text{g cat})^{-1}\cdot\text{h}^{-1}$ to investigate the effects of GHSV on the hydrogenation process. The results are shown in Fig. 7. With the increase of GHSV from 1200 to $6000\text{ ml}\cdot(\text{g cat})^{-1}\cdot\text{h}^{-1}$, the conversion of nitrobenzene increased from 23.6% to 98.9% , and the selectivity of aniline changed slightly. The increase of GHSV provided enough hydrogen sources for the hydrogenation reaction, leading to a higher conversion of nitrobenzene. Although the conversion of nitrobenzene was not the highest when the GHSV was $4800\text{ ml}\cdot(\text{g cat})^{-1}\cdot\text{h}^{-1}$, this value was chosen as the optimal GHSV considering the comparable data and the economics of reaction.

3.5.4. Stability of Ni/bentonite catalyst

The stability of the Ni/bentonite-20 catalyst was studied in the aniline synthesis via nitrobenzene/ H_2 at $300\text{ }^{\circ}\text{C}$ with $\text{GHSV} = 4800\text{ ml}\cdot(\text{g cat})^{-1}\cdot\text{h}^{-1}$ and $\text{LHSV} = 4.8\text{ ml}\cdot(\text{g cat})^{-1}\cdot\text{h}^{-1}$, and a Ni/ $\gamma\text{-Al}_2\text{O}_3$ -20 catalyst was used as a comparison. The results are shown in Fig. 8.

As a comparison, the Ni/ $\gamma\text{-Al}_2\text{O}_3$ -20 catalyst deactivated quickly, and the conversion of nitrobenzene decreased from 99.2% to 64.7% during the 5 h reaction process. Moreover, the selectivity of aniline

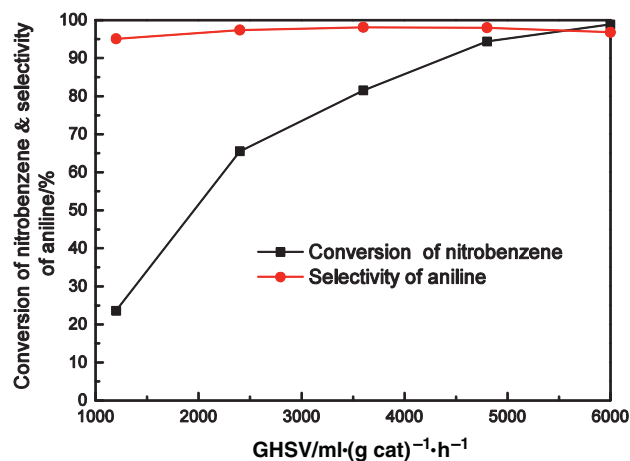


Fig. 7. Effect of gaseous H_2 space velocity (GHSV) on the catalytic hydrogenation of nitrobenzene to aniline over Ni/bentonite-20. Reaction conditions: $T = 300\text{ }^{\circ}\text{C}$, $\text{LHSV} = 4.8\text{ ml}\cdot(\text{g cat})^{-1}\cdot\text{h}^{-1}$, $\text{GHSV} = 1200\text{--}6000\text{ ml}\cdot(\text{g cat})^{-1}\cdot\text{h}^{-1}$.

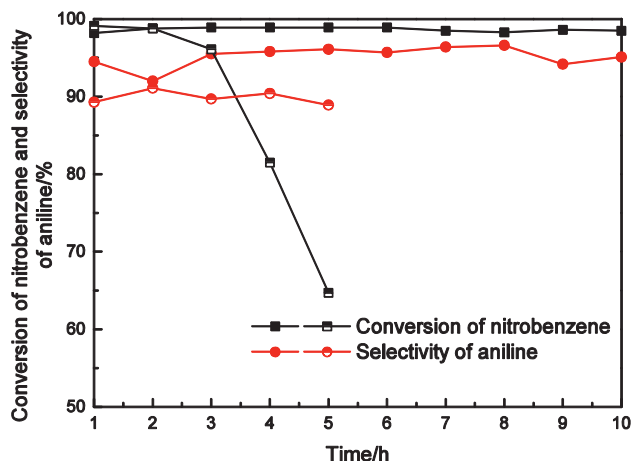


Fig. 8. Conversion of nitrobenzene and selectivity of aniline over Ni/bentonite-20 (solid) and Ni/γ-Al₂O₃-20 (half-solid) catalysts with time on stream. Reaction conditions: $T = 300\text{ }^{\circ}\text{C}$, LHSV = $4.8\text{ ml}\cdot(\text{g cat})^{-1}\cdot\text{h}^{-1}$, GHSV = $4800\text{ ml}\cdot(\text{g cat})^{-1}\cdot\text{h}^{-1}$.

was approximately 90%. For the Ni/bentonite-20 catalyst, the selectivity of aniline and the conversion of nitrobenzene remained almost constant during the whole reaction process, which indicated that the Ni/bentonite-20 was a stable catalyst for the nitrobenzene catalytic hydrogenation to aniline, producing an aniline selectivity of approximately 95.0% and a nitrobenzene conversion of approximately 98.0% after 10 h.

4. Conclusions

Ni/bentonite catalysts were prepared with different nickel contents and were used for the hydrogenation of nitrobenzene to synthesize aniline. Compared to other Ni/bentonite catalysts, Ni/bentonite-20 exhibited better catalytic properties in the hydrogenation process, producing 95.7% conversion of nitrobenzene and 98.8% selectivity of aniline. Both the small crystallite size of NiO and the high dispersion of NiO contributed to the conversion of nitrobenzene and selectivity of aniline. The catalytic stability of the Ni/bentonite-20 catalyst was very high when the LHSV was $4.8\text{ ml}\cdot(\text{g cat})^{-1}\cdot\text{h}^{-1}$.

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