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Promotion of Ni/SBA-15 catalyst for hydrogenation of naphthalene by pretreatment with ammonia/water vapour

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ABSTRACT

The activities of nickel supported on SBA-15 catalysts, which were prepared by pretreatment with ammonia/water vapour, were investigated by hydrogenation of naphthalene. Comparing with the un-pretreated catalysts, the pretreated catalysts exhibited significant activity, and naphthalene conversion was improved approximately 100% over the un-pretreated catalysts. The formation of NH_4NO_3 during pretreatment, which helped to reduce NO_2/O_2 generation thus enhancing the dispersion of NiO, was considered to be the main reason for the increased Ni^0 dispersion and the enhanced activity of the catalyst pretreated with ammonia/water vapour.

1. Introduction

Supported nickel catalysts have been widely studied because of their wide application in various industrially important chemical processes such as (de)hydrogenation, methanation, reforming, hydrocracking and so on [1,2]. To obtain supported nickel catalyst with high dispersion by impregnation method, several approaches and techniques such as using aqueous chelated metal complexes [3], organic nickel precursor [4], directly reduced with hydrogen without calcination in air [5] etc. have been reported.

It is interesting that, with a so-called VIH (ammonia/water vapour-induced internal hydrolysis) method, a relatively large amount of active components such as zirconia, alumina can be coated on the pore walls of SBA-15 without significant pore blocking, and the properties of the catalyst such as acidity can be enhanced greatly [6,7]. The reason can be ascribed to the formation of metal hydroxide due to the induced internal hydrolysis by ammonia/water vapour. Since the process to prepare supported nickel catalyst is similar to coat zirconia or alumina on SBA-15 support, the VIH method may have the same promotion on the supported nickel catalyst. However, this effect of the pretreatment with ammonia/water vapour on the catalytic performance of supported nickel catalyst is not reported according to our knowledge. At the same time, Jong et al. recently found that the decomposition products (NO_2, N_2O, O_2 and H_2O), especially NO_2 and O_2 of nickel nitrate supported on SBA-15 during air calcination had a great influence on the dispersion of NiO [8–10]. Low concentrations of NO_2 and O_2 formed during the thermal decomposition of nitrate prefers to form high dispersion of NiO, and the high dispersion of NiO can be achieved by the thermal decomposition in the presence of NO [9] or H_2 [10]. Therefore, the supported nickel catalyst with high nickel dispersion seems to be obtained by a suitable treating method on supported nickel nitrate samples to diminish the amount of NO_2 and O_2 formed during air calcination. Similarly to the case of zirconia or alumina supported on SBA-15 [6,7], the dispersion of supported nickel species should be altered by the pretreatment with ammonia/water vapour, and it may be greatly affected by the decomposition products from the supported nickel nitrate during air calcination, and also the catalytic properties of the supported nickel catalyst should be adjusted. Nevertheless, how to influence the decomposition products of supported nickel nitrate during air calcination and the catalytic properties of the supported nickel catalyst by this pretreatment are unclear.

Hydrogenation of naphthalene is normally used for catalytic test, because it is not only a useful model reaction for the activity evaluation of metal catalysts, but also is of commercial importance in the upgrading of coal liquids and diesel fuels [11]. Herein we report a pretreatment method with ammonia/water vapour to promote the activity of the nickel supported on SBA-15 catalyst by hydrogenation of naphthalene. The mechanism of the catalytic activity promoted by this pretreatment is also discussed.

2. Experimental

2.1. Catalyst preparation

The required amount of nickel nitrate supported on SBA-15 was prepared by impregnating SBA-15 (1.0 g, supplied by Shanghai Novel

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Chemical Technology Co., Ltd) with an aqueous solution containing nickel nitrate ($Ni(NO_3)_2.6H_2O$, 0.3 M) under stirring at 60 °C until dryness, and drying at 100 °C overnight. The dried sample were pretreated by ammonia/water vapour with the method mentioned in references [6,7]. In a typical procedure, 20 ml 14% NH_3 solution was added in a Teflon lined autoclave of 100 ml capacity, and 1.0 g of the precursor-loaded SBA-15 was charged into an open glass vial and kept inside the autoclave without contact with the ammonia/water solution. The tightly closed autoclave was then treated at 70 °C for 1.0 h. After treatment the material was dried at room temperature for 6 h and then at 100 °C overnight. The dried material was finally calcined at 550 °C for 4.0 h under air to obtain NiO/SBA-15 sample. The NiO/SBA-15 sample was then reduced at 550 °C in H_2 flow of 30 ml min^{-1} for 4 h and passivated in a nitrogen-diluted oxygen (1.0 vol.% O_2) gas stream at room temperature for 3 h to obtain Ni/SBA-15 catalyst. The same nickel-loaded catalysts calcined at 550 °C without ammonia/water treatment were also prepared as comparison. The catalysts were named based on the amount of nickel loading and prepared method and expressed as Ni/SBA-15(XT) or Ni/SBA-15 (XU), in which X was nickel loading (wt%), T denoted to the catalyst prepared by ammonia/water vapour pretreatment and U denoted the catalyst prepared without ammonia/water vapour treatment. The nickel loadings of different catalysts were determined by flame atomic absorption spectroscopy (TAS-990F, Beijing Purkinje General Instrument Co., Ltd.).

2.2. Catalyst characterization

XRD data were collected from a Shimadzu XD-3A diffractometer with Cu Kα-radiation (λ = 0.15418 nm) at 40 kV and 40 mA. H_2-TPR and H_2-TPD experiments were carried out in a Quantachrome equipment (ChemBET 3000). For each H_2-TPR measurement, NiO/SBA-15 sample (50 mg) was placed in a quartz U-tube reactor and heated from room temperature to 900 °C at a rate of 10 °C min^{-1} in a 10% H_2–Ar with 40 ml min^{-1}. H_2 consumption was detected by a thermal conductive detector. Before H_2-TPD measurement, the Ni/SBA-15 catalyst (50 mg) was heated to 550 °C in a flow of 10% H_2–Ar at a rate of 20 °C min^{-1}, and kept at this temperature for 0.5 h. After cooling to 40 °C, the catalyst was kept at this temperature for 0.5 h. Then, H_2–Ar flow was switched to pure Ar for a period of 0.5 h at 40 °C. Finally, the catalyst was heated from 40 °C to 500 °C at a rate of 10 °C min^{-1} with Ar flow at 40 ml min^{-1}, and H_2-TPD curve was recorded. The area under the TPD curve was used for the calculation of volume of H_2 chemisorbed. The TPD area was calibrated by running pure H_2 pulse-titration experiment on a blank sample. The Ni surface area (S, m^2/g-Ni.), dispersion of metallic Ni (D, %) and the average particle size of metallic Ni (d, nm) were calculated from the volume of H_2 chemisorbed using the reported method [12]. FT-IR measurements were carried out on a PE-Spectrum One IR spectrometer at ambient temperature. Samples for the FT-IR measurement were prepared by mixing the sample with KBr and the mixture was pressed into a pellet. Mass spectra (MS) of the decomposition gaseous products of nickel nitrate supported on SBA-15 during calcination with air flow were recorded with a mass spectrometer (Hiden QIC-20). Typically, about 50 mg samples were used, and the heating rate was 5 °C min^{-1}.

2.3. Catalytic hydrogenation of naphthalene

Hydrogenation of naphthalene was performed in a 60 mL stainless steel autoclave (Ordino CS340, Premex) equipped with a heating system and a magnetic-coupled paddle stirrer. In a typical run, 10 g of the solution of naphthalene in an n-dodecane (5–20 wt%) and 0.12 g of Ni/SBA-15 catalyst were loaded into the reactor. The reaction conditions were 300 °C and 5.0 MPa H_2. Each catalytic test was performed for 2 h. The reaction products were analyzed by gas chromatograph (GC-7890II, TechCom) equipped with an OV-1 column (*30 ×0.25 ×0.33* μm) and a flame ionization detector.

3. Results and discussion

3.1. Catalyst characterization

Fig. 1A shows the small-angle XRD patterns of the different Ni/SBA-15 catalysts. Three well resolved diffraction lines being indexed as the (100), (110) and (200) lattices of a unit cell with a hexagonal (*P6mm*) symmetry could be observed in the patterns. It demonstrates that the impregnation, drying, calcination and reduction steps during the preparation of the catalyst have no significant effect on the long-range order of the mesopores of support.

Fig. 1B, C shows the XRD patterns of the NiO/SBA-15 and Ni/SBA-15 catalysts with and without pretreatment. Comparing with the unpretreated catalysts, the peak intensities of nickel oxide (2θ = 37.3°, 43.3° and 62.9°, Fig. 1B) and nickel metal (2θ = 44.4°, 52.0°, Fig. 1C) decreased, and the widths of the peak at half height increased

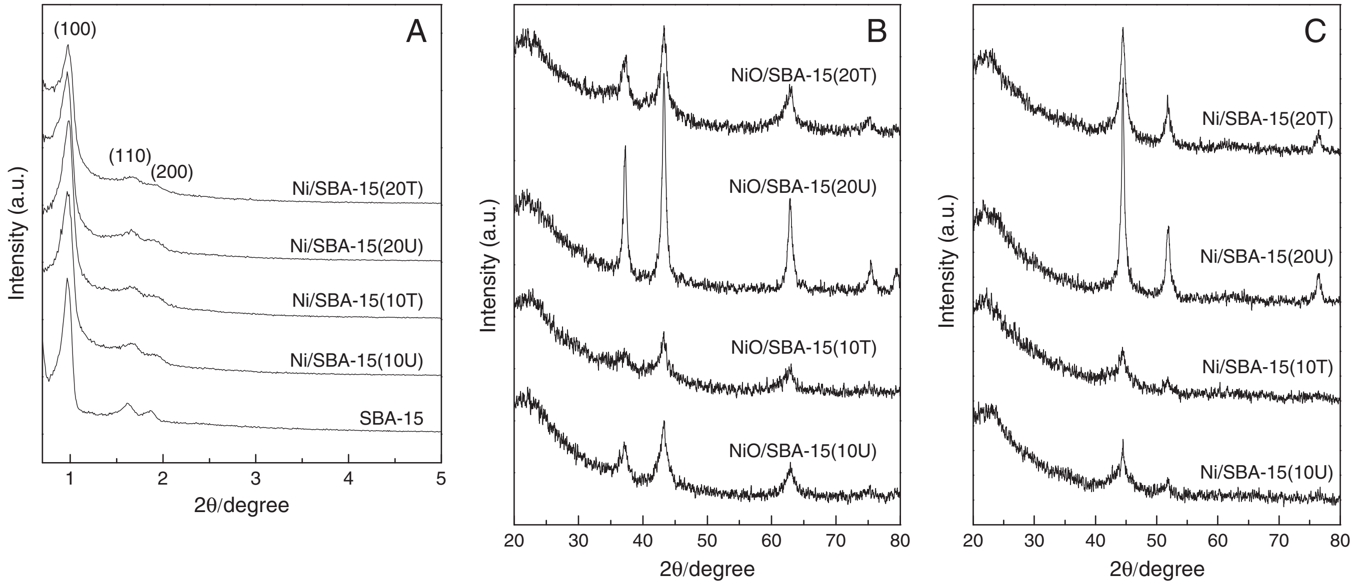

Fig. 1. XRD patterns of (A) different Ni/SBA-15 catalysts (small angel XRD patterns) (B) NiO/SBA-15 samples and (C) Ni/SBA-15 catalysts prepared with or without pretreatment.

obviously for the pretreated catalysts, especially for NiO/SBA-15 (20T) and Ni/SBA-15 (20T) catalysts. This indicates that nickel oxide and nickel metal particle sizes of the un-pretreated catalysts are larger than that of the pretreated catalysts, suggesting that the dispersion of nickel oxide and nickel metal can be enhanced by the pretreatment with ammonia/water vapour.

In order to further explore the effect of ammonia/water vapour pretreatment on the dispersion of the nickel species in NiO/SBA-15 samples, H_2-TPR of different NiO/SBA-15 samples were measured as shown in Fig. 2. It could be observed that the nickel species were reduced at low temperature and high temperature separately. The nickel species reduced at low temperature can be attributed to the NiO un-interacted with support, and the nickel species reduced at high temperature can be attributed to the NiO interacted strongly with support to form a few surface layers of silicate-type compounds [13]. It could be obviously observed that the ratios of peak area at high temperature to low temperature in the pretreated NiO/SBA-15 samples, especially for NiO/SBA-15 (20T) sample, were greater than the values of the un-pretreated NiO/SBA-15 samples. This demonstrates that the amount of the nickel species interacted strongly with support in NiO/SBA-15 sample can be improved by ammonia/water vapour pretreatment. Generally the strong interaction between the nickel species and support favors to enhance NiO dispersion. Therefore the dispersion of NiO in NiO/SBA-15 sample is promoted by ammonia/water vapour pretreatment, and it is accordance to the result of XRD mentioned above.

Fig. 3 shows H_2-TPD of different Ni/SBA-15 catalysts. Comparing with the catalyst without the pretreatment (Fig. 3a, c), the area under the TPD curve of the pretreated catalyst increased obviously (Fig. 3b, d). It indicates that the pretreated catalyst consists of more exposed surface Ni atoms. Based on the peak area of the H_2-TPD profiles and assuming the adsorption of one H atom per metal atom [12], the H_2 chemisorption uptake, surface area, dispersion and particle size were estimated as shown in Table 1. It clearly shows that the nickel metal particle sizes decrease (which is accordance with the results calculated by the Scherrer equation from XRD data) and the surface area and dispersion increase for the pretreated catalysts, suggesting the dispersion of the catalyst being promoted by the pretreatment of ammonia/water vapour.

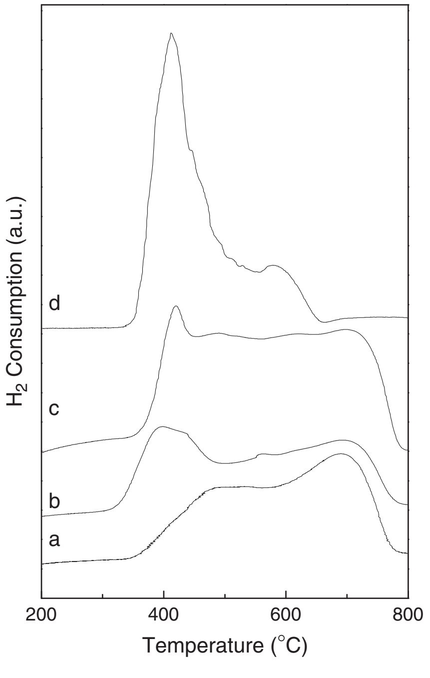

Fig. 2. H_2-TPR of different NiO/SBA-15 samples: (a) NiO/SBA-15 (10T); (b) NiO/SBA-15 (10U); (c) NiO/SBA-15 (20T); (d) NiO/SBA-15 (20U).

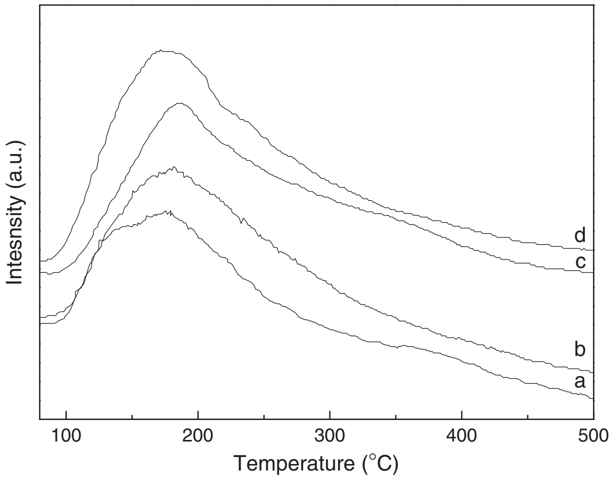

Fig. 3. H_2-TPD of the different catalysts: (a) Ni/SBA-15 (10U); (b) Ni/SBA-15 (10T); (c) Ni/SBA-15 (20U); (d) Ni/SBA-15 (20T).

3.2. Improvement of ammonia/water vapour pretreatment on the hydrogenation activity

In order to explore the effects of the pretreatment by ammonia/water vapour on the activity of the Ni/SBA-15 catalysts, the hydrogenation reactions of naphthalene were carried out on the Ni/SBA-15 catalysts. Table 2 shows the conversions of naphthalene and selectivities of main products. The main products of the hydrogenation were tetrain and decalin, and no hydrocracking product was observed. It could be observed from Table 2 that the pretreated Ni/SBA-15 catalysts had much higher catalytic activities for the naphthalene conversion compared with those of un-pretreated catalysts. For example, the naphthalene conversion increased from 72.0% of Ni/SBA-15 (10U) to 100.0% of Ni/SBA-15 (10T) when naphthalene content in feed was 5.0 wt%. In the mean time the selectivity of decalin also increased from 28.7% to 81.9%. Since decalin is produced through deep hydrogenating of tetralin, the increased selectivity of decalin is also correlated with the hydrogenating activity of the catalyst. So the total hydrogenating activity of the catalyst cannot be evaluated only using the conversion of naphthalene, and the selectivity of decalin should be also considered. When naphthalene content in feed increased from 5.0 wt% to 10.0 wt%, although naphthalene conversions over the catalysts with and without pretreatment obviously decreased, but selectivities of decalin on the two catalysts were almost zero (0% for Ni/SBA-15 (10U) and 2.6% for Ni/SBA-15 (10T)). In this case the hydrogenating activity of the catalyst could be accurately evaluated only using naphthalene conversion. Again, Table 2 clearly shows that when naphthalene content in feed is 20 wt%, the selectivity of decalin on the catalyst with or without pretreatment is almost zero, although the amounts of nickel-loaded in the catalyst increase to 20 wt%. The naphthalene conversion was 45.7% for the Ni/SBA-15 (20T) catalyst and it was improved and approximated at a 100% compared with the un-pretreated catalyst Ni/SBA-15 (20U) of 23.1%, indicating that the catalytic activity of Ni/SBA-15 catalyst could be strongly enhanced by ammonia/water vapour pretreatment.

3.3. Mechanism of the promotion of catalytic activity

In the case of zirconia or alumina, ammonia/water vapour is thought as hydrolyzing agent to induce the internal hydrolysis process, which is expected to precipitate zirconium hydroxide or aluminum hydroxide on the walls of SBA-15 in a highly dispersed manner and the calcination of the resulted composite material may lead to zirconia-coated or alumina-coated SBA-15 [6,7]. The first possible reason for the promotion of

Table 1
Hydrogen chemisorption data of different catalysts determined by H_2-TPD.

Catalyst	Nickel loading (wt.%)	H_2 chemisorption uptake (mL/g-Ni)	Surface area (m^2/g-Ni)	Dispersion (D, %)	Particle size (d, nm)	
					d[a]	d[b]
Ni/SBA-15 (10U)	9.91	45.6	79.57	11.9	8.5	8.7
Ni/SBA-15 (10T)	10.12	71.3	124.4	18.7	5.4	5.6
Ni/SBA-15 (20U)	20.10	36.8	64.0	9.6	10.5	12.9
Ni/SBA-15 (20T)	20.14	45.6	79.5	11.9	8.5	9.5

[a] Particle size was calculated from the volume of H_2 chemisorbed.

[b] Particle size was estimated using Scherrer's equation, $d = 0.89\lambda/(B\cos\theta_B)$, where λ is the wavelength (0.15418 nm), B the full width at half maximum (FWHM) of the peak, and θ_B the Bragg angle ($2\theta_B = 44.4°$).

Table 2
Catalytic hydrogenation activities of various catalysts.

Catalyst	Naphthalene content (wt.%)	Naphthalene conversion (%)	Selectivity (%)	
			Tetralin	Decalin
Ni/SBA-15 (10U)	5.0	72.0	71.3	28.7
	10.0	35.7	100.0	0.0
Ni/SBA-15 (10T)	5.0	100.0	18.1	81.9
	10.0	76.9	97.4	2.6
Ni/SBA-15 (20U)	20.0	23.1	100.0	0.0
Ni/SBA-15 (20T)	20.0	45.7	99.7	0.3

Reaction conditions: 10 g of the solution of naphthalene in n-dodecane (5.0, 10.0 or 20.0 wt.%), 0.12 g catalyst, 300 °C, 5.0 MPa H_2, 2.0 h.
The experiments were repeated 3 times.

catalytic activity of Ni/SBA-15 catalyst is that the highly dispersed nickel hydroxide may be formed in the presence of ammonia/water vapour, similar to the case of zirconia or alumina supported on SBA-15. In this case the absorption bands of the nickel hydroxide should be observed in the FT-IR spectra of the samples before calcination at high temperature. Unfortunately, the absorption band of the typical nickel hydroxide at ~3650 cm^{-1} [14] was not observed in the FT-IR spectra as shown in Fig. 4. This indicates that very few even no nickel hydroxide is formed by the pretreatment of ammonia/water vapour. Therefore the formation of the highly dispersed nickel hydroxide may not be responsible for the promotion of catalytic activity of Ni/SBA-15 catalyst by the pretreatment. Comparing with the samples without pretreatment (Fig. 4a, c), the new absorption bands at 3160 cm^{-1}, 3030 cm^{-1} and 2770 cm^{-1}, which are ascribed to the absorption of NH_4^+ group [15], were observed in the pretreated samples (Fig. 4b, d). It indicates that an amount of NH_3 is converted into NH_4^+ after pretreatment by ammonia/water vapour. In addition, the absorption bands at 1766 cm^{-1} and 832 cm^{-1}(amplified in Fig. 4), which are ascribed to the absorption of NH_4NO_3 [16], were also observed in the pretreated samples (Fig. 4b, d). This suggests that an amount of NH_4NO_3 is formed in the samples after pretreatment by ammonia/water vapour. In fact, the decomposition products (NO_2, N_2O, O_2 and H_2O) of nickel nitrate supported on SBA-15 during air calcination, in particular NO_2 and O_2, are found to play a key role to influence the dispersion of NiO [8–10]. And high dispersion of NiO is obtained when low concentrations of NO_2 and O_2 are formed during the thermal nitrate decomposition [9,10]. The thermal decomposition of NH_4NO_3 follows the equations [17,18] as follows:

$$NH_4NO_3 \rightarrow NH_3 + HNO_3 \tag{1}$$

$$HNO_3 + HA \rightarrow H_2ONO_2^+ \rightarrow NO_2^+ + H_2O \tag{2}$$

Where HA = NH_4^+, H_3O^+, HNO_3

$$NO_2^+ + NH_3 \rightarrow N_2O + H_3O^+ \tag{3}$$

$$\text{net reaction}: NH_4NO_3 \rightarrow N_2O + 2H_2O \tag{4}$$

Apparently, from the net reaction of NH_4NO_3 thermal decomposition (Eq. (4)), neither NO_2 nor O_2 appears in the decomposition products of NH_4NO_3. In other words, the concentrations of NO_2 and O_2 in the decomposition products of nickel nitrate supported on SBA-15 can be diminished with the decomposition of NH_4NO_3 instead of nickel nitrate. According to the MS analysis results (shown in Fig. 5), little NO_2 (Mass fraction 46) formed during decomposition of NiO/

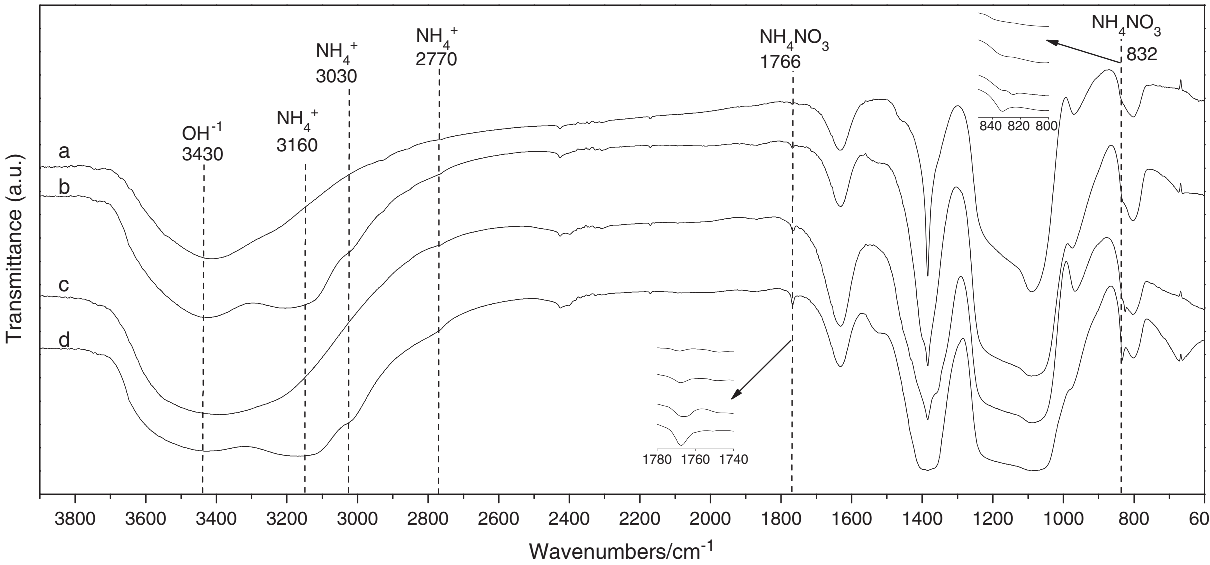

Fig. 4. FT-IR spectra of the NiO/SBA-15 samples without calcinations: (a) NiO/SBA-15 (10U); (b) NiO/SBA-15 (10T); (c) NiO/SBA-15 (20U); (d) NiO/SBA-15 (20T).

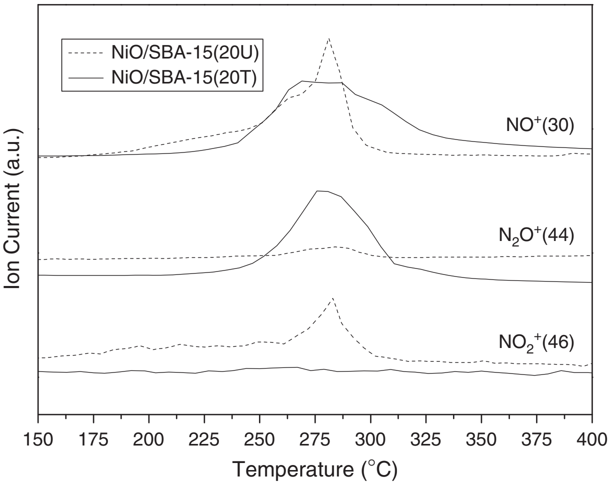

Fig. 5. MS results of the off gas during calcination in air flow of NiO/SBA-15 (20U) and NiO/SBA-15 (10T) samples.

SBA-15 (20T) sample, but significant amounts of NO_2 formed on NiO/SBA-15 (20U) sample. In the mean time, large amounts of N_2O (Mass fraction 44) formed on NiO/SBA-15 (20T) sample but little on NiO/SBA-15 (20U) sample. It is confirmed that the concentration of NO_2 decreases but N_2O increases in the thermal decomposition products of nickel nitrate supported on SBA-15 with the pretreatment of ammonia/water vapour. Then the dispersion of NiO is enhanced after calcination, which has been confirmed by the XRD and H_2-TPR characterization of NiO/SBA-15 samples mentioned above. As a result the Ni/SBA-15 catalyst with high dispersion of Ni^0 is obtained after the reduction of the high dispersion NiO/SBA-15 sample and gives higher activity for hydrogenation of naphthalene.

4. Conclusion

The effects of pretreatment by ammonia/water vapour on the properties and catalytic hydrogenation activity of Ni/SBA-15 were studied. The dispersion of Ni^0 and hydrogenating activity of Ni/SBA-15 catalyst were improved by the pretreatment. FT-IR showed that an amount of NH_4NO_3 formed in the nickel nitrate supported on the SBA-15 sample pretreated by ammonia/water vapour. During calcination, the concentrations of NO_2 and O_2 formed in the thermal decomposition products could be markedly lowered due to the decomposition of NH_4NO_3 instead of nickel nitrate, resulting in the promotion of the NiO dispersion over NiO/SBA-15 sample. Therefore Ni^0 dispersion of Ni/SBA-15 catalyst was improved after the reduction of the NiO/SBA-15 sample, and the catalytic activity of Ni/SBA-15 for hydrogenation of naphthalene was enhanced greatly by the ammonia/water vapour pretreatment.

Acknowledgements

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