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Article

Effect of calcination temperature of Ni/SiO₂-ZrO₂ catalyst on its hydrodeoxygenation of guaiacol

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ABSTRACT

SiO₂-ZrO₂ composites were synthesized by chemical precipitation and used to prepare a series of bifunctional Ni/SiO₂-ZrO₂ catalysts by impregnation. The effect of calcination temperature on the catalyst structure and its catalysis of the hydrodeoxygenation of guaiacol was investigated. Guaiacol was converted to cyclohexane by a synergism between the metal center and solid acid support. The catalyst calcined at 500 °C gave a maximum 100% guaiacol conversion and 96.8% selectivity for cyclohexane. The catalyst samples were characterized by N₂ adsorption, H₂ chemisorption, X-ray diffraction, H₂ temperature-programmed reduction, NH₃ temperature-programmed desorption, and Raman spectroscopy. The synthesized SiO₂-ZrO₂ was an amorphous oxide. The Ni/SiO₂-ZrO₂ catalyst calcined at 500 °C has more acidity, smaller NiO particles, and larger BET surface area and pore volume, which gave it the best catalytic performance.

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1. Introduction

Lignin, which is 15%–30% by mass and has 40% of the energy in woody biomass, is an important renewable carbon source. Unlike cellulose and hemicellulose, it cannot be converted by hydrolysis and fermentation, and it is usually removed as residue. Recently, various methods were explored to use it to produce phenolics such as alkyl-substituted phenols, guaiacols, and syringols [1,2]. However, these phenolic compounds cannot be used as transportation fuels directly owing to their high oxygen content, poor chemical stability, and immiscibility with hydrocarbon fuels [3,4]. Consequently, hydrodeoxygenation (HDO) is needed to make these products suitable as substitutes for conventional fuels.

The HDO catalyst is usually composed of an active metal and

a solid acid. The metal is used as the active component for hydrogenation. The base metals of Ni, Mo, and Cu and noble metals of Pt, Pd, and Ru were investigated for the HDO of oxygenated compounds [5–7].

A solid acid is usually used as the support, and it is another key factor in the HDO activity of the catalyst [8,9]. γ -Al₂O₃ was extensively used as the support in the initial research of bio-oil HDO. However, severe carbon deposition was found on the Lewis acid sites [10]. Moreover, γ -Al₂O₃ is partially transformed into boehmite under hydrothermal conditions [11]. To overcome these flaws, many support materials such as SiO₂ [12], TiO₂ [10], ZrO₂ [10,13,14], and zeolites [15] were explored in recent years. It was reported that ZrO₂ gave CoMoS catalysts relatively high catalytic activity [10,12], and carbon deposition on the ZrO₂-supported catalyst was lower than that on Al₂O₃-

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supported catalysts [16].

Mixed oxides have also been explored as the support for the HDO catalyst [17,18]. Mixed oxides have some unique physical and chemical properties, and they do not have some of the disadvantages of single oxides such as deteriorated texture and unstable crystal phase [18]. For example, in our previous studies, it was found that the mixed oxide $\text{SiO}_2\text{-ZrO}_2$ when used as the support of Ni and NiCu catalysts gave excellent catalytic activity for the HDO reaction of guaiacol [19,20].

In this work, the effect of calcination temperature on the catalytic performance of Ni/ $\text{SiO}_2\text{-ZrO}_2$ catalysts was investigated. Guaiacol was chosen as the probe reactant for the HDO reaction because its structure is similar to the monomer of lignin with the C–O bonds of $\text{C}_{\text{AR}}\text{-OH}$, $\text{C}_{\text{AR}}\text{-OCH}_3$, and $\text{C}_{\text{ARO}}\text{-CH}_3$. The catalysts prepared using different calcination temperatures were characterized by N_2 adsorption, H_2 chemisorption, H_2 temperature-programmed reduction ($\text{H}_2\text{-TPR}$), NH_3 temperature-programmed desorption ($\text{NH}_3\text{-TPD}$), and Raman spectroscopy to elucidate the effect of the calcination temperature of the catalyst on its texture and catalytic performance for the guaiacol HDO reaction.

2. Experimental

2.1. Preparation of catalyst

Precipitates of Si(OH)_4 and Zr(OH)_4 , respectively, were prepared by chemical precipitation using $\text{Na}_2\text{SiO}_3\cdot 9\text{H}_2\text{O}$ and $\text{ZrOCl}_2\cdot 8\text{H}_2\text{O}$ as precursors. The two precipitates were mixed with a Si/Zr molar ratio of 3 and stirred, then aged for 12 h at 75 °C. The mixed oxide precipitate was dried overnight at 120 °C and calcined at 500 °C for 5 h, after which the chloride ions were removed completely by filtering and the mixed oxide was washed with distilled water. The composite oxide $\text{SiO}_2\text{-ZrO}_2$ was designated as SZ. The preparation method for SZ had been reported in the literature by Zhang et al. [20].

An appropriate amount of nickel nitrate was dissolved in a measured volume of distilled water for a measured amount of the support, followed by agitating and evaporating to dryness. The solid that remained was dried at 120 °C overnight and then calcined for 5 h at 400, 500, 600, and 700 °C. The Ni loading (mass fraction) was 10% for all catalysts. The catalysts were denoted as Ni/SZ-400, Ni/SZ-500, Ni/SZ-600, and Ni/SZ-700. A Ni/ ZrO_2 catalyst with 10% Ni loading was also prepared using the same method. All the catalysts were crushed and sieved to the 75–125 μm size and reduced at 500 °C in a flow of reducing gas (5% H_2 + 95% N_2) before use.

2.2. Characterization of catalyst

The BET specific surface area, average pore diameter, and pore volume of the catalysts were determined by N_2 isothermal (–196 °C) adsorption using a QUADRASORB SI analyzer equipped with a QuadraWin software system. The catalyst was treated at 150 °C for 12 h under vacuum before N_2 adsorption. The nickel active surface was determined by H_2 chemisorption (Quantachrome, ASIQUACIV200-2). The supports and catalysts

were characterized by X-ray diffraction (XRD, XPert Pro MPD with Cu $K\alpha$ ($\lambda = 0.154\text{ nm}$) radiation, Philip). Scanning electron microscopy (SEM) images were recorded on a HITACHI S-4800 instrument operated at 20 kV.

$\text{H}_2\text{-TPR}$ and $\text{NH}_3\text{-TPD}$ were carried out in a quartz tube reactor with a thermal conductivity detector (TCD). Hydrogen consumption from 250 to 700 °C was calculated by the external standard method using the $\text{H}_2\text{-TPR}$ of CuO as the standard. The amount of reduced NiO was calculated from the hydrogen consumption, and the reduction degree was obtained by the amount of reduced NiO divided by the Ni loading. A similar procedure was described in the literature [21]. Thermogravimetric (TG) analysis was carried out with an air flow rate of 30 mL/min on an analyzer utilizing 10–15 mg sample and a 10 °C/min temperature increase.

Fourier transform infrared spectroscopy (FTIR) of the Ni/SZ-500 was acquired on a Nicolet 6700 FTIR spectrometer equipped with a DTGS detector. The catalyst sample was activated in the IR cell by heating from room temperature to 200 °C under vacuum ($1 \times 10^{-4}\text{ Pa}$) and evacuated at this temperature for 1 h. Pyridine was introduced in the IR cell at room temperature. Desorption was carried out at 50 °C, and the catalyst was evacuated for 10 min prior to recording the IR spectra. Laser Raman spectroscopy was carried out on a LabRAM HR800 (ORIBAJY) equipment with a charged coupled device detector and a Leica DMLM microscope. The excitation source was a 532 nm laser beam.

2.3. Catalytic activity test

The HDO reaction of guaiacol was carried out in a 500 mL stainless autoclave equipped with an electromagnetic stirrer. For each run, 1.5 g catalyst, 10.0 g of guaiacol, and 100.0 g of solvent dodecane were loaded into the autoclave. After displacing air, the reactor was pressurized with H_2 to 5.0 MPa and sealed. The autoclave was heated to 300 °C while the reagents were vigorously stirred at 800 r/min. Each HDO reaction was repeated twice. The data were the average of the results from the two experiments.

The liquid products were identified by a GC-MS equipped with a DB-5 packed column. Quantitative analysis of the liquid products was performed by GC (Shimadzu GC 2010 with an FID detector and a DB-5 column). The vaporization temperature was 250 °C, and the oven temperature program was from 50 to 250 °C at the rate of 5 °C/min.

3. Results and discussion

3.1. Thermal decomposition of the hydroxides

The TG and DTA curves of Zr(OH)_4 , Si(OH)_4 , and mixed oxide $\text{Zr(OH)}_4\text{-Si(OH)}_4$ are given in Fig. 1. Nominally, the weight losses of Zr(OH)_4 and Si(OH)_4 would be 22.6% and 37.5% when the Zr(OH)_4 and Si(OH)_4 are completely converted to ZrO_2 and SiO_2 , respectively. However, the actual weight losses of Zr(OH)_4 and Si(OH)_4 were 8.9% and 11.0%, respectively. The weight loss of the mixed oxide $\text{Zr(OH)}_4\text{-Si(OH)}_4$ was only 6%. The rea-

Fig. 1. TG and DTA profiles for the different hydroxides.

son may be that some SiO_2 and H_2SiO_3 were formed by dehydration during the preparation of $\text{Si}(\text{OH})_4$. That is, the $\text{Si}(\text{OH})_4$ sample contained some SiO_2 and H_2SiO_3 , thereby resulting in the lower weight loss. The weight losses of $\text{Zr}(\text{OH})_4$ and the mixed oxide $\text{Zr}(\text{OH})_4\text{-Si}(\text{OH})_4$ were less than their nominal values for probably the same reason.

The decomposition of $\text{Zr}(\text{OH})_4$ occurred at less than 400 °C, and its TG curve was relatively flat. A steep band from 190 to 260 °C was observed in the TG curve of $\text{Si}(\text{OH})_4$, which originated from the formation of H_2SiO_3 by the fast dehydration of $\text{Si}(\text{OH})_4$. H_2SiO_3 was converted into SiO_2 by further dehydration at higher temperatures.

A sharp endothermic peak was observed at 440 °C in the DTA profile of $\text{Zr}(\text{OH})_4$, but there was no weight loss in the corresponding TG curve. The reason is that the endothermic peak originated from the crystallization heat during the phase transformation from $t\text{-ZrO}_2$ to $m\text{-ZrO}_2$ [22]. However, the endothermic peak was not observed in the corresponding DTA profiles of the mixed oxide $\text{Zr}(\text{OH})_4\text{-Si}(\text{OH})_4$. The cause may be that the phase transformation of ZrO_2 was inhibited by the addition of SiO_2 . In addition, it was found that the heat of absorption of the mixed oxide $\text{Zr}(\text{OH})_4\text{-Si}(\text{OH})_4$ was more than that of the single component hydroxide when the calcination temperature exceeded 450 °C. This was because the formation of the Zr-O-Si bond was accompanied by the absorption of heat. In particular, it can be noticed that the absorbed heat further increased when the temperature was higher than 660 °C, suggesting that a higher calcination temperature favored the solid phase reaction between $\text{Si}(\text{OH})_4$ and $\text{Zr}(\text{OH})_4$ forming the Zr-O-Si bond.

3.2. XRD of the supports and catalysts

The XRD patterns of the different supports and catalysts are

Fig. 2. XRD patterns of the different samples.

shown in Fig. 2. A very broad weak feature between 26° and 37° was observed, suggesting that $\text{Zr}(\text{OH})_4$ is an amorphous material. Two coexisting structurally stable ZrO_2 phases, the monoclinic and tetragonal phases, were found in the XRD pattern of ZrO_2 obtained from the calcination of $\text{Zr}(\text{OH})_4$ at 500 °C. The 2θ peaks at 24.1°, 28.2°, 31.4°, and 34.1° were assigned to $m\text{-ZrO}_2$, and the peaks at 35.2°, 50.2°, and 60.3° were assigned to $t\text{-ZrO}_2$. The SZ complex oxide was also an amorphous material, and it showed no distinct XRD peaks apart from a very broad weak feature between 18° and 37°. It was suggested that the formation of ZrO_2 crystallite is inhibited in the calcination of mixed $\text{Zr}(\text{OH})_4$ and $\text{Si}(\text{OH})_4$ [23].

The Ni/SZ catalysts also exhibited a very broad weak feature between 18° and 37° like the SZ complex oxide. However, the shapes of the peaks varied with calcination temperature. The position of the highest peak in this broad weak feature was $2\theta = 23^\circ$ when the calcination temperature was 400 °C, which was shifted to $2\theta = 34^\circ$ when the calcination temperature was increased to 700 °C. This shift suggested that the structure of the catalyst had changed.

The characteristic peaks of NiO were seen clearly in the XRD patterns ($2\theta = 37.3^\circ$, 43.3° , and 62.9°). The crystallite size of NiO calculated by Scherrer equation is listed in Table 1. The crystallite size of NiO increased gradually with the increasing of the calcination temperature. The crystallite size of NiO supported on SZ was smaller than that of NiO supported on ZrO_2 . This suggested that the excellent textural structure of the SZ composite promoted the dispersion of NiO.

Table 1
NiO crystal size of the different catalysts.

Catalyst	FWHM (rad)	NiO crystal size (nm)
Ni/ ZrO_2	0.167	50.7
Ni/SZ-400	0.368	23.2
Ni/SZ-500	0.292	29.3
Ni/SZ-600	0.268	31.9
Ni/SZ-700	0.248	34.5

Table 2

Textural and structural properties of the Ni-based catalysts.

Catalyst	S_{BET} (m^2/g)	V_{total} (m^3/g)	D_p (nm)	N_{Ni} ^a (mmol/g)
Ni/ZrO ₂	6.2	0.06	41.4	0.01
Ni/SZ-400	212.7	0.79	14.9	0.17
Ni/SZ-500	228.8	0.69	12.1	0.16
Ni/SZ-600	191.8	0.62	14.7	0.13
Ni/SZ-700	179.0	0.64	16.2	0.07

^a The number of surface Ni atoms.

3.3. Texture and morphology of the catalysts

The results of the textural and structural analysis for the catalysts are exhibited in Table 2 and Fig. 3. The BET surface area, number of surface Ni atoms, and pore volume for Ni/ZrO₂ calcined at 500 °C were very small. Its pores were mainly distributed between 2 and 30 nm, and the average pore diameter was 41.4 nm. An increase in the BET surface area and total pore volume was observed for the SZ supported catalysts, indicating that the addition of SiO₂ led to changes in the physical properties. The pores of the catalysts were mainly distributed at 10 nm.

The surface area of the catalysts was affected by the calcination temperature from 400 to 700 °C. For the Ni/SZ-400 catalyst, the BET surface area was 212.7 m²/g. There was a slight increase in the BET surface area of Ni/SZ-500, which was attributed to the removal of the residues and decomposition products of Ni(NO₃)₂ from the inner surfaces of the blocked pores at the higher temperature. However, the BET surface area of the catalysts then decreased gradually with further increase in calcination temperature (600 and 700 °C). The reason may be pore structure destruction by calcination.

The SEM images of the Ni/SZ catalysts are presented in Fig. 4. For the Ni/ZrO₂ catalyst, many particles with size of approximately 70 nm were stacked compactly on the surface of catalyst due to the poor structural properties of the support. However, the surface morphology of the Ni/SZ-500 catalyst was rough, and the NiO particles were well dispersed on the SZ composite oxide. For the Ni/SZ-600 catalyst, the rough surface morphology was smoothed by the sintering at the higher temperature. Moreover, a small amount of NiO crystallites were

Fig. 3. Pore size distribution of different catalysts. **Fig. 4.** SEM images of the Ni-based catalysts. (a) Ni/ZrO₂; (b) Ni/SZ-500; (c) Ni/SZ-600; (d) Ni/SZ-700.

observed. When the calcination temperature was further increased to 700 °C, many octahedral NiO crystallites were clearly observed on the surface of catalyst. These results were in good agreement with the number of surface Ni atoms on the catalyst, which decreased with increased calcination temperature, indicating that calcination temperature had obvious effects on the structure and surface morphology of the catalysts.

3.4. H₂-TPR of the catalysts

H₂-TPR experiments for the Ni-based catalysts calcined at different temperatures were carried out. The results are presented in Fig. 5 and Table 3. The profile of the Ni/ZrO₂ catalyst showed a two stage reduction behavior. A reduction peak at 405 °C was observed, which was attributed to the reduction of bulk NiO. Another reduction peak at 480 °C was produced due to mass transport limitation caused by the large size of NiO. In addition, an interaction between NiO and ZrO₂ can be another reason for the appearance of the peak at 480 °C. Only one reduction peak at 398 °C was observed from Ni/SZ-400. The amount of H₂ consumption by the catalyst based on the peak area was 1.30 mmol/g. Thus, the reduction degree of NiO calculated from the amount of H₂ consumption divided by the

Fig. 5. H₂-TPR profiles of the Ni-based catalysts.

Table 3Results of H₂-TPR of the various Ni-based catalysts.

Catalyst	Peak position (°C)		H ₂ consumption (mmol/g)	NiO reduction degree (%)
	<i>t</i> ₁	<i>t</i> ₂		
Ni/ZrO ₂	405	480	1.36	79.3
Ni/SZ-400	398		1.30	75.8
Ni/SZ-500	405	480	1.26	73.5
Ni/SZ-600	427	560	1.16	67.7
Ni/SZ-700	490	655	1.04	60.7

catalyst was 75.8%. The excellent reducibility of Ni/SZ-400 was due to two reasons: (1) the NiO particles were small because NiO was well dispersed on the SZ complex oxide, which has excellent textural and structural properties; (2) the interaction between NiO and the support is negligible at the calcination temperature of 400 °C.

For the Ni/SZ-500 catalyst, two reduction peaks were observed. The peak at 405 °C was attributed to the reduction of surface NiO, and the other peak at the higher temperature was attributed to the reduction of NiO that interacted with the support. The interaction between NiO and the support is essentially the coordination of ZrO₂ in the mixed oxide (SiO₂-ZrO₂) with the lone pair electrons of NiO because ZrO₂ is a P-type semiconductor. The amount of H₂ consumption was 1.26 mmol/g, and its reduction degree was 73.8%. A shift of the NiO reduction peak towards higher temperature was found with the Ni/SZ-600 catalyst. The temperatures of the two reduction peaks were shifted to higher temperatures compared with Ni/SZ-500, suggesting that there was a stronger interaction between NiO and the support. For the Ni/SZ-700 catalyst, the first reduction peak was further shifted to an even higher temperature (490 °C), and the second reduction peak was shifted to 655 °C because of the stronger interaction between NiO and support, which could also cause the inefficient H₂ reduction. H₂ consumption decreased to 1.04 mmol/g, and the reduction degree of NiO was reduced to 60.7% for Ni/SZ-700. In addition, the reduction peak broadened gradually with the increasing of temperature due to mass transport limitation, which was additional evidence for the aggregation of NiO with increased calcination temperature.

3.5. Characterization of catalyst acidity

The NH₃-TPD profiles of different catalysts are presented in Fig. 6. The number of acidic surface sites on the catalysts can be deduced from the NH₃ desorption peak area. From Fig. 6, it can be seen that the peak for NH₃ desorption of Ni/ZrO₂ was very weak, implying that the number of acidic sites was small. For the SZ complex oxide supported catalysts, clear peaks at about 220 °C were observed, which were attributed to the adsorption of NH₃ on acidic sites. The enhanced acidity of the Ni/SZ catalysts relative to that of Ni/ZrO₂ was due to the Zr–O–Si bonds formed in the mixed oxide.

Generally, the number of acidic sites on catalyst decreases with increased calcination temperature [24]. However, compared with Ni/SZ-400, the Ni/SZ-500 catalyst exhibited an obvious increase in the acidic site number. The reason may be that the higher calcination temperature led to the removal of

Fig. 6. NH₃-TPD profiles of the different catalysts.

the residues and decomposition products of Ni(NO₃)₂, which covered the acidic surface sites. When the calcination temperature was higher than 500 °C, the number of acidic sites decreased with increasing temperature, suggesting that the SZ complex oxide was destroyed, resulting in the disappearance of acidic sites. This conclusion agreed with the XRD analysis and textural analysis of the catalyst. It was reported that the Si–O–Zr bond is converted into a Si–Zr bond at a high calcination temperature, resulting in the loss of acidic sites [23].

The Lewis acid sites (1450 cm⁻¹) and Brønsted acid sites (1540 cm⁻¹) for the Ni/SZ-500 catalyst are clearly shown in Fig. 7. It is well known that pure SiO₂ has no Lewis or Brønsted sites, and ZrO₂ has Lewis acid sites. Hence, the appearance of the Brønsted acid centers can be ascribed to the Zr–O–Si linkages formed in the mixed oxide [18].

3.6. Raman characterization

The Raman spectra of the Ni/SZ catalysts calcined at different temperatures and the Ni/ZrO₂ catalyst are shown in Fig. 8. The Ni/ZrO₂ catalyst calcined at 500 °C showed strong Raman peaks. The characteristic peaks at 175, 304, 338, 375, 475, and 634 cm⁻¹ were assigned to monoclinic ZrO₂ [25]. Two weak

Fig. 7. Infrared spectra of pyridine adsorbed on 10%Ni/SZ-500 after evacuation at 50 °C.

Fig. 8. Raman spectra of different catalysts.

peaks observed at 531 and 745 cm^{-1} were assigned to the Ni–O stretching mode [26]. Generally, it is hard to observe the characteristic peaks of amorphous silica in the Raman spectra. With the SZ complex oxide supported catalysts, the corresponding Raman peaks for ZrO_2 were also not observed in the Raman spectra of the Ni/SZ-500 catalyst. The reason is that the formation of ZrO_2 crystallites was inhibited by the addition of SiO_2 during the calcination. However, the weak peaks at 175, 304, 338, 375, 475, and 634 cm^{-1} assigned to $m\text{-ZrO}_2$ were observed in the Raman spectra of Ni/SZ-700. The reason may be that the structure of the SZ complex oxide was destroyed, which resulted in the formation of ZrO_2 crystallites when the calcination temperature was increased to 700 $^{\circ}\text{C}$. In addition, peaks at 534, 555, 755, and 1060 cm^{-1} assigned to the Ni–O stretching mode were also observed in the Raman spectra of Ni/SZ-700. The reason is that the size of the NiO crystallites increased with increased calcination temperature due to aggregation. These conclusions are in agreement with the XRD analysis.

3.7. Activity studies for guaiacol HDO

As shown in Table 4, the conversion of guaiacol was 43.8% over the Ni/ZrO₂ catalyst calcined at 500 $^{\circ}\text{C}$, suggesting a low catalytic activity. There are two possible reasons for this. First, the smaller number of surface Ni atoms on the catalyst and the poor texture of the Ni/ZrO₂ catalyst are unfavorable for good catalytic activity. Second, the acidity of the Ni/ZrO₂ catalyst was

very weak, which was shown by the NH_3 -TPD experiments, and this is also unfavorable for the HDO reaction of guaiacol.

The catalytic performance of the Ni/SZ catalysts obtained using different calcination temperatures was compared. A maximum guaiacol conversion of 100% was observed over the Ni/SZ-500 catalyst. With the use of a higher calcination temperature, there was a decrease in conversion. Moreover, the selectivity to cyclohexane also decreased from 96.8% for Ni/SZ-500 to 78.7% for Ni/SZ-700. However, the selectivity for all oxygenated compounds (phenol, anisole, and catechol) increased with increased calcination temperature of the catalyst. Three causes can explain the decline of catalytic activity. First, from the H_2 -TPR, it is known that the catalyst calcined at a higher temperature cannot be reduced completely at 500 $^{\circ}\text{C}$. Unfortunately all the catalysts were reduced at 500 $^{\circ}\text{C}$ in this work, thereby causing the decline of catalytic activity. Second, the size of the Ni crystallites was enlarged, and the number of surface Ni atoms on the catalyst was decreased when the catalyst was calcined at a higher temperature, resulting in the decline of catalytic activity. Third, the decrease of the acidity of the catalyst caused by increasing calcining temperature is a key factor for the decline of HDO activity. The acidity of the catalyst is related to the hydrogenation, isomerization, and dehydration, and cracking functions [27]. The guaiacol molecule was activated first by the adsorption by the C–O polar bond on the acidic sites of the catalysts, followed by the hydrolysis of the C–O bond, hydrogenation of the benzene ring, dehydroxylation and dehydration, which complete the HDO reaction [20]. Obviously, strong acidic sites favor the HDO reaction of guaiacol. Moreover, apart from the catalytic cleavage of C–O bond, the acidic sites of catalyst can also catalyze the dehydration reaction during the HDO reaction, and they work well together with metal-catalyzed hydrogenation to promote the HDO reaction [20].

Interesting, the catalytic activity of Ni/SZ-400 was close to that of Ni/SZ-500 in the guaiacol HDO reaction. The reason is that the reduction of the Ni/SZ-400 catalyst is equivalent to calcination at 500 $^{\circ}\text{C}$.

To investigate the recyclability of the catalyst, a batch of Ni/SZ-500 was used repeatedly for guaiacol HDO at 300 $^{\circ}\text{C}$ and an initial pressure of H_2 of 5.0 MPa. The guaiacol conversions for four runs were 100%, 91.1%, 89.8%, and 86.5%. A significant drop in the conversion of guaiacol was observed after the catalyst was reused only once. Then the conversion decreased only slightly in the following two runs. This result may suggest that the catalyst has excellent recyclability for the guaiacol HDO reaction.

Table 4

Catalytic performance of the Ni/SZ catalysts for guaiacol HDO reaction.

Catalyst	Conversion (%)	Selectivity (%)							
		Benzene	Cyclohexane	Cyclohexene	Methyl-cyclohexane	Toluene	Anisole	Phenol	Catechol
Ni/ZrO ₂	43.8	0.3	75.4	1.6	7.4	9.9	0.7	1.2	3.5
Ni/SZ-400	98.2	0.2	93.7	—	2.1	1.1	—	2.3	0.6
Ni/SZ-500	100	0.2	96.8	1.6	1.1	0.3	—	—	—
Ni/SZ-600	91	0.4	87.8	1.2	1.6	3.3	0.8	3.9	1.0
Ni/SZ-700	79.4	0.4	78.7	0.9	4.9	3.6	1.3	7.7	2.5

Reaction conditions: 300 $^{\circ}\text{C}$, H_2 5.0 MPa, 8 h.

Graphical Abstract

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Effect of calcination temperature of Ni/SiO₂-ZrO₂ catalysts on its hydrodeoxygenation of guaiacol

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Cyclohexane was obtained with high selectivity by the hydrodeoxygenation of guaiacol over a bifunctional Ni/SiO₂-ZrO₂ catalyst. The catalytic performance was influenced significantly by the calcination temperature of the catalyst.

4. Conclusions

The characterization of Ni/SZ catalysts calcined at different temperatures was performed, and their catalytic performance was investigated. The Ni/SZ-500 catalyst exhibited excellent performance for the HDO reaction of guaiacol. Guaiacol was converted with conversion of 100% and cyclohexane selectivity of 96.8%. Increased calcination temperature significantly reduced the BET surface area, number of surface Ni atoms, and amount of acidic surface sites. The Raman spectra analysis indicated that the ZrO₂ contained in the SZ complex oxides tended to crystallize with increasing calcining temperature, resulting in the deterioration of the catalyst structure. NH₃-TPD results and the catalytic behavior revealed that the acidic sites on the surface of catalyst improved the HDO activity due to a synergistic effect between the metallic and acidic functions of the catalysts.

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Ni/SiO₂-ZrO₂催化剂焙烧温度对其催化愈创木酚加氢脱氧性能的影响

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摘要: 采用化学沉淀法合成了 $\text{SiO}_2\text{-ZrO}_2$ 复合氧化物载体,并以浸渍法制备了 $\text{Ni/SiO}_2\text{-ZrO}_2$ 双功能催化剂,考察了焙烧温度对催化剂结构及其催化愈创木酚加氢脱氧制环己烷性能的影响。结果表明,经 $500\text{ }^\circ\text{C}$ 焙烧催化剂的加氢脱氧活性最高,在Ni金属中心和 $\text{SiO}_2\text{-ZrO}_2$ 载体材料的协同作用下,愈创木酚转化率为100%,环己烷选择性为96.8%。对催化剂进行 N_2 物理吸附、 H_2 化学吸附、X射线衍射分析、 H_2 程序升温还原、 NH_3 程序升温脱附与Raman光谱等表征后发现,合成的 $\text{SiO}_2\text{-ZrO}_2$ 为无定形的酸碱两性氧化物;经 $500\text{ }^\circ\text{C}$ 焙烧的催化剂样品的有效比表面积和孔体积均明显增大,表面酸量最多,硝酸镍分解成小颗粒的NiO较易被 H_2 还原,这些特性是该催化剂样品具有高效加氢脱氧活性的原因。

关键词: 镍; 氧化硅; 氧化锆; 焙烧温度; 愈创木酚; 加氢脱氧; 环己烷

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