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The difference in hydrogenation performance between Ni-in-Al_2O_3 and Ni-on-Al_2O_3 for hydrotreating of crude 2-ethylhexanol

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Abstract−Two mesoporous material Ni/γ-Al_2O_3 catalysts were prepared and characterized by ICP-AES, XRD, and TPR. The differences in reaction activity between Ni-in-Al_2O_3 and Ni-on-Al_2O_3 were investigated for hydrotreating of crude 2-ethylhexanol. The results show that the Ni species (Ni-on-Al_2O_3) exhibit excellent hydrogenation activities at a wide range of H_2 pressure and space velocity, while the Ni species (Ni-in-Al_2O_3) exhibit similar activities with those of Ni-on-Al_2O_3 only at higher H_2 pressure and lower space velocity. Due to the presence of extensively exposed Ni species on the Ni-on-Al_2O_3 catalyst, its hydrogenation performance was increased significantly because of the low interphase mass transfer resistance.

Key words: Ni/γ-Al_2O_3, Ni Species, Reducibility, Hydrotreating, 2-Ethylhexanol

INTRODUCTION

2-Ethylhexanol is an important industrial material [1-3] usually obtained by the hydrogenation of 2-ethylhexenal. However, during the process of hydrogenation, the existence of unsaturated by-products (2-ethylhexanal and 2-ethylhexenol) and residual reactant (2-ethylhexenal) greatly affects the product purity. Thus, it is necessary to develop an effective hydrotreating catalyst and use it in a subsequent supplementary hydrogenation process for crude 2-ethylhexanol.

To date, various hydrotreating and hydrogenation catalysts have been reported in publications (e.g. Mo nitride [4], Ni/Si [5], Co(Ni) Mo/γ-Al_2O_3 [6], CoMo/Al_2O_3, NiMo/Al_2O_3 [7], Pa/TiO_2 [8], Mo/MCM-41 [9], Mo/$TiZrO_4$, CoMo/$TiZrO_4$ [10], Co/Al_2O_3 [11], Fe/SiO_2 [12]). Among these, Ni-based catalysts are currently used in industry. The choice of nickel is mainly due to its availability and reasonable cost compared to noble metals. Some studies found that the hydrogenation performance of Ni-based catalyst depends on various factors, including Ni loading [13,14], support [15,16], promoter [17,18], heating treatment condition [19,20], and preparation method [15,21]. These factors affect the surface Ni state more or less and then affect the hydrogenation performance. It is generally acknowledged that Ni loading and the reduction temperature are two important influence factors for surface active sites and catalytic performance. In fact, the effects of Ni loading and the reduction temperature are due to various Ni species. One difference between them is structure and composition; the other difference is active sites located positions for the support. Some Ni species are embedded in the lattices of support (nickel-aluminate spinel), while other Ni species are located on the surface of support (crystal NiO). The difference between them is not only in different reducibility but also in exposed active sites. The inner Ni species should have relatively less chance to contact reactants and exhibit low activity because of the existence of interphase mass transfer. Thus, we believe that the difference in hydrogenation activity between Ni in support and Ni on support can be identified by various H_2 pressure and space velocity, because they all can describe the contact chance between active sites and reactant molecules.

Motivated by the possible difference between Ni in support and Ni on support, we attempted to design two catalysts: one containing only Ni in support, and the other containing Ni on and in support. Moreover, the hydrogenation performance and the operating conditions were investigated on the two different catalysts for hydrotreating of crude 2-ethylhexanol. The results indicated that the two catalysts all exhibited excellent activities at 120 °C, 2.5 MPa, and 3 h^{-1}.

EXPERIMENTAL

1. Catalyst Preparation

The supported catalyst samples were prepared by wet impregnation with $Ni(NO)_3 \cdot 6H_2O$ solutions on a commercial γ-Al_2O_3 (surface area=190 m^2 g^{-1}, mean pore diameter=10 nm). 10.0 g of γ-Al_2O_3 particles (20-60 mesh) were placed in 20 mL 0.2 or 1.65 mol L^{-2} $Ni(NO)_3 \cdot 6H_2O$ solutions at room temperature. Approximately 3 h contact time was enough to reach the equilibrium adsorption. After impregnation, the samples were dried at 120 °C for 3 h and then calcined at 500 °C for 3 h in air. The resultant samples were designated NiL and NiL-R before and after reduction, where L was Ni loading and R was reduction temperature.

2. Catalyst Characterization

The samples were dissolved in mixed acids, and their chemical compositions were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Powder X-ray Diffraction (XRD) patterns of the samples were obtained with a Rigaku diffractometer/MAX-RB by nickel-filtered Cu Kα radiation (λ=1.54056 A°).

Temperature programmed reduction (TPR) measurements were carried out in a TPDRO 1100 series (Thermo electron corporation)

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instrument. About 50 mg catalyst was placed in a U-shaped quartz sample tube. Prior to TPR studies, the catalyst sample was pretreated in an inert gas (N_2, 40 mL min^{-1}) at 200 °C for 1 h. After pretreatment, the sample was cooled to ambient temperature, the carrier gas consisting of 5% hydrogen balance argon (40 mL min^{-1}) was allowed to pass over the sample, and the temperature was increased from ambient to 950 °C at a heating rate of 10 °C min^{-1}.

3. Activity Test

The hydrotreating of crude 2-ethylhexanol was performed in a continuous-flow system. Before any measurement, 6.0 mL catalyst was pretreated at scheduled temperature in a 400 ml min^{-1} flow of hydrogen for 180 min, followed by cooling in hydrogen flow to the desired reaction temperature. The liquid feed and hydrogen were dosed by an HPLC pump and a mass flow controller, respectively. Both reactants were mixed before they entered the reactor. The reactants and the products were collected in cold traps and analyzed by an offline gas chromatograph (SP-3420). The hydrogenation activities of 2-ethylhexanal, 2-ethylhexenal, and 2-ethylhexenol on the catalysts were determined by the equation:

$$\text{Conversion (mol\%)} = 100 \times \frac{X_{in} - X_{out}}{X_{in}}$$

where X_{in} and X_{out} stand for the 2-ethylhexanal, 2-ethylhexenal, and 2-ethylhexenol contents in feed and product, respectively.

RESULTS AND DISCUSSION

1. Catalyst Characterization

1-1. XRD

Fig. 1 shows XRD patterns of the catalyst samples and the support (γ-Al_2O_3). The support exhibits three peaks at 2θ=37.6°, 45.8° and 66.7°, corresponding to the planes (311), (400) and (440) of γ-Al_2O_3 (JCPDS 29-0063), respectively. Ni6 also exhibits three similar intensive peaks with those of γ-Al_2O_3. Clearly, their intensities are more intensive than those of the support, which are attributed to the formation of nickel-aluminate spinel because the characteristic peaks of nickel-alumina are similar to those of γ-Al_2O_3 [22]. Compared with Ni6, Ni20 exhibits some new crystal phase peaks besides nickel-aluminate spinel phase, which are due to the phases of crystal NiO. Peaks at 2θ=43.29°, 62.85°, and 75.40° are associated with NiO (012), (110), and (113) (JCPDS 44-1159), indicating that crystal NiO occurs at high Ni loading. The difference in the XRD patterns between Ni6 and Ni20 may result in different catalytic performance. First, the reducibility of Ni6 and Ni20 should be different because of various Ni species on them, which is important for the hydrogenation reaction. Second, the occupied position of Ni atom on/in the support is different. For instance, a larger number of Ni atoms mainly occupy the lattices of the support and form nickel-aluminate spinel when Ni loading is low, which may decrease the contact chance between reactants and the active sites because interphase mass transfer may occur. However, Ni species located on the surface of the support (crystal NiO), besides reducing easily, should have more chance to contact the reactant molecules because a majority of them are exposed on the surface of the support. We named the Ni species exposed on the surface of the support as Ni-on-Al_2O_3 and those in the lattices of the support (nickel-aluminate spinel) as Ni-in-Al_2O_3. The reducibility and hydrogenation performance of these different Ni species (Ni in or on Al_2O_3) will be further discussed later.

1-2. TPR

The TPR characterization is often used to analyze Ni/Al_2O_3 catalysts for surface Ni species, reducibility, and metal-support interaction [23-26]. To clarify the difference of reducibility between Ni-on-Al_2O_3 and Ni-in-Al_2O_3, Ni6 and Ni20 were characterized by TPR and shown in Fig. 2. As can be seen, Ni6 exhibits two reduction peaks, while Ni20 presents four peaks. Peaks at 660 and 810 °C on Ni6 are attributed to Ni_{OC}^{2+} (Ni^{2+} in an octahedral geometry) and Ni_{T}^{2+} (Ni^{2+} in a tetrahedral geometry) [27], which are nickel-aluminate spinel and correspond to Ni-in-Al_2O_3. Compared with Ni6, Ni20 presents four reduction peaks. Peaks at 620 and 740 °C should also be due to the reduction of Ni_{OC}^{2+} and Ni_{T}^{2+} which are reduced more easily than those of Ni6, suggesting that some of the Ni species (Ni-in-Al_2O_3) on Ni6 are embedded more deep in the support than those on Ni20. Besides the two high temperature reduction peaks, Ni20 exhibits two low temperature peaks around 300 and 520 °C which are attributed to the Ni species on the surface of support (Ni-on-

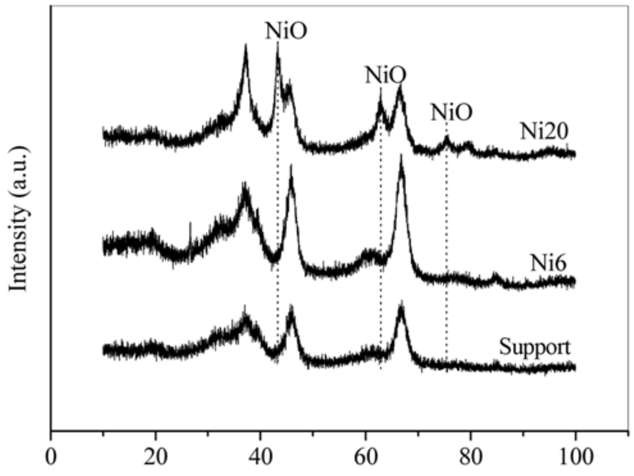

Fig. 1. XRD patterns of samples.

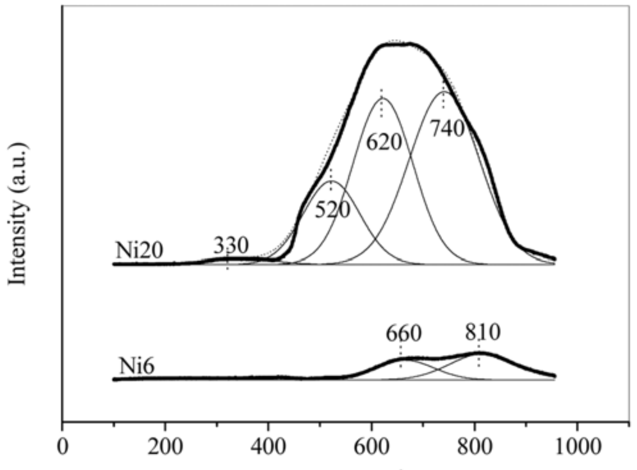

Fig. 2. TPR profiles of samples.

Al_2O_3).

Peak areas of the TPR profiles were estimated quantitatively by fitting the curves with a combination of Gaussian curves of variable proportion. The results indicated that area percentages of 660 and 810 °C corresponding Ni species on the Ni6 are 48.3 and 51.7%, and those of 330, 520, 620 and 740 °C on Ni20 are 1.9, 15.4, 38.1, and 44.6%, respectively. Thus, based on the area percentages of various Ni species and the loading of the Ni-20 catalyst, the content of Ni-in species including in the Ni-20 sample can be estimated and is about 16.54% ((38.1+44.6)%×20%=16.54%), which may be a threshold value for the formation of Ni-on species in this preparation conditions.

2. Catalyst Test

2-1. Reducibility and Intrinsic Activity of Various Ni Species

To investigate the difference in reducibility of various Ni species and their catalytic activities, Ni6 and Ni20 were reduced at five different temperature points and employed to test in the hydrogenation of crude 2-ethylhexanol. Fig. 3 shows the effect of reduction temperature on the conversions of 2-ethylhexanal, 2-ethylhexenal, and 2-ethylhexenol over the Ni/γ-Al_2O_3 catalysts. Note that: (i) at low reduction temperature (<600 °C), Ni6 exhibits very poor hydrogenation activities, even a negative conversion for 2-ethylhexanal at 400 °C. The appearance of negative conversion indicates that the content of 2-ethylhexanal increases during the reaction process, which is due to the incomplete reaction of 2-ethylhexenal (only C=C is hydrogenated) into 2-ethylhexanal. However, at high reduction tem-

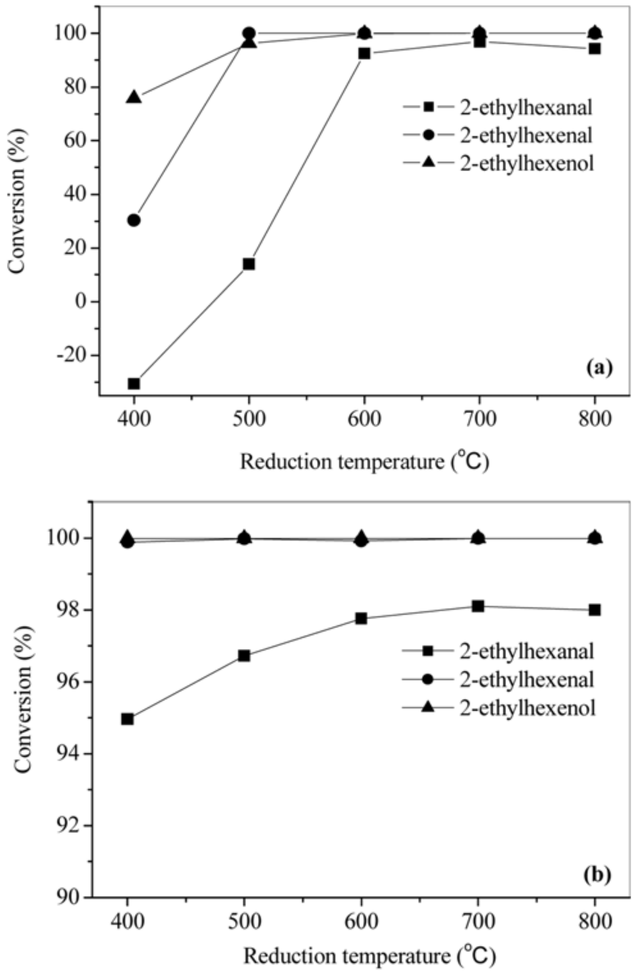

Fig. 3. Effect of reduction temperature on hydrogenation performance over: (a) Ni6 and (b) Ni20. Reaction conditions: T=120 °C, P=2.5 MPa, and LHSV=3.0 h^{-1}.

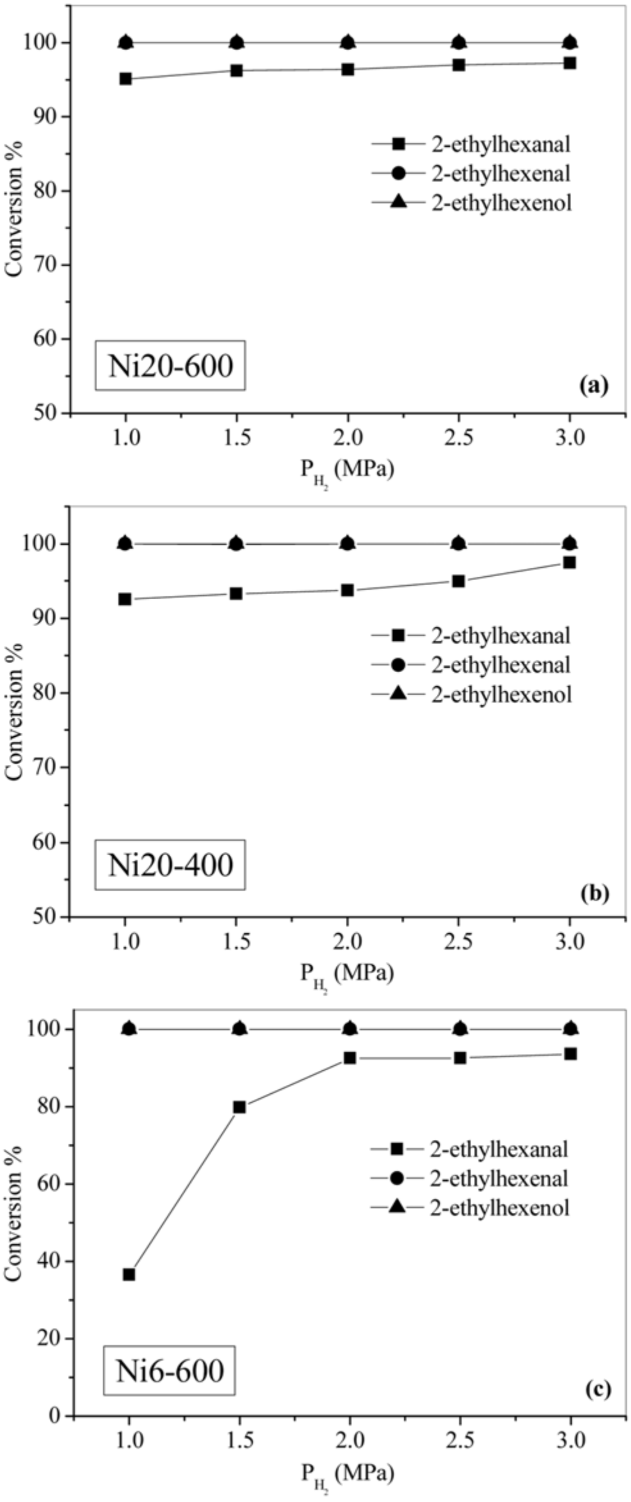

Fig. 4. Effect of H_2 pressure on reaction performance over: (a) Ni20-600, (b) Ni20-400, and (c) Ni6-600. Reaction conditions: T=120 °C and LHSV=3.0 h^{-1}.

perature (>600 ºC), the catalyst exhibits relatively high hydrogenation activities not only for 2-ethylhexenal and 2-ethylhexenol but also for 2-ethylhexanal; (ii) compared with Ni6, Ni20 exhibits better hydrogenation performance for the three unsaturated compounds at a wide range of reduction temperature from 400 to 800 ºC. The result is attributed to the fact that the Ni species in Al_2O_3 cannot be reduced easily at low temperature; in contrast, the Ni species on Al_2O_3 can be reduced easily. Although the difference of reducibility between Ni6 and Ni20 is obvious, the hydrogenation activities of Ni6 reduced above 600 ºC are similar with those of Ni20 reduced at a wide range of temperature, suggesting that Ni species in or on Al_2O_3 all exhibit hydrogenation activities in this system as long as they are reduced to metallic Ni^0. This also indicates that the intrinsic activity of Ni species in Al_2O_3 is similar to that of Ni species on Al_2O_3.

2-2. The Difference of Catalytic Activity between Ni-in-Al_2O_3 and Ni-on-Al_2O_3

To identify the difference of hydrogenation between Ni in Al_2O_3 and Ni on Al_2O_3, as well as obtain the optimum reaction conditions for the hydrotreating of crude 2-ethylhexanol, the effects of H_2 pressure, space velocity, and reaction temperature on the catalytic performance were investigated over Ni20-600, Ni20-400, and Ni6-600. Generally, the chance of reaction molecules contacting the active sites of catalyst is affected by H_2 pressure and space velocity because of the existence of interphase mass transfer. Thus, we expect that the difference between Ni-in-Al_2O_3 and Ni-on-Al_2O_3 can be well distinguished at various H_2 pressure and space velocity.

Fig. 4 shows the effect of H_2 pressure on hydrogenation activities of 2-ethylhexanal, 2-ethylhexenal, and 2-ethylhexenol. The conversions of 2-ethylhexenal and 2-ethylhexenol are almost not affected by H_2 pressure and remain constant at 100% on the three catalysts. However, an obvious difference is present at low H_2 pressure for 2-ethylhexanal hydrogenation on various catalysts. The result should be attributed to the fact that the initial contents of 2-ethylhexenal and 2-ethylhexenol are far lower than that of 2-ethylhexanal. Thus, the 2-ethylhexanal conversion is lower than the conversion of 2-ethylhexenal and 2-ethylhexenol at low H_2 pressure. As can be seen, the hydrogenation performance of Ni20-600 and Ni20-400 was very similar in the wide range of H_2 pressure from 1.0 to 3.0 MPa. However, very low hydrogenation activity occurs at low H_2 pressure for 2-ethylhexanal over Ni6-600. The result is not due to the difference of intrinsic activity between Ni-in Al_2O_3 and Ni-on Al_2O_3 but to the effect of interphase mass transfer. On Ni20-600 and Ni20-400, the H_2 molecule can easily contact the active Ni atom on the surface of support and then be activated immediately; however, on Ni6-600, H_2 molecule contacting the active sites must overcome the interphase mass transfer resistance because the Ni species are in the inner lattice of support. When H_2 pressure was increased, the chance of H_2 molecule containing and escaping the active sites in support should also have been increased. Thus, the conversion of 2-ethylhexanal reached a relatively high value (above 90%) at 2.0 MPa.

Fig. 5 shows the influence of space velocity on hydrogenation activities of 2-ethylhexanal, 2-ethylhexenal, and 2-ethylhexenol. Note that Ni20-600 and Ni6-400 all exhibit excellent hydrogenation performance for the three unsaturated compounds at a wide LHSV range from 1.5 to 9 h^{-1}. When the LHSV was increased to 12 h^{-1}, only 2-ethylhexanal conversion was slightly decreased to around 80%. However, Ni6-600 exhibits poor hydrogenation performance for the 2-ethylhexanal at a wide LHSV range, especially at high space velocity (above 6 h^{-1}). The results indicate that the effect of space velocity on the hydrogenation performance is similar to that of H_2 pres-

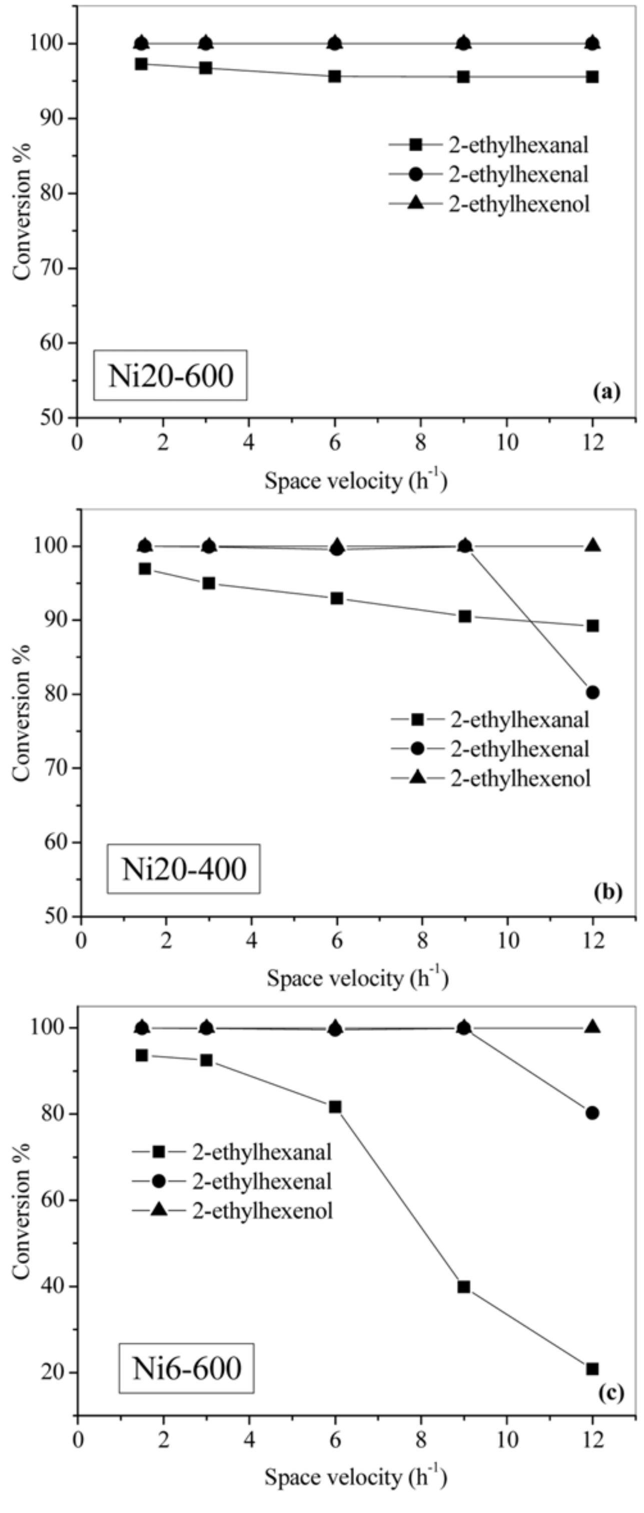

Fig. 5. Effect of space velocity on reaction performance over: (a) Ni20-600, (b) Ni20-400, and (c) Ni6-600. Reaction conditions: T=120 ºC and P=2.5 MPa.

sure. In fact, the influence of space velocity (LHSV) on hydrogenation performance reflects the contact time of the three unsaturated compounds and active sites. The higher the space velocity, the shorter the contact time. A shorter contact time may result because there is no more time for the reactants to contact active sites on the catalyst, especially on the Ni species in Al_2O_3 (i.e. Ni6-600), which is similar with the effect of H_2 pressure.

Fig. 6 illustrates the influence of reaction temperature on hydrogenation activities of 2-ethylhexanal, 2-ethylhexenal, and 2-ethylhexenol. The activity profiles obtained in the temperature range 80-160 °C follow a similar trend on the three catalysts, suggesting that

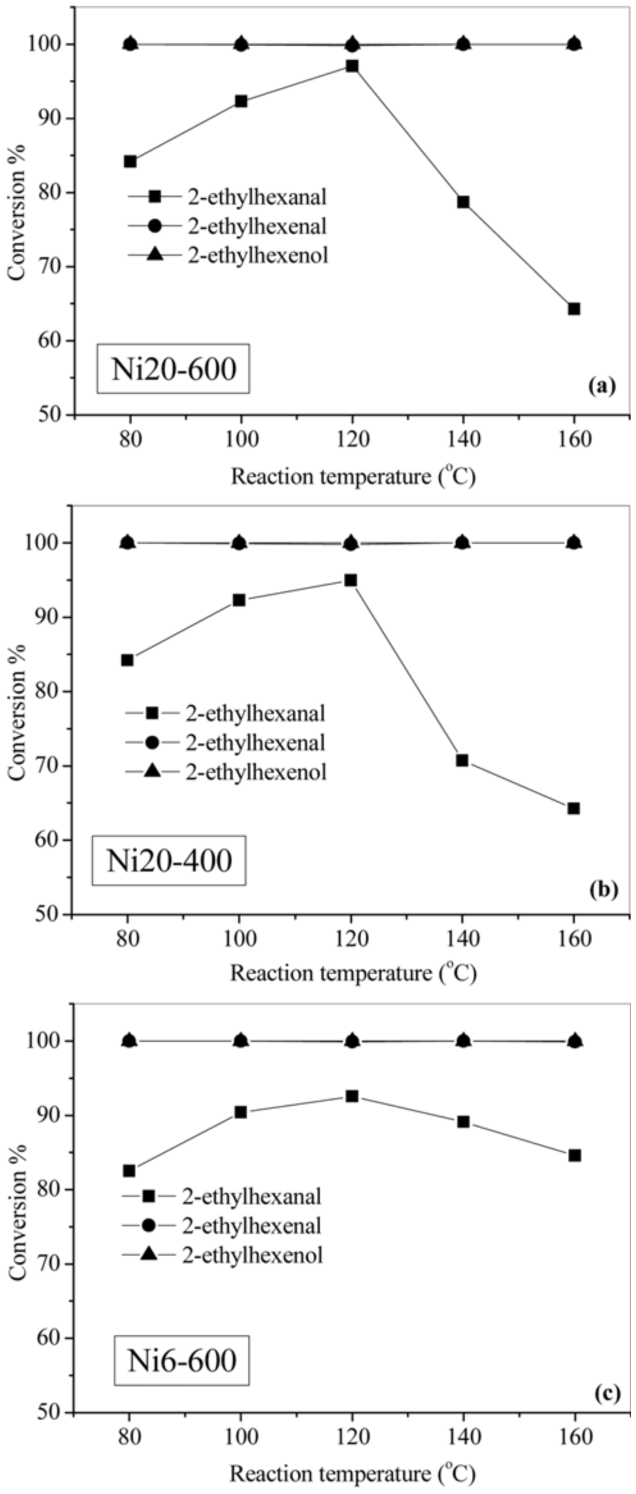

Fig. 6. Effect of reaction temperature on reaction performance over: (a) Ni20-600, (b) Ni20-400, and (c) Ni6-600. Reaction conditions: P=2.5 MPa and LHSV=3.0 h^{-1}.

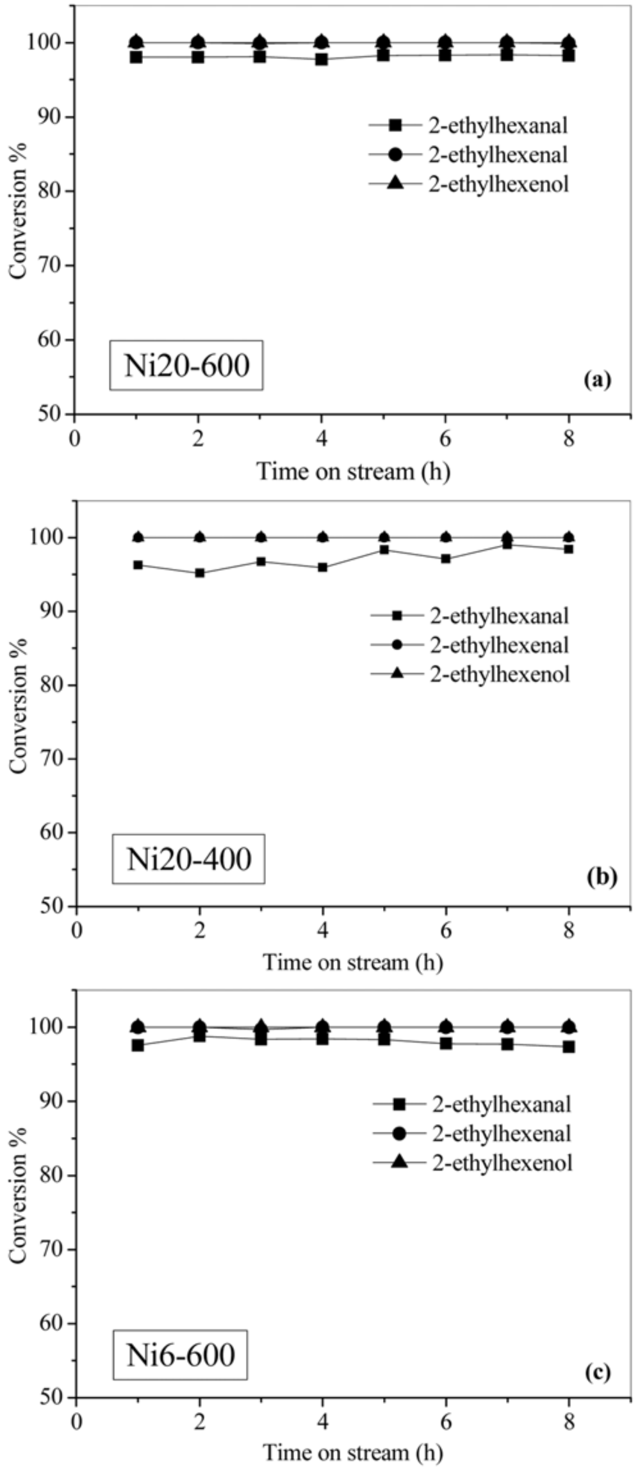

Fig. 7. Conversions as functions of time on stream over: (a) Ni20-600, (b) Ni20-400, and (c) Ni6-600. Reaction conditions: T=120 °C, P=2.5 MPa, and LHSV=3.0 h^{-1}.

the hydrogenation performance of the three unsaturated compounds at various reaction temperatures is nearly not affected by different Ni species (Ni in or on Al_2O_3). The hydrogenation conversions of 2-ethylhexenal and 2-ethylhexenol remain at a high value (100%) at a wide range of reaction temperature. However, the effect of reaction temperature on the hydrogenation performance of 2-ethylhexanal is very distinct. Note that at low temperatures (<120 °C), the conversion of 2-ethylhexanal increases gradually with increasing temperature, while a converse trend presents at high temperature (>120 °C). From a thermodynamic standpoint, these reactions are slightly exothermic and favor at low temperature. The excessive heat will result in inactivation of the catalyst and will affect the thermodynamic equilibrium [28]. Such phenomenon may also be associated with carbon deposition which may happen at high temperature. Based on these considerations, the optimum reaction temperature is about 120 °C for this system.

2-3. Effect of Time on Stream

Fig. 7 shows the conversions of 2-ethylhexanal, 2-ethylhexenal, and 2-ethylhexenol as functions of time on stream. The quite high active was presented immediately for 2-ethylhexanal conversion (97%), 2-ethylhexenal conversion (100%), and 2-ethylhexenol conversion (100%) on Ni20-600 and Ni6-400. The conversions were quite stable with time on stream at the fixed reactions conditions: T=120 °C, P=2.5 MPa, and LHSV=3.0 h^{-1}. A slight fluctuation in the hydrogenation performance of 2-ethylhexanal can be found on Ni20-400 in Fig. 7(b), which can be due to experimental error. Time on stream studies show that the conversions of the three unsaturated compounds are stable up to 8 h of reaction on Ni20-600, Ni20-400, and Ni6-400, indicating that the Ni species in or on the support are effective and stable in this reaction system.

2-4. Reaction Mechanism of 2-Ethylhexanal, 2-Ethylhexenal, and 2-Ethylhexenol

The synthesis of 2-ethylhexanol from 2-ethylhexenal may involve three reaction routes (Fig. 8): (i) the C=C bond hydrogenation of 2-ethylhexenal to intermediate product 2-ethylhexanal and then the C=O bond hydrogenation to 2-ethylhexanol; (ii) the C=O bond hydrogenation of 2-ethylhexenal to intermediate product (2-ethylhexenol) and then the C=C bond hydrogenation of 2-ethylhexenol to 2-ethylhexanol; and (iii) the synchronous hydrogenation of the C=C and C=O bands of 2-ethylhexenal to 2-ethylhexanol.

In fact, the first pathway is the main reaction route based on the foregoing results of 2-ethylhexanal, 2-ethylhexenal, and 2-ethylhexenol hydrogenation conversions in this system. From hydrogenation activities of the three unsaturated reactants, the 2-ethylhexenal and 2-ethylhexenol always exhibit higher hydrogenation conversions than 2-ethylhexanal; especially, 2-ethylhexanal exhibits a negative conversion on the catalysts with low Ni surface active sites. The appearance of negative conversion of 2-ethylhexanal indicates that hydrogenation of 2-ethylhexenal to intermediate product 2-ethylhexanal must occur. Thus, the results indicate that the hydrogenation of C=C band is easier than that of C=O band for 2-ethylhexenal on the $Ni/\gamma\text{-}Al_2O_3$ catalysts.

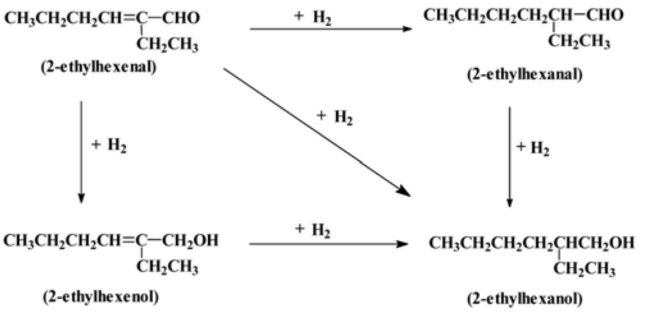

Fig. 8. Reaction scheme for 2-ethylhexenal hydrogenation to 2-ethylhexanol.

CONCLUSIONS

The differences in reaction activity between Ni-in-Al_2O_3 and Ni-on-Al_2O_3 were investigated. The results show that their activities are obviously different in various H_2 pressure and space velocity, suggesting that the number of exposed active sites is an important factor for hydrogenation performance because of the existence of interphase mass transfer. Moreover, the operating conditions on these Ni-based catalysts have been investigated for hydrotreating crude 2-ethylhexanol--they all exhibited excellent activities at 120 °C, 2.5 MPa, and 3 h^{-1}.

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