Hindawi Publishing Corporation
Journal of Nanomaterials
Volume 2015, Article ID 791529, 6 pages
http://dx.doi.org/10.1155/2015/791529

Research Article

Synthesis and Catalytic Performance of Ni/SiO$_2$ for Hydrogenation of 2-Methylfuran to 2-Methyltetrahydrofuran

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Received 22 October 2014; Accepted 26 December 2014

Academic Editor: Bhanu P. S. Chauhan

A series of Ni/SiO$_2$ catalysts with different Ni content were prepared by sol-gel method for application in the synthesis of 2-methyltetrahydrofuran (2-MTHF) by hydrogenation of 2-methylfuran (2-MF). The catalyst structure was investigated by X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and temperature programmed reduction (TPR). It is found that structures and catalytic performance of the catalysts were highly affected by the Ni content. The catalyst with a 25% Ni content had an appropriate size of the Ni species and larger BET surface area and produced a higher 2-MF conversion with enhanced selectivity in 2-MTHF.

1. Introduction

2-Methyltetrahydrofuran (2-MTHF) is a chemical intermediate in synthesis of chloroquine phosphate and oryzanin (thiamine monochloride), a good additive for fuel gasoline (to a content as high as 55%), as well as an alternative solvent due to its moderate boiling point and easy separation from water; 2-MTHF also behaves as a Lewis base similar to tetrahydrofuran (THF) [1–3]. 2-MTHF has found applications as a solvent in the preparation of Grignard reagents, in cross-coupling reactions [4, 5], in enantioselective 1,4 additions and other synthetic procedures, and even in the enzyme-catalyzed C-C bond formation reactions [6, 7].

At present, the main raw materials for production of 2-MTHF are glycols, inner esters, and furfural. In the glycol route, the most frequently used glycol is the expensive 2-methyl-1,4-butanediol, which was seldom obtained as a byproduct in large quantity and therefore renders its industrialization problematic [8, 9]. As for the inner ester route, although the 2-MTHF yield is high (82.3%), cobalt-60 has to be used for producing X-rays to irradiate the reactant inevitably resulting in pollution [10]. Nevertheless, the synthesis of 2-MTHF from hydrogenation of furfural (usually derived from biomass) has attracted considerable attention because furfural is cheap and easily available. Two steps are included in this route: first, hydrogenation of furfural gives 2-MF with the use of a copper-based catalyst; next, hydrogenation of 2-MF provides 2-MTHF that implies either a noble metal catalyst or a Ni-based catalyst [11–14]. This route has been industrialized. However, the cost for the second step is in a dilemma: if noble metal catalyst is adopted, the catalyst is expensive, while if relative cheaper Ni-base catalyst is applied, the apparatus and operation costs will be higher because the reaction pressure is as high as 15–20 Mpa. It is well known that the performance of the catalyst is highly dependent on the structure, constituents, and preparation method. Recently considerable efforts have been focused on the development of the catalyst for the second step. The hydrogenation process can be completed by both homogeneous and heterogeneous catalytic reactions. Compared with homogeneous hydrogenation, the heterogeneous process has the advantages of an easy purification of the product and low cost. Therefore, attention has been focused on investigation of the heterogeneous catalysts. In this paper, a series of Ni/SiO_2 catalysts with different Ni contents were prepared by a sol-gel method. We have tried to complete the second step of the reaction at a relatively lower pressure with nonnoble Ni-based catalysts. To better understand the effect of the Ni content on the performance of the catalyst, we characterized these catalysts by means of most adequate techniques such as nitrogen physisorption, X-ray diffraction (XRD), temperature-programmed reduction (TPR), and transmission electron microscopy (TEM). Therefore, this work can not only provide a research foundation/basis for development of industrial catalysts for the synthesis of 2-MTHF via 2-MF but also brings insight into the design of highly active nickel-based catalysts for other reactions.

2. Experimental Section

2.1. Catalyst Preparation. The Ni/SiO_2 catalysts, abbreviated as x-Ni/SiO_2 (where x stands for the NiO theoretical mass fraction of the catalyst), were prepared by a sol-gel method. All the reagents were of analytical grade and were used without further purification. In a typical procedure, Ni $(NO_3)_2{\cdot}6H_2O$ was dissolved in a certain amount of deionized water, so that the concentration of Ni^{2+} was 0.5 M. Then the solution was added dropwise to 85 mL silica sol (JA-25, Qingdao Haiyang Chemical Ltd.) under vigorous stirring. The resulting gel was aged for 2 hours and evaporated at 80°C for removing the solvent (water). Next, the gel was dried at 120°C for 12 hours. Then, the catalyst was prepared with an extruder and the extruded catalyst was calcined at 600°C for 4 hours.

2.2. Catalyst Characterization. XRD measurements were performed on a Rigaku D/max 2500pc X-ray diffractometer with Cu-Kα radiation (λ = 1.54156 Å) at a scan rate of 4° min^{-1} at 50 kV and 250 mA. The grain size was calculated from the XRD spectra by using the Scherrer equation.

BET surface areas were measured by N_2 adsorption at −196°C using a Quantachrome Autosorb 1-C, before measurements samples were degassed under vacuum at 300°C for 4 hours.

H_2-TPR was also conducted using Quantachrome chemisorption to examine the catalyst reducibility. 50 mg of the catalyst was heated in He at 400°C for 60 min, followed by cooling to room temperature. The temperature was then raised, in 30 mL/min of 10% H_2/Ar, using a ramp rate of 10°C/min to 900°C.

TEM images were obtained on a JEOL JEM 2010 transmission electron microscope with accelerating voltage of 200 kV.

The XPS measurement was made on a Thermo Spectrometer (VG ESCALAB250) equipped with a monochromatic Al Ka (1486.6 eV) radiation source. To eliminate the effect of possible charge development in the sample during the XPS measurements, the observed peak position calibrated the C1s peak (284.6 eV) as a reference.

2.3. Catalyst Testing. Activity and selectivity measurements of the catalysts were carried out in a continuous-flow fixed-bed reactor made of stainless steel (i.d. = 10 mm). Prior to the measurements, the catalysts were reduced in a stream of 20% H_2/N_2 at 600°C for 10 h, under atmospheric pressure. Then the reactor was cooled to 180°C, and the catalyst bed was fed with 2-methylfuran (2-MF) and H_2 (H_2/2-MF is 10.7), and the pressure was raised to 1.6 MPa. The 2-MF was supplied by a syringe pump (SSI), vaporized, and mixed with the H_2 feed in an electrically heated stainless steel preheater. The hydrogen feed was controlled by the mass flow controllers. The exit gases were cooled down to room temperature in a water-cooled condenser. The liquid product was collected and analyzed by means of a gas chromatograph (Beijing Benfenruili Ltd., 3420) equipped with a FID detector.

3. Results and Discussion

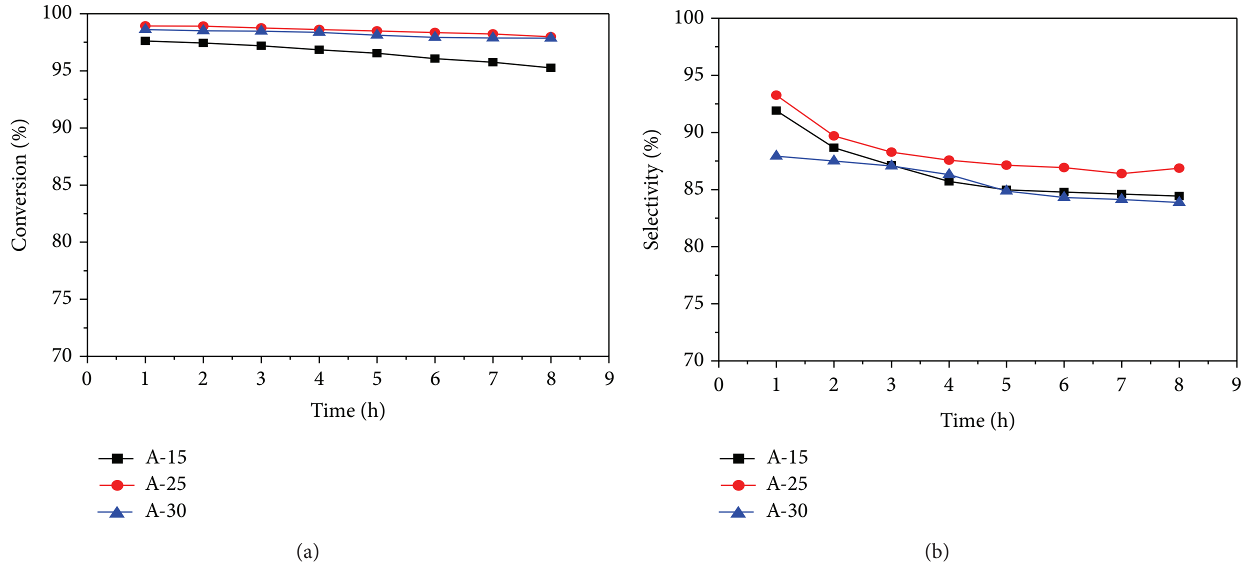
3.1. Catalytic Performance of Ni/SiO_2 Catalysts. The catalytic properties of the reduced Ni/SiO_2 catalysts with different contents of nickel were tested for 2-MF hydrogenation to 2-MTHF. The major product was 2-MTHF, and the side products included tetrahydrofuran, pentyl alcohol, and 2-pentyl alcohol. The conversion of 2-MF and the selectivity in 2-MTHF are shown in Figure 1. It can be found that the conversion of 2-MF and the selectivity of 2-MTHF first increase and then decrease with increasing Ni content to reach 98.0% and 86.8%, respectively, for the 25-Ni/SiO_2 catalyst after 8 hrs. It is understandable that the performance of Ni/SiO_2 catalysts improves with increasing Ni content because Ni is the active species for the reaction. More active species means more reaction centers that can be supplied. However, it should be noted that if the Ni content exceeds certain values, for example, of 30-Ni/SiO_2 catalyst, the performance of the catalyst deteriorates. This can be caused by changes in the Ni dispersion within the catalysts [15]. Further characterization to explore the effect of Ni content in the catalyst is shown in Sections 3.2–3.3.

3.2. The Structure of the Catalysts. Figure 2 shows the XRD patterns of the as-prepared Ni/SiO_2 catalysts. The strong and sharp peaks observed in Figure 2 confirm that the catalysts are all well crystallized. For all the Ni/SiO_2 catalysts, the diffraction peaks appearing at 37.1°, 43.1°, 62.5°, and 79.0° can be attributed to the NiO phase (JCPDS 65-2901) while the broad peak at 22.3° can be ascribed to the SiO_2 phase (JCPDS 39-1425) [16]. With increasing of Ni content from 15% to 30%, the intensities of the diffraction peaks of Ni become sharper and the width of the peaks gradually becomes narrower, which indicates that the Ni crystal size increases with the Ni content [17]. The Ni crystallite size calculated by using the Scherrer equation is in good agreement with the above-mentioned trend, as shown in Table 1.

The BET surface area (S_{BET}) values of the catalysts change a little with an increasing Ni content: they first increase and then decrease, as listed in Table 1. The catalyst 25-Ni/SiO_2 shows the maximum S_{BET} of 97.0 m^2/g, and 30-Ni/SiO_2 gives the minimum S_{BET} of 95.1 m^2/g, which indicates that S_{BET}

Table 1: The physiochemical properties of the Ni/SiO$_2$ catalysts.

Samples	S_{BET} (m^2/g)	V (cm^3/g)	D_{NiO} (nm)	D_{Ni} (nm)
A-15	96.2	0.352	14.4	11.5
A-25	97.0	0.365	14.6	14.3
A-30	95.1	0.362	15.6	16.4



(a)

(b)

Figure 1: Catalytic performances of the Ni-SiO$_2$ catalysts: (a) conversion of 2-MF; (b) selectivity of 2-Me-THF.

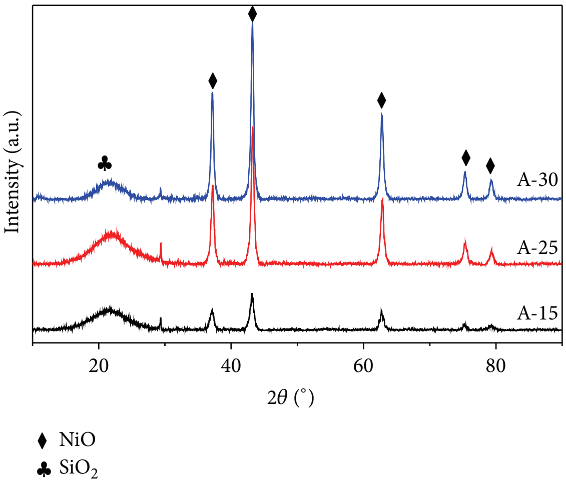


Figure 2: XRD patterns of as-prepared Ni/SiO$_2$ catalysts.

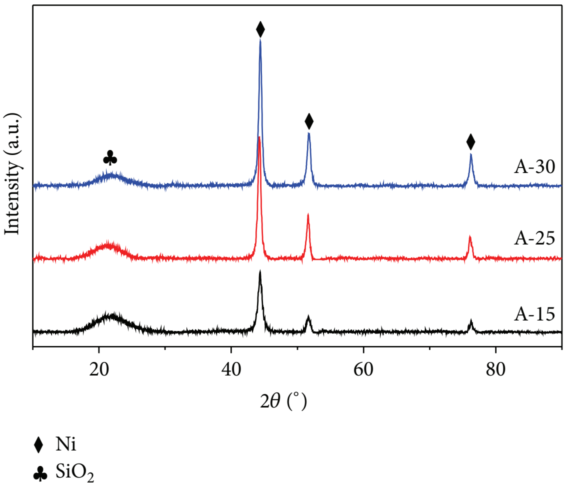
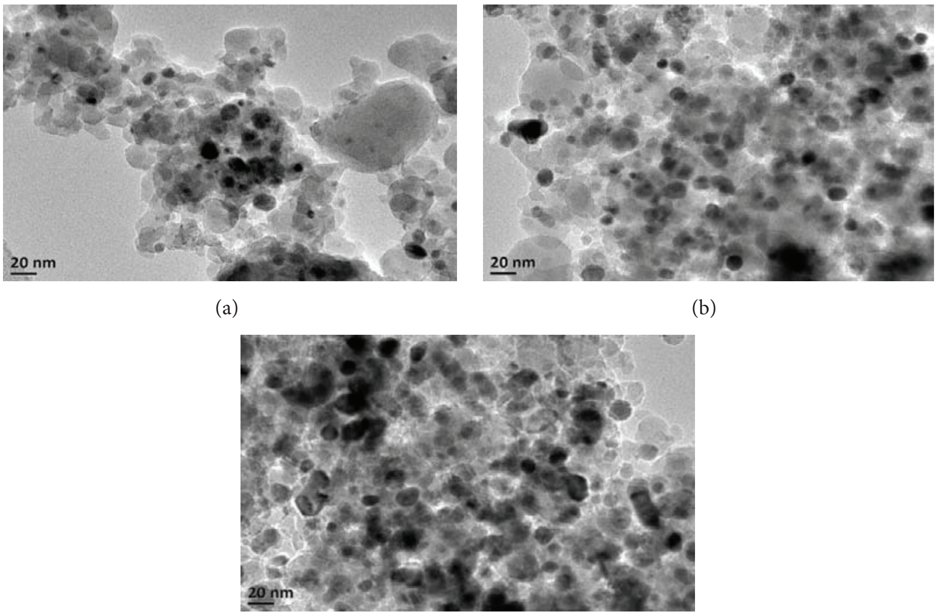


Figure 3: XRD patterns of the reduced Ni/SiO$_2$ catalysts.

may not be the main reason accounting for the catalytic performance of the catalysts.

The XRD patterns of the reduced catalysts are shown in Figure 3. It can be observed that the XRD patterns show diffraction peaks at 2θ values of 44.3°, 51.4°, and 76.1°, which can be related to the crystal planes of (111), (200), and (220) of metallic nickel phase, respectively (JCPDS 65-0380), whereas the broad peak at 22.3° can be ascribed to the SiO$_2$ phase. No diffraction peaks belonging to NiO phase can be detected in any of the catalysts, suggesting that all NiO species have been reduced to nickel. The calculated grain sizes of Ni using Scherrer's equation are also listed in Table 1. As can be seen, the grain size slightly increases from 15-Ni/SiO$_2$ to 30-Ni/SiO$_2$. It is reasonable that the Ni grain size increases with the metal content because of an aggregation of the Ni species [18]. The changing trend of the Ni grain size is the same as that of NiO.



(a) (b)

(c)

Figure 4: TEM images of reduced catalysts: (a) 15-Ni/SiO_2; (b) 25-Ni/SiO_2; (c) 30-Ni/SiO_2.

The Ni nanoparticle size can also be observed from the TEM images. Figure 4 shows images of the reduced Ni/SiO_2 catalysts with different Ni contents. It is observed that the Ni species are distributed uniformly over the Ni/SiO_2 catalyst; that is, the average particle sizes are about 11 and 14 nm for 15-Ni/SiO_2 and 25-Ni/SiO_2 catalyst, respectively. On the contrary, the average Ni particle size is about 16 nm when the Ni content is high (30-Ni/SiO_2). In addition, some Ni particles obviously aggregate together, implying poor Ni dispersion within the catalyst. Combined with results listed in Table 1, Ni aggregation will cause a decrease in performance of the catalyst.

Figure 5 gives the spectra of the x-Ni/SiO_2 sample after reduction. The binding energy of Ni $2p_{3/2}$ was 852.1 eV with the corresponding satellite peak at about 857 eV. The binding energy of about 852.1 eV is related to metallic Ni^0 at the surface in good agreement with the literature result (852.0 eV [19]), which indicated the presence of only metallic Ni^0. No NiSi alloy (853.5 eV [20]) was observed and therefore these species can be discarded at the surface.

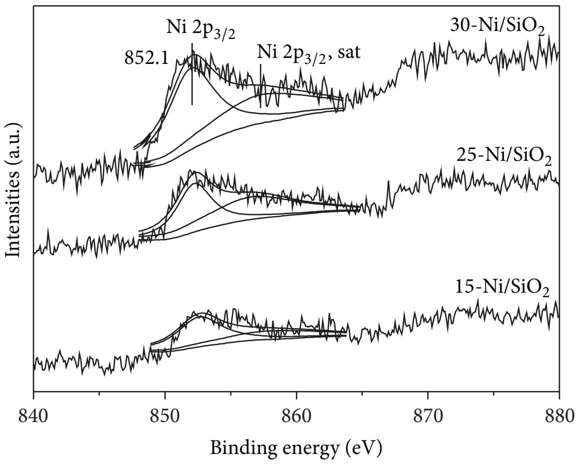


Figure 5: XPS spectra in the Ni 2p region.

3.3. The Reducibility of the Catalysts. In order to investigate the reducibility of the catalysts, H_2-TPR was performed, and the obtained results are shown in Figure 6. As illustrated, TPR profiles of the catalysts exhibit two broad peaks of H_2 consumption. Obviously, the peaks are asymmetric, indicating an overlapping of two reduction processes [21]. To get a deeper insight into the TPR results, the broad peaks are denoted by α and β peaks, respectively. Under the experimental conditions used in this study, SiO_2 in these catalysts is nonreducible. Consequently, α and β peaks occurring in the range of 400 to 800°C in the TPR profiles imply the presence of different NiO species with slight differences in ease of reducibility. Similar results have also been reported for other Ni/SiO_2 catalysts: α peak (the low-temperature reduction peak) being attributed to the reduction of NiO weakly interacts with the support and β peak (the high-temperature reduction peak) being attributed to the reduction of NiO strongly interacts with silica [22]. The TPR profiles show that the areas of α and β peaks become larger with an increasing Ni content, indicating that both highly dispersed and bulk NiO species increase. Moreover, with a growing Ni content, α peaks for 15-Ni/SiO_2 and 25-Ni/SiO_2 increase more than the β peaks, or this illustrates that the dispersed NiO becomes more significant; for 30-Ni/SiO_2, the relative area of the α peak lessens again. This may be another reason for the poorer performance of 30-Ni/SiO_2. At the same time, α and β peaks maxima shift

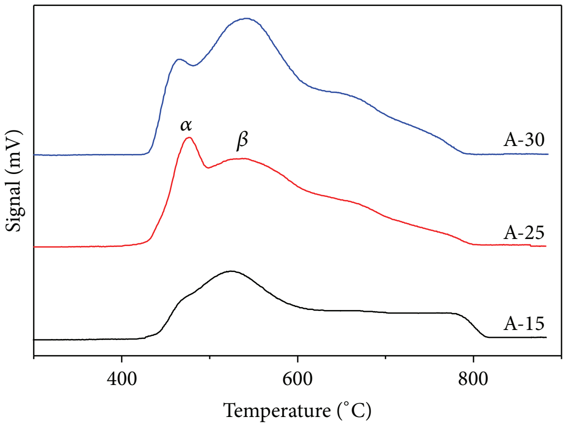


Figure 6: TPR profiles of different Ni/SiO_2 catalysts.

to higher temperature, which implies that increasing the Ni content during preparation does not facilitate reducibility [23].

4. Conclusions

In summary, herein the effect of Ni content on the structure and the catalytic performance of Ni/SiO_2 catalysts applied in synthesis of 2-MTHF from 2-MF hydrogenation has been investigated. Results show that the appropriate Ni grain size (about 14 nm) obtained in Ni/SiO_2 catalysts with a 25% Ni content exhibited superior catalytic performance. With 25Ni/SiO_2, under a reaction pressure of 1.6 Mpa, at 180°C, the 2-MF conversion and 2-MTHF selectivity are 98% and 86.8% after 8 hrs, respectively.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

The authors thank National Nature Science Foundation of China (51301114, 21201123, and 21203125), Liaoning Educational Department Foundation (L2011065), and LNET (LJQ2013044) for financial support.

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