Preparation of highly dispersed nickel metal catalysts supported on silica by heat treatment with water

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Abstract: Highly dispersed nickel metal catalysts supported on silica gel were prepared by heat treatment of conventional supported nickel catalysts with water and carbon dioxide. The treatment increased the number of nickel metal atoms on the surface from 65 to 433 mmol g^{-1} and decreased the size of nickel metal particles to 3 nm. The obtained catalysts showed higher activity (methylcyclohexane yield 75%) for toluene hydrogenation than the conventional supported catalyst (methylcyclohexane yield 18%).
Keywords: Supported nickel catalyst, Nanoparticle, Toluene hydrogenation.

1. Introduction

Supported nickel metal catalysts are active for various hydrogenations such as toluene hydrogenation, and alumina, zirconia etc. are used as catalyst supports. Silica is one of the most important supports because of high surface area. Use of silica supports, however, leads to sintering of nickel particles in the calcination, which is necessary to remove anions of nickel salts as nickel sources.[1] To prepare dispersed nickel catalysts supported on silica, several methods such as sol-gel[2] and co-precipitation[3] methods have been reported.

We have reported the preparation of highly dispersed copper metal catalysts supported on silica for partial hydrogenation of 5-hydorxymethylfurfural.[4] When supported copper catalysts prepared by the conventional impregnation method, which had copper metal particles with ca. 150 nm size, were heated in the presence of a small amount of water, the copper particle size decreased to 3 nm.

In this work, highly dispersed nickel metal catalysts supported on silica were prepared by heat treatment of the conventional nickel catalysts supported on silica with a small amount of water. We also demonstrated hydrogenation of toluene using the dispersed nickel metal catalysts.

2. Experimental

The supported nickel catalysts were prepared by conventional impregnation of nickel nitrate on silica gel (Q-15, Fuji Silysia Chemical Ltd.), calcination at 500 °C for 6 h and reduction under a hydrogen stream at 600 °C for 1 h (imp-Ni/SiO_2). Water (1 mL) and imp-Ni/SiO_2 (0.4 g) were put in an autoclave at 150 °C for 3 days (water treatment), and subsequently the catalyst was reduced at 800 °C for 1 h (wt-Ni/SiO_2). When CO_2 (CO_2:O_2 = 3:2) was charged in the autoclave, imp-Ni/SiO_2 (0.4 g) was heated at 80 °C for 17 h, and reduced at 600 °C for 1 h (wt-CO_2-Ni/SiO_2).

Toluene hydrogenation was carried out at 180 °C using a fixed-bed flow reactor. The pressures of toluene and hydrogen were 11 and 84 kPa, respectively. The catalyst amount and WHSV were 0.10 g and 7.01 h^{-1}, respectively.

3. Results and discussion

Figure 1 shows TEM images of imp-Ni/SiO_2, wt-Ni/SiO_2 and wt-CO_2-Ni/SiO_2. The nickel particle size of imp-Ni/SiO_2 was ca. 20 nm. Water treatment decreased the particle size to 10 nm; however, the size was not satisfactory, and long treatment time and high temperature were necessary for dispersion. Moreover, the shape of silica was changed and looked like films. Charging CO_2 to the autoclave greatly improved the dispersion of the nickel particles (3 nm), and lower temperature (80 °C) and shorter time (17 h) were enough to disperse the nickel particles. The silica shape was not changed with water treatment with CO_2 probably because of lower treatment temperature.

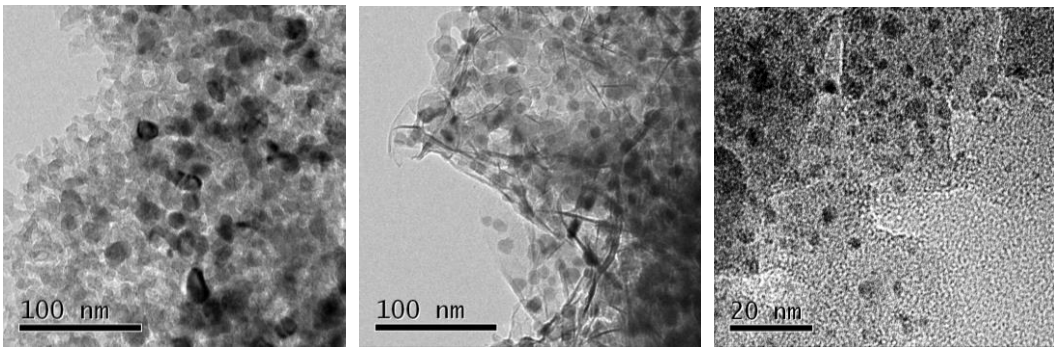

Figure 1. TEM images of imp-Ni/SiO_2 (left), wt-Ni/SiO_2 (center) and wt-CO_2-Ni/SiO_2 (right).

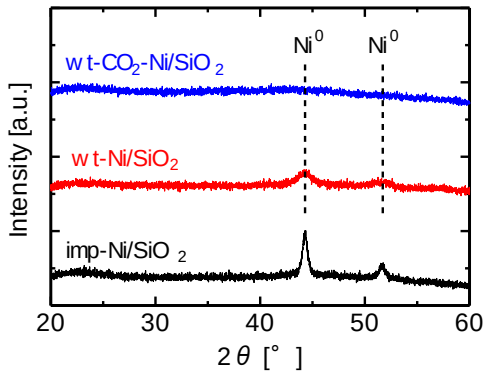

Figure 2. XRD patterns of imp-Ni/SiO_2, wt-Ni/SiO_2 and wt-CO_2-Ni/SiO_2.

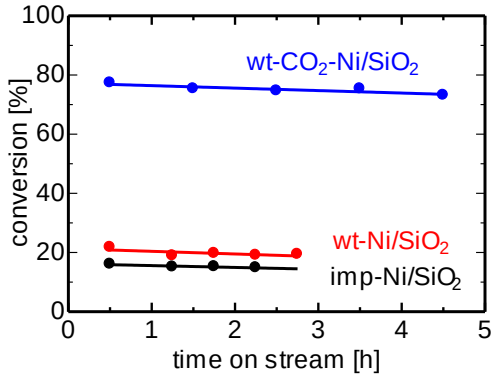

Figure 3. Time courses of toluene conversions in the hydrogenation of toluene catalyzed by imp-Ni/SiO_2, wt-Ni/SiO_2 and wt-CO_2-Ni/SiO_2.

The XRD patterns of imp-Ni/SiO_2, wt-Ni/SiO_2 and wt-CO_2-Ni/SiO_2 are shown in Figure 2. After water treatment without CO_2, the peaks due to metallic nickel still remained. When imp-Ni/SiO_2 was heated with water and CO_2, the peaks completely disappeared. Furthermore, the number of nickel metal atoms on the surface was examined using the reaction of nickel with N_2O.[5] The numbers of the nickel atoms in imp-Ni/SiO_2 and wt-CO_2-Ni/SiO_2 were estimated to be 65 and 433 μmol g_{SiO2}^{-1}, respectively. These results also indicate that water treatment with CO_2 made the nickel particles dispersed highly. CO_2 might be dissolved in the water to form an acidic solution, which might accelerate oxidation of the nickel metal particles (rate determining step of dispersion) to dissolve the nickel in the acidic water.

The catalytic activity of the dispersed nickel catalysts was examined. Toluene hydrogenation was carried out at 180 °C using the fix-bed flow reactor. The toluene conversion was ca. 15%, when imp-Ni/SiO_2 was used as a catalyst. Water treatment improved the conversion, especially the treatment with CO_2, and the conversion reached 75%.

4. Conclusions

The preparation method of highly dispersed nickel metal catalysts supported on silica was developed. Heat treatment of the impregnated nickel catalysts with a small amount of water and CO_2 resulted in formation of nickel nanoparticles and enhancement of catalytic activity.

References

1. C. Thunyaratchatanon, A. Luengnaruemitchai, N. Chollacoop, Y. Yoshimura, Fuel 163 (2016) 8.
2. T. Ueckert, R. Lamber, N.I. Jaeger and U. Schubert, Appl. Catal. A 155 (1997) 75.
3. M. P. González-Marcos, J. I. Gutiérrez-Ortiz, C. Gonzalez-Ortiz de Elguea, J. R. González-Velasco, J. Mol. Catal. A, 120 (1997) 185.
4. M. Okamoto, F. Kawamura, Y. Fukuda, TOCAT 7, O-D03.
5. S. Tada, M. Yokoyama, R. Kikuchi, T. Haneda, H. Kameyama J. Phys. Chem. C 117 (2013) 14652.