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Preparation of monodispersed NiO particles in SBA-15, and its enhanced selectivity for reverse water gas shift reaction

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ABSTRACT

The preparation of monodispersed NiO particles in SBA-15 using the direct hydrothermal synthesis method with various combinations of metallic salt precursors and acids was investigated in detail. With NiO/SBA-15 containing less than 1 wt% NiO, the NiO particles were monodispersed in the SBA-15 framework using the HCl + $Ni(NO_3)_2$ combination, whereas when the NiO amount exceeded 2 wt%, the NiO particles aggregated. However, with NiO/SBA-15 containing less than 25 wt% NiO, the NiO particles were monodispersed in the SBA-15 framework using the HCl + $NiSO_4$ combination, whereas when the NiO amount exceeded 30 wt%, the NiO particles aggregated. In addition, the reverse water gas shift (RWGS) reaction was studied using NiO/SBA-15 obtained by different combinations. Regardless of the combination and temperature, the CO selectivity was 100% using monodispersed NiO particles. In the presence of aggregated NiO particles, the CO selectivity was 100% only at high temperature; by contrast, the CO selectivity was less than 100% at low temperature. To achieve high CO_2 conversion and 100% CO selectivity, the HCl + $Ni(NO_3)_2$ combination was not desired due to small metal loading, whereas the HCl + $NiSO_4$ combination was necessary owing to large metal loading. Moreover, NiO/SBA-15 had relatively high thermal stability.

Introduction

Nickel (Ni)-based catalysts are the most extensively studied well-dispersed materials, and high loading is always desirable for high performance. Although ordered mesoporous materials with an adjustable pore size and a high specific surface area can be used to prepare well-dispersed Ni catalysts, two crucial problems are usually encountered: (1) the blockage of nanochannels because of high NiO loading [1]; and (2) poor catalytic activity because of the small amount of NiO [2,3]. The discovery of the ordered mesostructured silica SBA-15 [4,5] provides a wide range of opportunities for achieving high NiO loading. NiO/SBA-15 has been obtained with a NiO loading of 18.55 wt% by using the hydrophobic encapsulation route (HER) [6], with a loading range 20–69 wt% by using the complex internal gelation (IG) method [7], with a loading of 20 wt% [8] or 10–20 wt% [9] by using the impregnation method, and with loadings of 20 and 70 wt% by using the simple calcination method [10–12]. Because these are post synthesis methods in which the mesoporous SBA-15 support is impregnated with Ni precursors in the solution phase followed by thermal treatment or direct thermal treatment, NiO nanoparticles generated on SBA-15 typically lack uniformity as regards size and shape due to particle aggregates. Therefore, it is a serious technological challenge to design a synthesis approach for preparing NiO nanoparticles that are well dispersed (monodispersed) in SBA-15.

We have obtained monodispersed NiO particles in SBA-15 using the direct synthesis method in the presence of H_2SO_4 + $Ni(NO_3)_2$ [13,14], and employed them for a detailed investigation of the RWGS reaction. We found that when the NiO particles were monodispersed, the CO selectivity was 100%, regardless of the reaction temperature. By contrast, at a low reaction temperature CH_4 was formed in the presence of aggregated NiO particles, resulting in low CO selectivity. However, the formation mechanism and characterizes of monodispersed NiO particles in SBA-15 have not been yet clear.

For RWGS reaction as an equilibrium reaction, to achieve 100% CO selectivity, small Ni loading is not desired due to low CO_2 conversion, whereas large Ni loading is required. After considering the above options, we investigated two different combinations of Ni salt precursors and acids using the direct thermal synthesis method for preparing monodispersed NiO particles with large loading in SBA-15, namely the HCl + $Ni(NO_3)_2$ and HCl + $NiSO_4$ combinations. In addition, we studied its catalytic property using the RWGS reaction.

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Experimental

Direct synthesis of NiO/SBA-15 using HCl + Ni(NO$_3$)$_2$

In accordance with a previously reported direct synthesis method [13,14], an attempt was made to synthesize NiO/SBA-15 using hydrochloric acid (HCl, Junsei Chemical, Japan, 35–37.0 wt%) instead of sulphuric acid (H_2SO_4). The block copolymer Pluronic P123 (Aldrich, $EO_{20}PO_{70}EO_{20}$, $M_{av} = 5800$) was dissolved in 105 g of deionized water, and then 28.6 g of HCl and an appropriate amount of nickel (II) nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$, Wako Chemical, Japan, 99.5 wt%) were added at room temperature. The mixture was stirred for 30 min, and then 8.52 g of tetraethylorthosilicate ($Si(OC_2H_5)_4$, TEOS, Wako Chemical, Japan, 95.0 wt%) was added. The starting mixture obtained was aged at 60 °C until a white precipitate appeared, and then immediately evaporated at 100 °C overnight (≈14 h). The resulting solid product was dried at room temperature, and then calcined at 550 °C for 10 h and at 800 °C for 2 h.

Direct synthesis of NiO/SBA-15 using HCl + NiSO$_4$

An attempt was also made to synthesize NiO/SBA-15 using the direct synthesis method in the presence of HCl + $NiSO_4$ (nickel (II) sulphate hexahydrate, $NiSO_4 \cdot 6H_2O$, Kanto Chemical, Japan, 99.0–102 wt%). Pluronic P123 block copolymer (Aldrich, $EO_{20}PO_{70}EO_{20}$, $M_{av} = 5800$) was dissolved in 105 g of deionized water, and then 28.6 g of HCl and an appropriate amount of $NiSO_4 \cdot 6H_2O$ were added at room temperature. The mixture was stirred for 30 min, and then 8.52 g of tetraethylorthosilicate ($Si(OC_2H_5)_4$, TEOS, Wako Chemical, Japan, 95.0 wt%) was added. The starting mixture obtained was aged at 60 °C until a white precipitate appeared, and then immediately evaporated at 100 °C overnight (≈14 h). The resulting solid product was dried at room temperature, and then calcined at 500 °C for 10 h and at 800 °C for 2 h.

Characterization

The X-ray diffraction (XRD) patterns of the solid products were collected by a powder X-ray diffractometer (Bruker AXS D8 Advance) with graphite monochromatized Cu Kα radiation at 40 kV and 40 mA. Nitrogen adsorption isotherms at −196 °C were obtained using a conventional volumetric apparatus (Quadrasorb USA). Before the adsorption measurements were made, the powders (≈0.1 g) were subjected to a temperature of 300 °C for 5 h in a vacuum. The specific surface area was calculated with the Brunauer–Emmett–Teller (BET) method. The pore size was calculated from the desorption branch of nitrogen adsorption–desorption isotherms by the Barrett–Joyner–Halenda (BJH) method. The pore volume was taken at a single point $p/p_0 = 0.95$. The solid product was observed using a transmission electron microscope (TEM, JEM-2100F) at an electron acceleration of 200 kV. TEM-EDX analyses were conducted with an electron beam approximately 1 nm in diameter.

Catalytic property

The RWGS reaction was used as a model reaction to study the catalytic property of NiO/SBA-15 obtained using various combinations. Before the RWGS reaction, the catalysts were pre-reduced in situ in an 80% H_2/N_2 stream for 2 h with a total gas flow of 50 ml/min at 900 °C and a heating ramp rate of 100 °C/h. The RWGS reaction was performed at atmospheric pressure in a fixed-bed quartz reactor with a 20-mm inside diameter in an initial temperature range 400–900 °C. A 30-mm-long catalyst between two layers of quartz wool was loaded into the reactor. A thermocouple was inserted directly into the center of the catalyst bed to measure the actual pretreatment and reaction temperatures in situ. The reactor was heated in a furnace (KTF-035N, Koyo Thermo Systems, Co., Ltd.) equipped with a temperature controller. All reactant gases were monitored with a mass flow meter (E-40) and a controller (PE-D20) (HORIBA STEC, Co., Ltd.). The flow of the product was measured with a film flow meter (VP-3, HORIBA STEC, Co., Ltd.) and analyzed with a gas chromatography–thermal conductivity detector (GC-TCD) after the RWGS reaction had become stable.

Results and discussion

Direct synthesis of NiO/SBA-15 using HCl + Ni(NO$_3$)$_2$

In our previous research [13,14], where we employed H_2SO_4 instead of the HCl used in the conventional SBA-15 synthesis method and added $Ni(NO_3)_2 \cdot 6H_2O$ to the starting synthesis mixture of SBA-15, in NiO/SBA-15 containing less than 15 wt% NiO, the NiO particles were monodispersed in the SBA-15 framework using a direct hydrothermal synthesis. Firstly, we used HCl instead of H_2SO_4 and attempted to obtain monodispersed NiO particles in SBA-15. Fig. 1(a) shows the wide-angle XRD pattern of the as-synthesized products with 1 wt% NiO obtained using the HCl + $Ni(NO_3)_2$ combination. A broad peak at around $2\theta = 23°$ caused by the amorphous SiO_2 structure of SBA-15 was clearly observed, indicating that the ordered mesoporous SBA-15 structure was not disturbed by the incorporation of nickel salt. However, the peak caused by nickel salt was hardly seen, perhaps due to the coexistence of small nanoparticles of nickel salt in the SBA-15nanochannels.

As with NiO/SBA-15 obtained using the H_2SO_4 + $Ni(NO_3)_2$ combination, in the small-angle XRD pattern (not shown in here) of NiO/SBA-15 obtained using the HCl + $Ni(NO_3)_2$ combination,

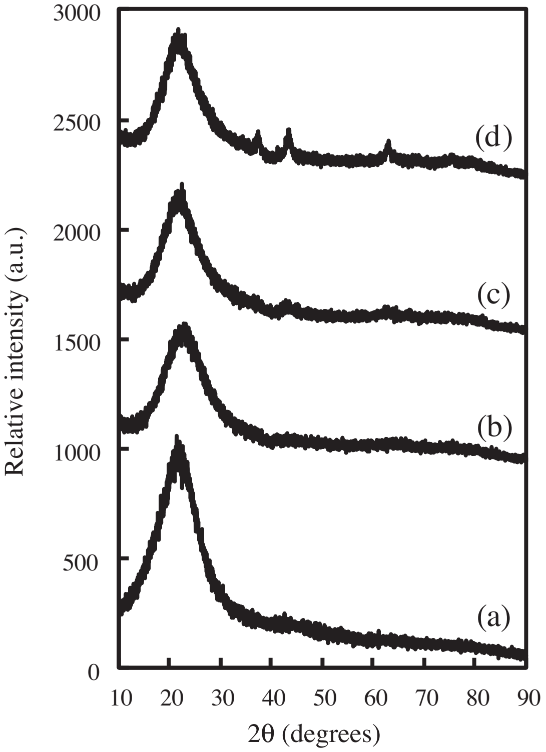

Fig. 1. Wide-angle XRD patterns of products with different NiO amount obtained using HCl + $Ni(NO_3)_2$. Sample no.: (a) as-synthesized product with 1 wt% NiO, (b) 1, (c) 2 and (d) 3.