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Fabrication of Pt nanoparticles encapsulated in single crystal like silicalite-1 zeolite as a catalyst for shape-selective hydrogenation of C_6 olefins

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ABSTRACT

In this work, a dual-functional catalyst with (1) catalytic activity of metal catalysts and (2) shape-selectivity of zeolites has been developed. We have fabricated Pt nanoparticles encapsulated in core-shell single crystal like silicalite-1 zeolite (CS-Pt/s-1) by a crystalline overgrowth method. The CS-Pt/s-1 catalyst showed much higher catalytic hydrogenation activity of *n*-hexene compared to cyclohexene.

1. Introduction

Zeolites have been widely known as multi-functional materials with shape selectivity, solid acidity and ion exchange capacity. In fact, zeolites have been applied as catalysts, adsorbents and membrane in various chemical processes. To give zeolites other catalytic properties besides solid acidity, it is effective to modify zeolites with various metal nanoparticles [1–22]; however, the nanoparticles are often located on the external surface of zeolite crystals, where shape selectivity does not work.

Zeolite-based membrane-reactors have been developed as one of the solutions to the problem. Some papers reported that MFI zeolite membranes with Pt nanoparticles exhibit high catalytic performances for xylene isomerization and hydroisomerization of C_6 olefins [23–27]. In addition, core-shell structured membrane catalysts also have been developed; e.g., Al_2O_3 and Pt/TiO_2 particles coated with a silicalite-1 (MFI type all silica zeolite) membrane show high selectivity to *p*-xylene on disproportionation of toluene [28] and to *n*-hexene on hydrogenation of liner and branched C_6 olefins, respectively [29]. In addition, LTA type zeolite-based membrane catalyst also has been developed; e.g., Pt/Al_2O_3 particles coated with LTA zeolite membrane can catalyze selective oxidation of CO in the mixture of CO and *n*-butane [30]. However, it is difficult to fabricate these zeolite-based membranes without defects that drastically deteriorate the shape-selectivity. Such defects often form during reactions or heating processes due to the mechanical vulnerability of zeolite polycrystalline membranes.

We have developed core-shell structured MFI zeolite catalysts [31–38], which are single crystal like zeolites without the above-mentioned large defects and mechanically tougher than polycrystalline zeolite-based membranes. In this work, we have fabricated Pt nanoparticles encapsulated in core-shell single crystal like silicalite-1 zeolite (CS-Pt/s-1) by an epitaxial crystalline overgrowth method (Scheme 1). And we discuss the shape-selectivity of the Pt-encapsulated zeolite catalyst on hydrogenation.

2. Experimental

Firstly, we synthesized a core silicalite-1 zeolite using 95 wt% tetraethyl orthosilicate (TEOS, Wako Pure Chemical Industries Co.), 10 wt % tetrapropylammonium hydroxide (TPAOH, Wako Pure Chemical Industries Co.) and deionized water. The molar ratio of precursor solution was 2.0 SiO_2: 0.5 TPAOH: 170 H_2O. The precursor was stirred at room temperature for 24 h. The solution was transferred into Teflon-lined autoclave and heated under hydrothermal conditions at 453 K for 24 h. The resultant powder was washed by deionized water several times, followed by dried at 363 K overnight. Finally, to remove TPA ions (structure directing agent), calcination under air was performed at 823 K for 5 h.

To load Pt nanoparticles on silicalite-1, 10 mM Pt nanoparticles-dispersed solution (particle size: 1–6 nm, Renaissance Energy Research) was used as a Pt source. The synthesized silicalite-1 (1.5 g) was added into the Pt nanoparticles-dispersed solution (7.5 mL). The solution was evaporated at 363 K. The dried mixture powder was calcined at 823 K for 5 h. The obtained sample was donated as Pt/s-1.

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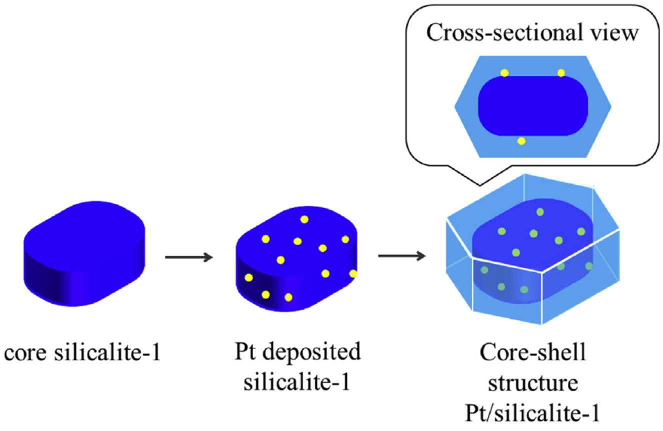

Scheme 1. Fabrication method of core-shell structure Pt/silicalite-1.

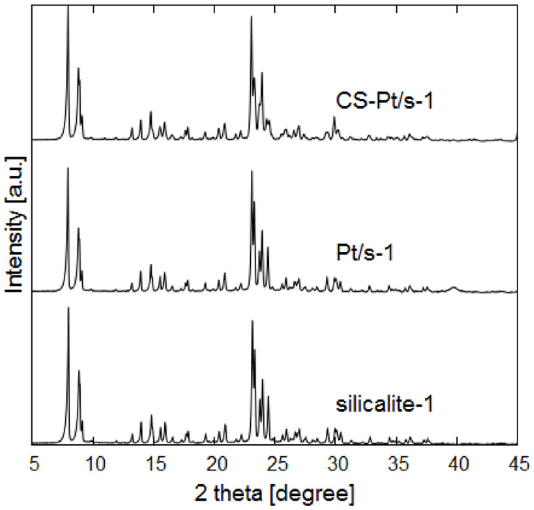

Fig. 1. XRD patterns of silicalite-1, Pt/s-1 and CS-Pt/s-1.

Fumed silica (Aldrich), TPAOH, ethanol (EtOH, Wako Pure Chemical Industries Co.) and deionized water were used for silicalite-1 coating. The molar ratio of the precursor was 1 SiO_2: 0.08 TPAOH: 16 EtOH: 240 H_2O. The above solution was stirred at room temperature for 1 h. Then, Pt/s-1 was added to the resulting solution, and the solution was placed in a Teflon-lined autoclave and heated under hydrothermal conditions at 453 K for 24 h with rotation (3 rpm). The resultant powder was washed by deionized water several times and then dried at 363 K and was calcined at 823 K for 5 h. The sample was donated as CS-Pt/s-1.

X-ray diffraction (XRD) measurements, Energy dispersive X-ray spectrometry (EDX) analysis and Transmission Electron Microscope (TEM) observations were carried out for the Pt/s-1 and CS-Pt/s-1 samples.

Hydrogenation of mesitylene, *n*-hexene and cyclohexene was performed using a fixed bed reactor. The mesitylene vapor was balanced by H_2 and fed by a saturator. The partial pressure of mesitylene was 162 Pa, and the contact time ($W/F_{mesitylene}$) was 58.2 g h/mol. As for the hydrogenation of *n*-hexene and cyclohexene, the vapor was balanced by 50% He and 50% H_2 (v/v) and fed by a saturator. The partial pressure of *n*-hexene and cyclohexene was 8.0 kPa, and the contact time (W/F_{hexene}) was 14.2 g h/mol.

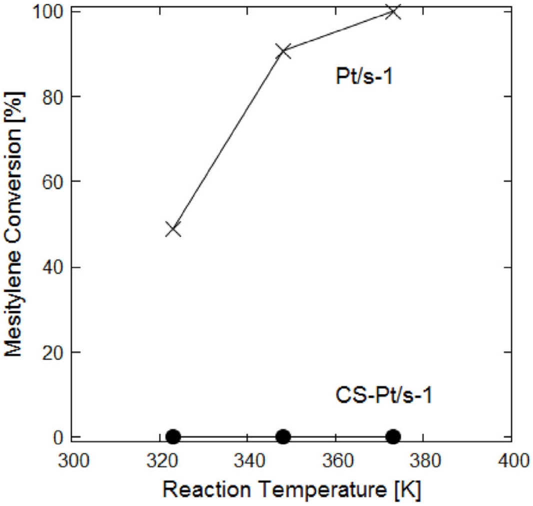

Fig. 3. Conversion of mesitylene on hydrogenation over Pt/s-1 and CS-Pt/s-1.

3. Results

XRD patterns were shown in Fig. 1. The peaks derived from Pt were not clearly observed even in the XRD patterns of uncoated Pt/s-1. This is because the amount of Pt was very low and the particle size of Pt was very small. The XRD pattern of CS-Pt/s-1 was similar to those of silicalite-1 and Pt/s-1, and the intensity was also similar, indicating that amorphous silica was not formed even after the silicalite-1 coating.

TEM images were shown in Fig. 2. Pt nanoparticles were observed on the external surface of silicalite-1 crystals for Pt/s-1 (Fig. 2(b)). Meanwhile, Pt nanoparticles were not clearly observed on the external surface of core-shell silicalite-1 crystals for CS-Pt/s-1 (Fig. 2(c)) although the presence of Pt was confirmed by an EDX analysis, which indicates that Pt nanoparticles were encapsulated in single crystal like silicalite-1. Crystalline boundary lines between the core and shell crystals were observed, suggesting that crystalline overgrowth occurs successfully and the surface of the core silicalite-1 was fully covered with the shell silicalite-1 layer. The Pt nanoparticles seem to locate in the core-shell crystalline boundary.

To confirm the encapsulation of Pt nanoparticles, we performed hydrogenation of mesitylene. The molecular size of mesitylene was larger than MFI zeolitic micropores [39,40]. Therefore, hydrogenation of mesitylene does not occur if Pt nanoparticles are completely covered with silicalite-1 layers. The result of hydrogenation of mesitylene was

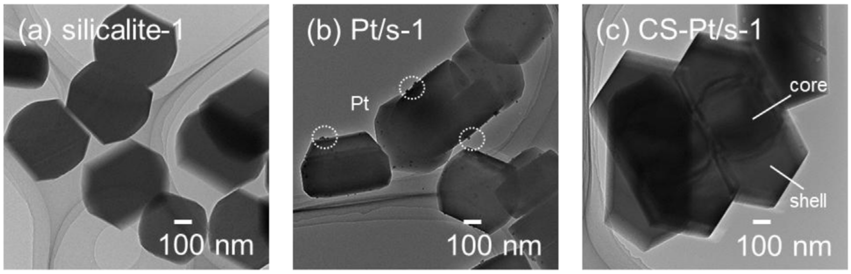

Fig. 2. TEM images of silicalite-1, Pt/s-1 and CS-Pt/s-1.