

Synthesis of Birdcage-type zeolite encapsulating ultrafine Pt nanoparticles and its application to dry reforming of methane

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Highlights

- Birdcage-type Pt@Silicalite-1 catalyst was prepared by a w/o microemulsion method.
- Pt nanoparticles with < 2 nm diameter were encapsulated in MFI zeolite particles.
- Pt@Silicalite-1 showed high and stable catalytic activity for DRM at 620 °C over 24 h.
- Birdcage structure efficiently suppressed sintering of Pt nanoparticles.

1. Introduction

Zeolite supported metal catalysts are widely used in many industrial processes. However, the metals on the pore surface of zeolite prepared by conventional impregnation method easily aggregate to form large particles on the external surface of zeolite during catalytic reactions, leading to catalytic deactivation and to lose molecular-sieve ability of zeolite. To overcome this problem, we have proposed Birdcage-type zeolite catalyst encapsulating ultrafine metal nanoparticles (NPs). Since the metal NPs are surrounded with zeolite, it is expected that the sintering of metal NPs is physically hindered, so that the thermal stability of catalysts is improved. In this research, Birdcage-type zeolite catalysts encapsulating Pt NPs were prepared emulsion method, in which Pt NPs were prepared in w/o microemulsion, followed by addition of zeolite sources and hydrothermal treatment^[1,2]. The obtained Birdcage zeolites were applied for dry reforming of methane (DRM) to investigate the catalytic activity of the prepared catalysts.

2. Methods

Two types of 0.1 wt% Pt loaded zeolite catalysts, Birdcage type zeolite (Pt@Silicalite-1) and impregnated catalyst (Pt/Silicalite-1), were prepared. Pt@Silicalite-1 was synthesized in a w/o microemulsion. First, the microemulsion was prepared by adding aqueous H₂PtCl₆ into surfactant and organic solvent mixture solution consisting of polyoxyethylene (15) oleyl ether and cyclohexane. After 1 h of stirring, hydrazine and polyvinylpyrrolidone aqueous solution were added to the microemulsion to form Pt NPs, followed by addition of tetraethyl orthosilicate (TEOS) as Si source and tetrapropylammonium hydroxide (TPAOH) as OSDA to form zeolite on the surface of Pt NPs. The solution was poured into Teflon-sealed stainless steel autoclave and heated to 100 °C for 72 h. The precipitate thus obtained was centrifuged, washed with isopropanol, dried at 110 °C overnight, and calcined at 550 °C for 12 h. Pt/Silicalite-1 was prepared by a conventional impregnation method. For the prepared catalysts, the morphology of zeolite, BET surface area, and Pt particle size were measured by an X-ray diffraction spectrometer (XRD), N₂ physisorption isotherm at -196 °C, and a transmission electron microscopy (TEM), respectively.

Dry reforming of methane was carried using a fixed-bed flow reactor at ambient pressure. The catalyst was pretreated in 10 % H₂ containing nitrogen stream at 670 °C for 1 h and then cooled to 620 °C in nitrogen stream. The reactant gas (CH₄/CO₂/Ar/He = 2/2/4/1) was fed to the reactor at the predetermined flow rate to fix the W/F value at 1.1 h g-catalyst/g-CH₄. The effluent was analyzed by an on-line gas chromatograph equipped with a thermal conductivity detector. Carbon balances were closed with deviations lower than 2 %.

3. Results and discussion

The XRD pattern for Pt@Silicalite-1 corresponded to that for MFI type zeolite as shown in **Figure 1**. N₂ physisorption isotherms showed that Pt@Silicalite-1 had well-developed micropores and BET surface area of 362 m²/g. **Figure 2 (a) and (b)** show TEM photographs of the obtained samples. While the Pt particles

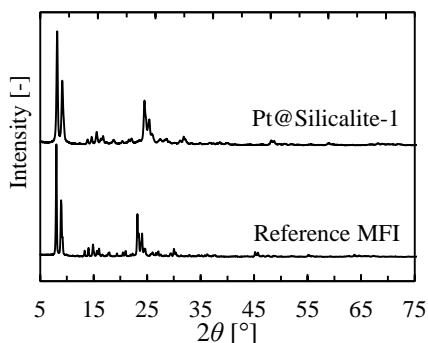


Figure 1. XRD patterns for Pt@Silicalite-1

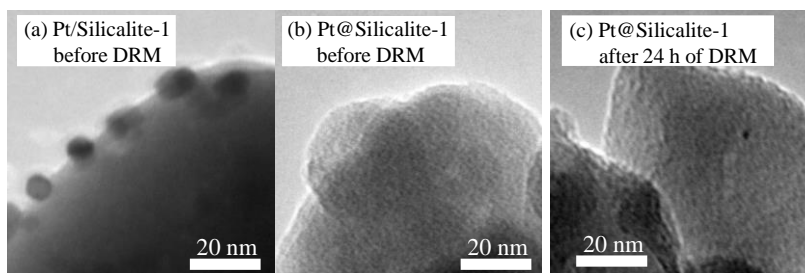


Figure 2. TEM images of the prepared catalysts before and after DRM

with the diameter larger than 10 nm were observed on the external surface of zeolite support in Pt/Silicalite-1, the Pt NPs with the diameter of < 2 nm were finely dispersed within zeolite particles for Pt@Silicalite-1. Accordingly, the Pt@Silicalite-1 catalyst with Birdcage structure is successfully obtained using microemulsion method.

Figure 3 shows the conversion of methane over the prepared catalysts at $620\text{ }^{\circ}\text{C}$. Pt/Silicalite-1 showed almost no activity due to the large particle size of Pt. In contrast, although the conversion of methane over Pt@Silicalite-1 was slightly decreased at the initial reaction time, the catalyst exhibited the stable activity for 24 h. The sintering of Pt particle was partly observed. The decrease in the conversion of methane during the initial reaction time was ascribed to the slight sintering of Pt, the size of which was approximately less than 8 nm. However, it was found that the Pt NPs remained small with the size of approximately 2 nm after the 24 h of DRM reaction at $620\text{ }^{\circ}\text{C}$ as shown in Figure 2(c). Since the Pt NPs in Pt@Silicalite-1 were surrounded with Silicalite-1 zeolite, the immobilized Pt NPs possess strong resistance to sintering. Moreover, the stable activity of DRM shown in Figure 3 indicates that the reactants CH_4 and CO_2 diffuse through the zeolitic pore of Silicalite-1 and effectively reach on the active sites of Pt surface.

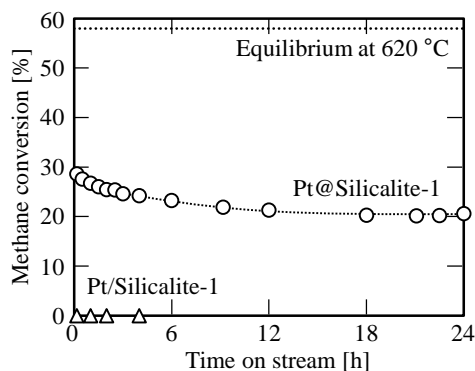


Figure 3. CH_4 conversion over the prepared catalysts. $T = 620\text{ }^{\circ}\text{C}$, $W/F = 1.1\text{ h g-cat./g-CH}_4$

4. Conclusions

Birdcage-type MFI zeolite encapsulating Pt NPs with the diameter of < 2 nm was successfully prepared in a microemulsion. Birdcage-type Pt@Silicalite-1 showed stable and high activity for DRM at $620\text{ }^{\circ}\text{C}$ over 24 h. Pt NPs in Birdcage-type Pt@Silicalite-1 are encapsulated in zeolite structure and prevented from sintering, resulting in a high activity and high thermal stability.

References

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Keywords

Birdcage-type zeolite, Thermal stability, Dry reforming of methane