

Influence of porous properties on mesoporous silica supported Pt catalysts for cinnamaldehyde hydrogenation in supercritical CO₂

Taichi Shimizu, Masaki Ota, Yoshiyuki Sato, Hiroshi Inomata*

Research Center of Supercritical Fluid Tech., Graduate School of Engineering, Tohoku University,
6-6-11-404 Aoba, Aramaki, Aoba, Sendai, 980-8579, JAPAN
inomata@scf.che.tohoku.ac.jp, +81-22-795-7283

ABSTRACT

Platinum catalysts for hydrogenation were effectively confined in the mesopores of MCM-41 and MSU-H silica by using supercritical CO₂ as impregnation solvent. After impregnation, calcination step was conducted to control the size of platinum particles, and the influence of calcination probably depended on the pore structure of mesoporous silica. The catalysts were characterized by nitrogen adsorption and transmission electron microscopy (TEM). While big and irregular platinum particles produced on MCM-41 with relatively small pore size (2.7 nm) upon calcination at 873 K, homogeneous and small platinum nanoparticles maintain inside MSU-H with relatively large pore size (8.4 nm). The hydrogenation of cinnamaldehyde using the catalysts was carried out in supercritical CO₂. Pt/MCM-41 which was calcined at 873 K displayed the highest catalytic activity.

INTRODUCTION

Metal nanoparticles on mesoporous silica have been considered as one of the future hybrid functional catalysts possessing highly active and selective reaction capabilities. Wakayama *et al.* firstly reported that supercritical CO₂ can be a good solvent to allow metal precursors penetrating into mesoporous silica due to its high diffusivity and low surface tension, leading to better dispersion of penetrated metal [1]. Our group utilized this method could obtain highly dispersed cobalt catalysts [2]. This method could be considered to consist of three steps: (1) the dissolution of the metallic precursor in the supercritical CO₂, (2) adsorption of the metallic precursor on the substrate, (3) conversion of the precursor to its metal form by calcination or reduction. However, it is limited that the knowledge about the effect of porous structure on the size and thermal stability of metal nanoparticles supported on mesoporous silica. Furthermore, there have been few reports to investigate catalytic activities of the catalyst prepared by supercritical impregnation method. In this work, we examined the effect of calcination conditions on size of platinum particles on various types of mesoporous silica and conducted cinnamaldehyde hydrogenation to investigate catalytic activities.

MATERIALS AND METHODS

1. Catalyst Preparation

Experimental apparatus and procedure by supercritical impregnation method were described in our previous work [2]. In experiments, 0.055 g of Pt(acac)₂ was introduced into the reactor whose internal volume is 50 cm³. The basket containing 0.5 g of silica was first placed on the aluminum stage in the reactor, and then the reactor was set in the air bath. After the temperature reaching 333 K, CO₂ was pressurized up to 20 MPa using a high-pressure pump. The reaction time was assumed to be the elapsed time after reaching the desired pressure. During the reaction, the reactor contents were mixed mechanically using a magnetic stirrer. After 24 h, the system was gradually depressurized to atmospheric pressure in order to stop the reaction. The collected samples in the basket were calcined under air or inert (argon gas) condition in a muffle oven at 673-873 K and 3 h. The final material was named Pt/MCM-41(X) or Pt/MSU-H(X) representing the catalyst calcined at X K.

2. Catalytic activity measurement

The hydrogenation of cinnamaldehyde in supercritical CO₂ solvent was carried out in a 100 cm³ stainless steel batch reactor. 500 mg of catalyst and 2.0 g of the reactant were loaded into the reactor. The reactor was sealed, flushed with CO₂ at 2 MPa pressure for three times to remove air and maintained at 323 K for 90 min to stabilize the temperature. Hydrogen was firstly loaded into the reactor to a 4 MPa. After that, liquid CO₂ was charged into the reactor using a high-pressure liquid pump and then compressed to 9-18 MPa. The reaction mixture was stirred continuously with a magnetic stirrer during the reaction for 3 h. After the reaction, the reactor was cooled in ice-cold water to quench the reaction. The reaction products were analyzed using a gas chromatography equipped with FID.

RESULTS

1. Characterization of Catalyst Structure

Figure 1 shows TEM images of Pt/MCM-41 calcined under air or argon atmosphere. Aggregation of platinum particles was observed in Pt/MCM-41(air). On the other hand, highly dispersed platinum particles were observed in Pt/MCM-41(argon). The difference of dispersion between Pt/MCM-41(air) and Pt/MCM-41(argon) can be explained by the existence of PtO [3]. Pt(acac)₂ can decompose to PtO by calcination under air. When the temperature further increases, the small and mobile PtO particles merge which leads to a low metal dispersion because of the high mobility of PtO. On the other hand, PtO particles are not produced under argon condition, therefore Pt/MCM-41(argon) showed high metal dispersion.

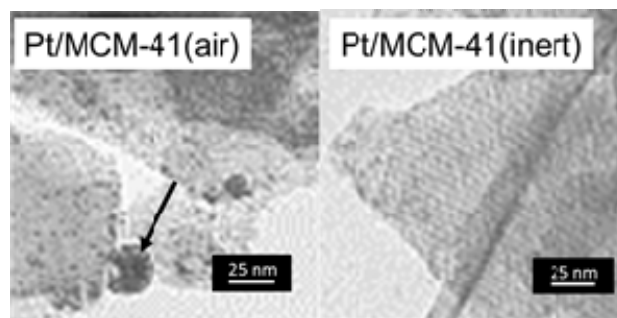


Figure 1 TEM images of Pt/MCM-41 catalysts calcined by air or inert gas (argon) at 473 K

Figure 2 and Figure 3 show TEM images of Pt/MCM-41 and Pt/MSU-H calcined at 473-873 K under argon atmosphere, respectively. The size of platinum particles increased with an increase of calcination temperature in each silica supports. This is because the increase of mobility of platinum particles with an increase calcination temperature. Compared with the size of platinum particles on each supports, Pt/MSU-H catalysts have relatively smaller platinum particles in comparison with Pt/MCM-41 catalysts. This tendency cannot explain the pore size of each supports because MSU-H has relatively larger pore size. The results of nitrogen adsorption showed MSU-H has micro pores of which size 0.8 nm. The micro pores might act as anchors of platinum particles, therefore Pt/MSU-H catalysts maintain the high dispersion of platinum.

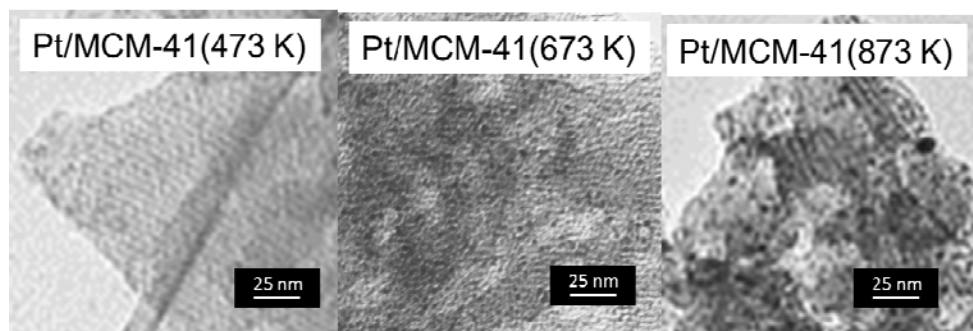


Figure 2 TEM images of Pt/MCM-41 catalysts calcined at 473-873 K under argon

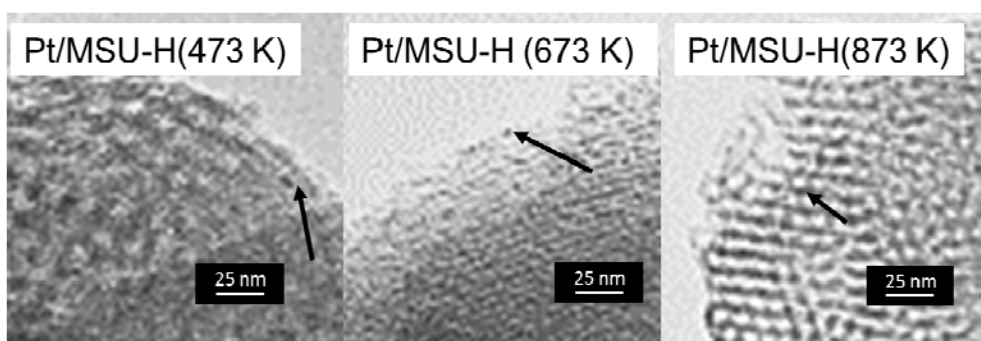


Figure 3 TEM images of Pt/MSU-H catalysts calcined at 473-873 K under argon

2. Catalytic Activity

Fig. 4 shows the effect of CO₂ pressure on catalytic activity. The conversion of CAL increased with an increase of CO₂ pressure until 10 MPa, and then decreased with a decrease with an increase in pressure. On the other hand, the selectivity to COL slightly increased with an increase of CO₂ pressure. Considering phase behavior, the reaction mixture exists in two phases from 5 MPa to 10 MPa, and then transforms into a single phase [4]. In the two phase region (5-10 MPa), the conversion increased with an increase of CO₂ pressure because of 'expanded liquid effect' described above. On the other hand, in the single phase region, the concentration of cinnamaldehyde decreased significantly compared with two phase region, leading to the decrease conversion above 12 MPa.

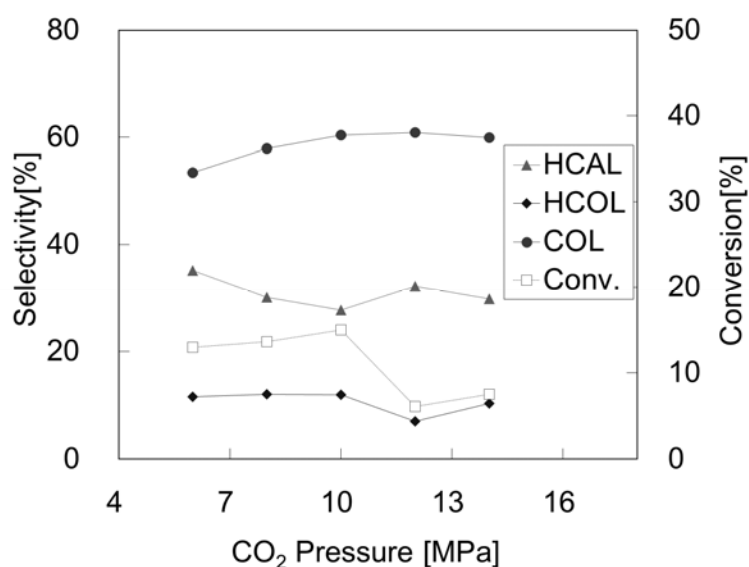


Figure 4 Effect of CO₂ pressure on catalytic activity of the Pt/MCM-41 catalyst calcined at 873 K (reaction conditions: catalyst 0.05 g, CAL 2 g, H₂ 4 MPa, 3 h)

Figure 5 and Figure 6 show catalytic activities of Pt/MCM-41 and Pt/MSU-H, respectively. The higher conversion was obtained by using the catalyst which has larger platinum particles in both Pt/MCM-41 and Pt/MSU-H catalysts. Englisch et al. mentioned that smaller Pt particles favored side reactions [5]. Smaller Pt particles can be more selective for the formation of byproduct due to electronic and steric effects. The electronic effect in small Pt particles, i.e. a decrease in electron density of the d-orbitals favors the interactions of both the double bonds in unsaturated aldehyde. Smaller metal particles, exhibiting low coordination, have more edges and corners compared to the larger Pt particles. These features of smaller platinum particles can attribute to the selectivity. Compared in the result of Pt/MCM-41 catalysts, Pt/MSU-H catalysts showed relatively lower conversions despite Pt/MSU-H catalysts have large pore size. Now we are investigating the reason why Pt/MSU-H showed lower catalytic activity by analyzing electron state of platinum surface, surface silanol density of silica, and so on.

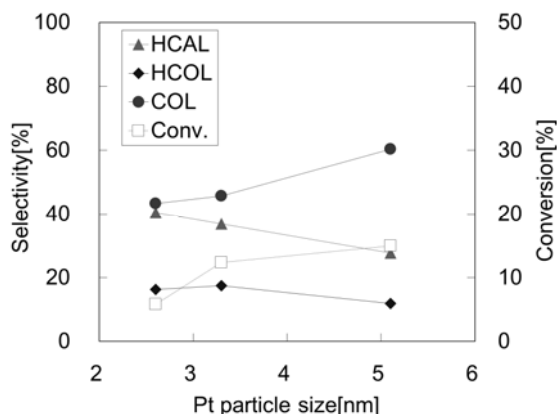


Figure 5 Catalytic activities of the Pt/MCM-41 catalysts (reaction conditions: catalyst 0.05 g, CAL 2 g, CO₂ 10 MPa, H₂ 4 MPa, 3 h)

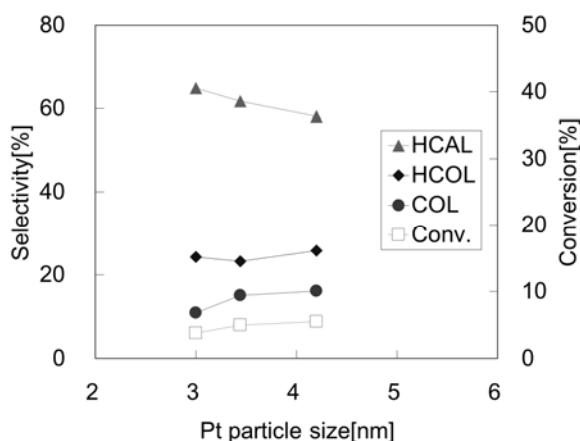


Figure 6 Catalytic activities of the Pt/MSU-H catalysts (reaction conditions: catalyst 0.05 g, CAL 2 g, CO₂ 10 MPa, H₂ 4 MPa, 3 h)

CONCLUSION

We demonstrated the preparation of platinum particles on the different silica supports using a supercritical CO₂. When MCM-41 with small pore size was used as support material, platinum nanoparticles migrate out easily and agglomerate on the external surface of the support. In MSU-H with larger pore size, generated platinum nanoparticles remain stable within the mesoporous channels. We have also conducted cinnamaldehyde hydrogenation with the obtained catalysts as a model reaction to investigate the catalyst structure. Pt/MCM-41 which is calcined at 873 K displayed the highest catalytic activity. The result indicates that larger size of platinum particles is better to get higher catalytic activity.

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