In-situ Synthesis of Zeolite with Encapsulated Pt and Its Hydrogenation Activity at High Levels of Sulfur

Song Chen*, Lianhui Ding, Jinwen Chen, Craig Fairbridge, Yu Shi

***Abstract*—In-situ synthesis of a zeolite with encapsulated Pt was conducted to prepare a sulfur-resistant noble metal catalyst based on concepts of shape selectivity and hydrogen spillover. The prepared zeolite was of the sodalite type, in which the pore openings allow H_2 to enter the pores but not H2S. Chemisorption with H_2/CO was conducted to verify the most of Pt atoms distribution in the cage of Pt/SOD prepared by hydrothermal method. The catalyst was tested for hydrogenation activity using light cycle oil with high contents of multi-ring aromatics and sulfur. The catalyst showed reasonable hydrogenation activity even at high levels of sulfur.**

***Index Terms*—hydrothermal synthesis, hydrogenation, Pt zeolite, sulfur resistance**

I. INTRODUCTION

Aromatics in diesel fuel have been considered as a source of environmental pollution due to incomplete combustion and the formation of soot particles [1]. Noble metal catalysts have excellent hydrogenation activity. However, they are very susceptible to poisoning by sulfur compounds [2-4]. In the past several decades many approaches have been explored to improve the sulfur resistance of noble metal catalysts [5-9].

Based on the concepts of shape selectivity and hydrogen spillover, a novel noble metal catalyst for hydrogenation and/or ring opening has been proposed in our research group [10]. The core of the concept is to enclose noble metal particles in zeolite with pore openings that allow access by H_2 but not by H_2S.

Theoretically, the size of zeolite pore openings required to suit the above-mentioned concept should be between the kinetic diameters of H_2 (0.289 nm) and H_2S (0.36 nm). Two zeolites, namely, modified zeolite A and Zeolite Rho (RHO), which have pore openings of about 0.41 nm and 0.36 nm[11], respectively, were selected to prove the concept [10, 12]. Sodalite (SOD) is another good candidate since it has a pore opening size of 0.28 nm.

This paper describes an in-situ hydrothermal synthesis method used to prepare a sodalite-based zeolite catalyst that was then used for hydrogenation of light cycle oil (LCO), a low-value middle distillate containing high levels of multi-ring aromatics and sulfur.

II. EXPERIMENTAL

A. *Zeolite synthesis*

A suspended gel was made by commixing a clear sodium aluminate aqueous solution, ammonium chloroplatinic acid, and 40 wt% SiO_2 colloidal hydrogel, with vigorous stirring for 1 h at room temperature. The mixture was then transferred into an autoclave that was kept at 140°C for 168 h. After crystallization, the solid product was filtered, washed, dried, and calcined at 400°C for 8 h. The final product was designated as Pt/SOD. As referring sample, ion exchange Pt-NaA is prepared by ion-exchanged NaA (Aldrich 4A) with $Pt(NH_3)4Cl_2 \cdot H_2O$ aqueous solution at 50°C for 3h. The exchanged solid was washed , dried, and calcined at 400°C for 8 h.

B. *Characterization*

The crystalline phases of the synthesized Pt/SOD sample were characterized by powder XRD using a Bruker D8 Advanced Instrument equipped with twin Co X-ray monochromating parabolic mirrors on the incident and diffracted beam sides. High-resolution field emission SEM (FESEM) was performed using a Hitachi S-4800 field-emission scanning electron microscope with voltages ranging from 0.5 to 30 kV. The bulk Pt elemental composition was measured by inductively coupled plasma–mass spectrometry (ICP-MS). Pt distribution on the zeolite surface was also determined by transmission electron microscopy (TEM) on a JEOL 2010 STEM, operated at 200keV. H_2 and CO chemisorption was performed using a Micromeritics ASAP 2010C unit. Before doing chemisorption, the reduction was carried out by flowing hydrogen at 400°C for 6 h (5 °C /min ramp rate) and the system was evacuated at 300°C for 60 min. The method published by Prado-Burguete et al. was used to calculate the hydrogen and CO uptakes as well as metal dispersion [13]. Therefore, the linear portion of the isotherm in the pressure range from 300 to 600 mmHg was extrapolated to zero pressure to determine the hydrogen uptake and metal dispersion.

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Song Chen is with Upgrading Program, CanmetENERGY, Natural Resources Canada, Devon, AB, Canada T9G1A8 (corresponding author to provide phone: 780-987-8713; fax: 780-987-5349; e-mail: song.chen@nrcan-rncan.gc.ca).

Lianhui Ding is with Upgrading Program, CanmetENERGY, Devon, AB, Canada T9G1A8 (e-mail: lianhuiding@nrcan-rncan.gc.ca).

Jinwen Chen is with Upgrading Program, CanmetENERGY, Devon, AB, Canada T9G1A8 (e-mail: jinwen.chen@nrcan-rncan.gc.ca).

Craig Fairbridge is with Upgrading Program, CanmetENERGY, Devon, AB, Canada T9G1A8 (e-mail: craig.Fairbridge@nrcan-rncan.gc.ca).

Yu Shi is with Upgrading Program, CanmetENERGY, Devon, AB, Canada T9G1A8 (e-mail: yu.shui@nrcan-rncan.gc.ca).

C. *Catalyst preparation*

Large-pore alumina, MoO_3, $Ni(NO_3)_2{\cdot}6H_2O$, and the prepared Pt/SOD were mixed evenly. An micro-pore alumina binder and an appropriate amount of water were added to make an extruding paste, which was extruded to form a cylindrical catalyst of 1.2mm diameter. The extrudate was broken into small pieces (about 5 mm long), dried in an oven at 110°C overnight, and calcined at 500°C for 4 h.

D. *Hydrogenation Activity Tests*

The hydrogenation activity tests were conducted using a fixed-bed bench-scale reactor. The high-pressure reaction setup used in this study simulates the process that takes place in industrial hydrotreaters. Three (3) mL of the prepared catalyst was crushed to 30–80 mesh and diluted with 36-mesh silicon carbide at a 1:1 volumetric ratio for loading into the middle of the reactor (a stainless steel tube 6 mm in diameter and 400 mm in length). At start-up, the catalysts were reduced in flowing H_2 at 400°C for 16 h. The reactor was pressurized to 880 psi and the LCO feed was then pumped into the reactor at a flow rate of 5.4 g/h with an H_2 flow rate of 4.8 NL/h at a reaction temperature of 320°C. after lined out for 24h, pilot installment collect product for 24h. The total liquid products were characterized following: simulated distillation (ASTM D-2887); hydrocarbon types by GC-MC (using specially configured gas chromatograph with a prefractionator and mass spectrography); boiling-point distributions of sulfur (using a GC with a Sievers sulfur chemiluminescence detectorsGC-SCD).

III. RESULTS AND DISCUSSION

Figure 1 illustrates the XRD profiles of Pt/SOD. The five characteristic peaks of the sodalite occur at 2θ 16.3°, 28.5°, 40.8°, 44.2°, and 50.6°. The XRD profile shown in Figure 1 indicates the successful in-situ hydrothermal synthesis of Pt-containing sodalite.

To enhance the catalyst activity and sulfur resistance, it is of great importance to obtain highly dispersed noble metal clusters inside the sodalite. Figure 2 shows the morphology of the Pt/SOD prepared by in-situ hydrothermal synthesis. The morphology of Pt/SOD is a homogeneous cloud form, which is different from the ball form of pure sodalites [14]. No significant agglomeration of Pt clusters is observed at the surface of the zeolite crystal grains, which was probably supported by no significant peak occurred at the characteristic peaks of Pt.

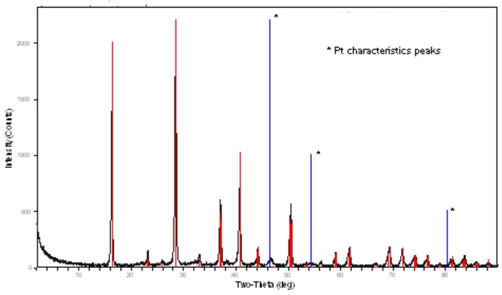


Figure 1. XRD result of Pt/SOD samples (synthesized by in-situ hydrothermal method)

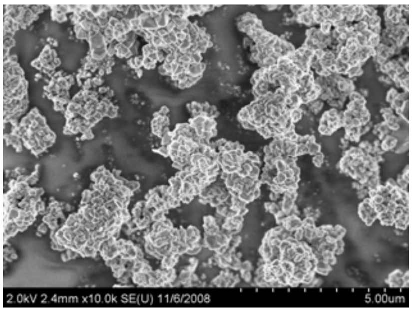
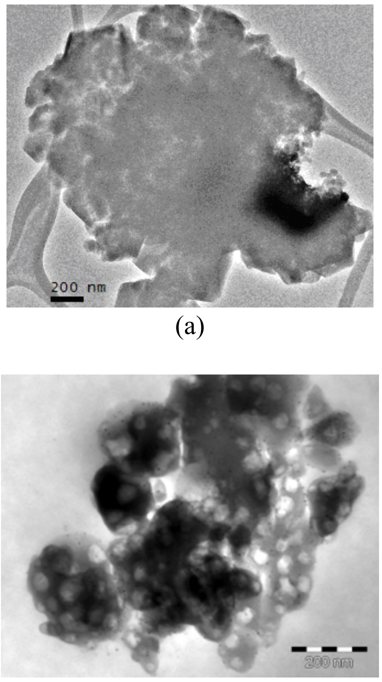


Figure 2. SEM photo of Pt/SOD prepared by in-situ hydrothermal synthesis.

The encapsulation of Pt in the sodalite can be inferred in the TEM image in Figure 3 (a), compared to the ion-exchanged Pt/NaA in Figure 3 (b) in which concentrated Pt clusters (dark spots) are observed at the surface. In Figure 3 (a) the subnanometer-sized Pt precursors most likely are constrained inside the cages of the zeolite, as no concentrated Pt clusters are observed in the image.

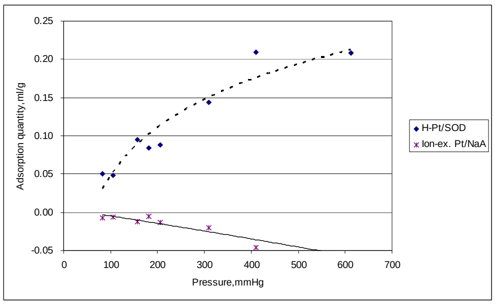


(a)

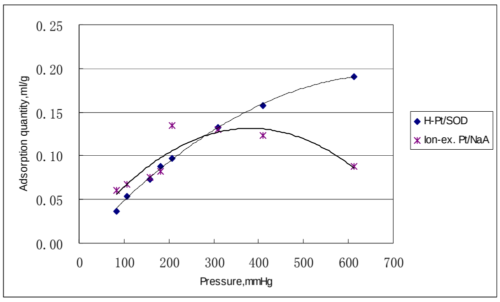
(b)

Figure 3. TEM photos: (a) Pt/SOD prepared by in-situ hydrothermal synthesis, (b) Pt/NaA prepared by ion exchange

The H_2 and CO chemisorptions for the Pt/SOD prepared by in-situ hydrothermal synthesis at 300°C are shown in Figure 4. The adsorption of H_2 increases almost monotonically with pressure for Pt/SOD while that for Pt/NaA prepared by ion-exchange shows completely different trends.



(a) H_2 Chemisorption



(b) CO Chemisorption

Figure 4. Chemisorption result at the temperature of 300°C

The kinetic diameters of H_2 and CO are 1.36Å and 2.8 Å, respectively. Theoretically, the pore openings of sodalite will allow H_2 to enter the cages, but not CO, since they are also about 2.8 Å in size. This suggests that the Pt particles in Pt/SOD are mainly in the sodalite cages while the Pt particles in ion-exchanged Pt/NaA are extensively distributed both inside and outside the sodalite cages, as verified by the reverse trends of adsorption shown in Figure 4 and Table 1. Ion-exchanged Pt/NaA has maximum CO chemisorption while Pt/SOD has maximum H_2 chemisorption.

Table 1 H_2/CO chemisorption amount

Item	Pt wt%	H_2* mL/g	CO* mL/g
Ion-exchanged Pt/NaA	0.65	0.050	0.180
H-Pt/SOD	0.67	0.210	0.040

* H_2/CO chemisorption at 300°C

LCO is a low-value product from fluid catalytic cracking (FCC) that contains high levels of multi-ring aromatics and sulfur. In this study, LCO was used as the feed to evaluate the hydrogenation activity of sodalite catalyst with encapsulated Pt at high levels of sulfur. As shown in Table 2, the hydrogenated product has a sulfur content of 1240 ppm, much higher than the 50 ppm value generally considered as the sulfur tolerance level of noble metal catalysts. Therefore this Pt catalyst (at reduced state) displays reasonable hydrogenation activity after high levels of sulfur exposure. As seen in Figure 5, while the reduced Pt catalyst has a certain capacity of hydrodesulfurization, the mono-aromatic content in the product increases while with the di-, tri-, and tetra-aromatic contents decrease, suggesting that the hydrogenation activity of the reduced catalyst remains reasonably high after high levels of sulfur exposure.

Table 2. Hydrogenation activity test results

Item	LCO	Product
Density, g/cm^3	0.9733	0.9659
Liquid yield, wt%		98.8
Aromatics, wt%		
S, ppm	2030	1240
N, ppm	285	222
Distillation, °C		
IBP	143.8	143.8
30%	254.4	253.6
50%	285.2	282.4
70%	328.2	324.6
FBP	503.8	453.6

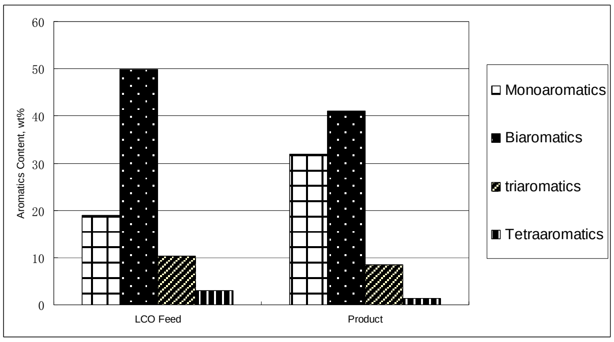


Figure 5. mono-, di-, tri- aromatic contents in the feed tested and hydrogenated product

IV. CONCLUSION

A zeolite catalyst with encapsulated Pt was prepared by in-situ hydrothermal synthesis, based on the concepts of shape selectivity and hydrogen spillover, and tested for hydrogenation activity and sulfur resistance. It was concluded that Pt was mainly encapsulated inside cages of the sodalite, which has the right size of pore opening to allow H2 to enter the cages, but not H_2S. Various characterizations, including H_2/CO chemisorption, SEM/TEM, and XRD, were performed to confirm the distribution of Pt inside the sodalite cages. Hydrogenation activity tests using LCO as the feed demonstrated reasonable activity of the prepared catalyst even after high levels of sulfur exposure..

REFERENCES

[1] A. Juva, A. Rautiola, P. Saikkonen, D. Le Breton, Preprints of the 13th World Petroleum Congress, Buenos Aires, Argentina, 1991.
[2] J. Barbier, E.Lamy-Pitara, P. Marecot, J. Boitiaux, J. Cosyns, F. Verna, Adv. Catal. 37 (1990) 279.
[3] C.H. Bartholomew, P.K. Agrawal, J.R. Katzer, Adv. Catal. 31 (1982) 135.
[4] J.T. Miller, D.C. Koningsberger, J. of Catal. 162 (1996) 209.
[5] R.A. Dalla Betta, M. Boudart, Proceeding of the fifth international congress on catalysis, Miami Beach, FL, 20-26 August 1972. 1329-1341.
[6] C. Song, A. Schmitz, Energy & Fuels 11 (1997) 656-661.

[7] T., B. Lin, C. A., Jan, J. R. Chang, 1995. Ind. Eng. Chem. Res. 34 (1995) 4284-4289.

[8] H. Yasuda, Y. Yoshimura, Catalysis Letters 46 (1997) 43-48.

[9] T. Fujikawa, K. Idei, K. Ohki, H. Mizuguchi, K. Usui, Applied Catal. A, 205 (2001) 71-77.

[10] H. Yang, H. Chen, J. Chen, O. Omotoso, Z. Ring, J. of Catal. 243 (2006) 36-42.

[11] H.W. Langmi et al., Journal of Alloys and Compounds, 356–357 (2003) 710–715

[12] H. Chen, H. Yang, O. Omotoso, L. Ding, Y. Briker, Y. Zheng, Z. Ring, Applied Catal. A, 358 (2009) 103-109.

[13] C. Prado-Burguete, A. Linares-Solano, F. Rodriguez-Eeinoso, C. Salinas-Martinez De Lecea, J. Catal. 128 (1991) 397.]

[14] Fechtelkord M. ,Microporous and Mesoporous Materials 28 (1999) 335–351.