

# A comparative study of the synthesis approaches and catalytic behaviors of $\text{Pt}/\text{SO}_4^{2-}/\text{ZrO}_2\text{—Al}_2\text{O}_3$ catalysts for *n*-hexane hydroisomerization

G.X. Yu<sup>a</sup>, X.L. Zhou<sup>a,\*</sup>, C. Tang<sup>a</sup>, C.L. Li<sup>a</sup>, J.A. Wang<sup>b</sup>, O. Novaro<sup>c</sup>

<sup>a</sup> *Petroleum Processing Research Center, East China University of Science and Technology, 200237 Shanghai, PR China*

<sup>b</sup> *Laboratorio de Catálisis y Materiales, ESIQIE, Instituto Politécnico Nacional, Col. Zacatenco, 07738 México DF, Mexico*

<sup>c</sup> *Instituto de Física, Universidad Nacional Autónoma de México, A. P.20-364, 01000 México DF, Mexico*

Received 13 December 2007; received in revised form 30 January 2008; accepted 10 February 2008

Available online 15 February 2008

## Abstract

Four Al-promoted  $\text{Pt}/\text{SO}_4^{2-}/\text{ZrO}_2\text{—Al}_2\text{O}_3$  (denoted as PtSZA) catalysts were prepared through different approaches to introduce alumina, including co-precipitation (CP), shaping (SH), suspension (SU) and mixing methods (MI). The effects of alumina incorporation methods to zirconia on the structure, surface acidity, reduction of the sulfur species and catalytic performance of PtSZA catalysts were studied. The results showed that PtSZA from SH introduction of alumina has better crystallization, better Pt promotion effect and higher catalytic performance in *n*-hexane hydroisomerization compared to the samples from other alumina introductions. Aluminum introduction method is a crucial step to prepare a PtSZA catalyst for *n*-hexane isomerization.

© 2008 Elsevier B.V. All rights reserved.

**Keywords:**  $\text{Al}_2\text{O}_3$  introduction method; *n*-hexane isomerization; Al-promoted sulfated zirconia; Shaping method

## 1. Introduction

Among solid acids, Sulfated zirconia (SZ) has attracted intense attention for its super strong acidity and activities in the catalysis of alkane isomerization at relatively mild conditions [1]. For this reason a large number of research works were focused on this catalyst and many reviews are available [2–5]. Nevertheless, SZ showed rapid deactivation during catalytic reactions. A number of transition metals promoters (e.g. Fe, Mn, and Ni) have been added to SZ, resulting in catalysts with higher activity than unmodified SZ [6]. However, rapid deactivation was still observed [7–9] and the marked promoting effect disappeared if the reaction was performed at temperatures higher than 250 °C [10,11].

Platinum loading on sulfated zirconia (SZ) would only significantly inhibit the formation of coke and thus improve the stability [12]; however, Gao [10] once reported that sulfated zirconia promoted by a little amount of alumina by CP exhibited excellent catalyst activity and also improved stability at high temperature higher than 250 °C for *n*-butane hydroisomerization. Since then, many contributions on Al-promoted zirconia (SZA) have been published [13–18], which confirmed that the introduction of alumina by CP or SU or MI could improve SZA catalyst activity and stability for alkane hydroisomerization. Platinum was also reported to be a good promoter to increase acidity as well as dehydrogenation–hydrogenation ability and therefore improve the activity for alkane isomerization [19]. SZ catalysts are in powdered form and its mechanical properties of pure extrudates are rather poor. To prepare an industrial hydroisomerization catalyst with better mechanical strength, incorporation of alumina and platinum to SZ to prepare Pt–Al-promoted SZ catalysts is

\* Corresponding author. Tel.: +86 21 64253049; fax: +86 21 64252041.  
E-mail address: [prrc\\_zy@ecust.edu.cn](mailto:prrc_zy@ecust.edu.cn) (X.L. Zhou).

necessary. However, catalytic performance of a PtSZA catalyst by shaping  $\text{Al}_2\text{O}_3$  and  $\text{Zr}(\text{OH})_4$  followed by sulfated (a detailed preparation method is given in Section 2) was not reported, and comparison of PtSZA catalyst performances, prepared through different alumina introduction methods were not systematically addressed yet.

In the present contribution, a PtSZA preparation method by alumina SH introduction was reported, and to compare the effect of alumina introduction methods on PtSZA catalysts, several preparation methods were applied for PtSZA catalyst preparation, including: co-precipitation, shaping, suspension and mixing methods, the other preparation parameters, such as pH value, drying and calcination temperatures, platinum content and impregnation conditions as well as  $\text{Al}_2\text{O}_3$  contents, remain the same. The effects of alumina incorporation methods to zirconia on the structure, surface acidity, reduction of the sulfur species and catalytic performance of PtSZA catalysts were studied. We found that  $\text{Al}_2\text{O}_3$  introduction methods have significant effect on PtSZA catalysts for *n*-C<sub>6</sub> hydroisomerization and a PtSZA catalyst from alumina SH introduction has higher catalytic performance than those from other alumina introductions.

## 2. Experimental

### 2.1. Sample preparation

The four samples were prepared by different methods to introduce  $\text{Al}_2\text{O}_3$  under the same preparation conditions, including pH in precipitation step, drying and calcination temperatures as well as  $\text{Al}_2\text{O}_3$  and Pt contents and impregnation conditions for the latter etc.

$\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  and  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  were dissolved in water. A 26% ammonia solution was dropwise added into the above solution at a rate of 0.5 ml/min up to pH of 10. The solution and precipitate was filtered after ageing at 338 K for 24 h. The obtained precipitate was washed with distilled water until the disappearance of chloride ions ( $\text{AgNO}_3$  test), dried overnight at 383 K for 24 h and then pulverized to particles below 290  $\mu\text{m}$ . Sulfation procedure was carried out by impregnation method with 0.5 M of  $\text{H}_2\text{SO}_4$  solution (15 ml/g) under continuous stirring at room temperature for 12 h. The sulfated  $\text{Al}(\text{OH})_3\text{—Zr}(\text{OH})_4$  was filtered without washing then dried overnight at 383 K and calcined at 873 K for 5 h. Subsequently, the above product was impregnated with  $\text{H}_2\text{PtCl}_6$  solution using the incipient wetness technique. At last, it was dried overnight

at 383 K before the final calcination at 773 K for 3 h. The sample was designated as CP15 by  $\text{Al}_2\text{O}_3$  introduction method where the number denoted alumina weight percent.

$\text{Zr}(\text{OH})_4$  was obtained by adding ammonia solution and then  $\text{Al}_2\text{O}_3$  ( $\gamma\text{-Al}_2\text{O}_3\text{H}_2\text{O}$ , 400 mesh) and  $\text{Zr}(\text{OH})_4$  were shaped (or kneaded). Other procedures and related conditions were the same as that for CP15 and the prepared sample in this method was designated as SH15 where the number denoted alumina weight percent.

$\text{Al}_2\text{O}_3$  ( $\gamma\text{-Al}_2\text{O}_3\text{H}_2\text{O}$ , 400 mesh) in powder form was mixed with  $\text{ZrOCl}_2$  solution and then  $\text{Al}_2\text{O}_3\text{—Zr}(\text{OH})_4$  was obtained by adding ammonia solution. Other procedures and related conditions were the same as that for CP15; so the prepared sample was designated as SU15 where the number denoted alumina weight percent.

SZ was first obtained and the SZ was shaped with  $\text{Al}_2\text{O}_3$  ( $\gamma\text{-Al}_2\text{O}_3\text{H}_2\text{O}$ , 400 mesh). The obtained solid was impregnated with  $\text{H}_2\text{PtCl}_6$  solution and then calcined. Other related preparation conditions were the same as that for CP15. So prepared sample was designated as MI15 where the number denoted alumina weight percent.

### 2.2. Characterization of catalysts

Compositions, textural properties and sulfur contents of all the samples by above four methods to introduce  $\text{Al}_2\text{O}_3$  were listed in Table 1.  $\text{N}_2$  adsorption–desorption isotherms were determined with a Micromeritics ASAP 2010 instrument. The total sulphur content of each sample was analyzed with a microcoulometer by the combustion method. The powder X-ray diffraction patterns (XRD) were recorded on a Rigaku D/Max 2550 X using  $\text{Cu K}\alpha$  ( $\lambda = 0.154 \text{ nm}$ ) radiation in a operating mode of 40 kV and 30 mA. Data were collected from  $2\theta = 20\text{--}80^\circ$  in steps of  $0.02^\circ/\text{s}$  in order to gain textural information about the crystalline phase of catalysts. A pyridine adsorption-FTIR spectroscopic technique on a Nicolet Magna-IR 550 spectrometer was also used for acidic property measurements. The sample was pressed to a 15 mm plate and put in a wafer. It was degassed in vacuum of  $10^{-4}$  Torr at  $450^\circ\text{C}$  for 2 h and lowered the temperature to  $200^\circ\text{C}$ . Pyridine was adsorbed for 10 min and took 30 min for equilibrium. Then it was scanned after being vacuumed for 40 min. Then raised the temperature to  $300^\circ\text{C}$  and recorded after 10 min for equilibrium. Same procedures were performed for  $400^\circ\text{C}$  and  $450^\circ\text{C}$ . The number of Brönsted and Lewis acid sites was calculated according to the integral area of the bands at  $1540 \text{ cm}^{-1}$  and  $1450 \text{ cm}^{-1}$ , respectively. TPR

Table 1  
Composition, tissue structure and surfur content of catalysts

| Sample | $\text{Al}_2\text{O}_3\%$ (wt) | Pt% (wt) | BET surface area ( $\text{m}^2 \text{ g}^{-1}$ ) | Total pore volume ( $\text{cm}^3 \text{ g}^{-1}$ ) | Average pore diameter (nm) | S% (wt) |
|--------|--------------------------------|----------|--------------------------------------------------|----------------------------------------------------|----------------------------|---------|
| CP15   | 15.0                           | 0.5      | 139                                              | 0.13                                               | 4.0                        | 3.23    |
| SU15   | 15.0                           | 0.5      | 138                                              | 0.17                                               | 5.0                        | 1.85    |
| SH15   | 15.0                           | 0.5      | 124                                              | 0.15                                               | 6.2                        | 2.21    |
| MI15   | 15.0                           | 0.5      | 127                                              | 0.15                                               | 5.1                        | 1.36    |

experiments were performed in Auto Chem II (Micromeritics, USA). The heating rate was 10 °C/min from 50 to 900 °C using a gas containing 7% hydrogen in argon. The hydrogen consumption was measured by a Shimadzu GC-8A gas chromatograph, equipped with a thermal conductivity detector.

### 2.3. Test of activity of the catalysts

The *n*-Hexane hydroisomerization reaction was carried out in a flow-type fixed-bed reactor loaded with 1.0 g catalyst. Prior to the reaction, the sample was pretreated with flowing dry air (40 ml/min) at 450 °C for 3 h to remove any water adsorbed on the catalyst sample. The system was cooled to 250 °C and the catalyst was reduced in flowing hydrogen for 3 h at 250 °C. Hydrogen and *n*-hexane mixture was then introduced into the reactor and hydroisomerization tests. Products were monitored and analyzed using an on-line GC-920 gas chromatograph with an FID detector and a 50-m OV-101 capillary column.

## 3. Results and discussion

Effect of the reaction temperature on *n*-C<sub>6</sub> isomerization behaviors was examined, shown in Fig. 1. It is seen that the SH15 has the best catalytic performance due to its highest

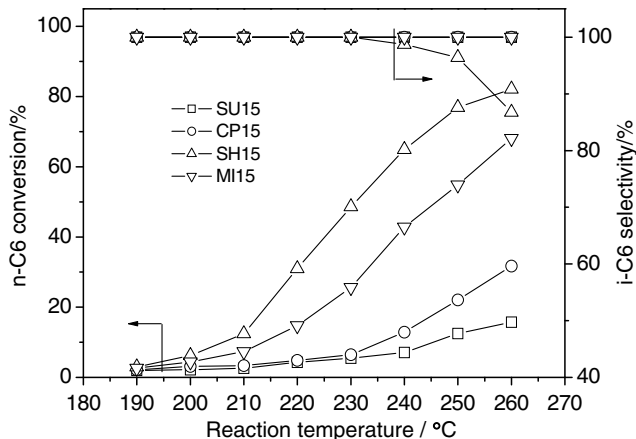


Fig. 1. Effect of reaction temperature on *n*-C<sub>6</sub> isomerization (catalyst loading = 1.0 g; WHSV = 2.0 h<sup>-1</sup>; Reaction pressure *P* = 2.0 MPa; *n*-C<sub>6</sub>:H<sub>2</sub> = 1:3).

conversion and selectivity in the reaction temperature ranging from 190 °C to 260 °C. Catalytic activities of these four samples were decreasing in the following order based upon *n*-C<sub>6</sub> conversion: SH15 > MI15 > CP15 > SU15. The selectivity of *i*-C<sub>6</sub> decreased only over SH15 catalyst above 230 °C because the cracking reaction took place over SH15.

Isomerization product distributions for the catalysts (time on stream = 480 min) were listed in Table 2. It is true that SZ deactivated very fast in hexane hydroisomerization, but it was also observed in our work that Pt- and Al-promoted SZ catalysts possessed markedly improved stability and activity compared to SZ. Table 2 listed the results after 480 min of time on stream (TOS) of the four catalysts where no deactivation appeared in this duration. At the reaction conditions, the conversion kept almost unchanged with stability of 100%, whilst the product distribution had only small changes at increasing TOS. Isohexanes yield over the catalysts was decreasing in the following order: SH15 > MI15 > CP15 > SU15. In addition, yields of 2,2-DMB as a high octane rating isomerization product are also the highest over SH15. Therefore, it is concluded that Al<sub>2</sub>O<sub>3</sub> introduction method has an important impact on the catalytic performance of PtSZA and the shaping method (SH) is preferred to be applied for catalyst preparation due to its highest enhancement of catalytic activity and selectivity.

Textural properties, contents of alumina, platinum and sulfur in the samples were summarized in Table 1. The surface areas of these catalysts vary from 124 to 139 m<sup>2</sup>/g, pore volumes are from 0.13 to 0.17 cm<sup>3</sup>/g and pore sizes are from 4.0 to 6.2 nm. Additionally, different Al<sub>2</sub>O<sub>3</sub> introduction methods cause a great difference in sulfur contents with the following order: CP15 > SH15 > SU15 > MI15.

It has been commonly recognized that the crystalline phase of the SZ catalysts plays a very important role in catalytic activity and the tetragonal crystalline phase shows a higher catalytic activity than that of monoclinic structure for alkane isomerization [21,22]. XRD patterns of these samples are shown in Fig. 2. The pattern of CP15 contains only a broad and low intensity reflection at 30° that indicates an amorphous structure. Olindo [20] reported that aluminum ions for coprecipitation method would retard the dehydration upon drying and hamper the growth of the small tetragonal crystallites of zirconia upon calcination. The sample SU15 is still amorphous, however, tetragonal zirconia

Table 2  
Conversion and selectivity for *n*-hexane isomerization over the samples

| Sample | i-C <sub>6</sub> H <sub>14</sub> yield (%) |       |         |         | Σ <i>i</i> -C <sub>6</sub> H <sub>14</sub> (%) | Selectivity (%) |
|--------|--------------------------------------------|-------|---------|---------|------------------------------------------------|-----------------|
|        | 3-MP                                       | 2-MP  | 2,3-DMB | 2,2-DMB |                                                |                 |
| SU15   | 2.15                                       | 2.86  | 0.62    | 0       | 5.63                                           | 100             |
| CP15   | 2.36                                       | 3.06  | 0.79    | 0       | 6.21                                           | 100             |
| SH15   | 14.91                                      | 23.19 | 6.58    | 3.66    | 48.34                                          | 100             |
| MI15   | 9.85                                       | 12.44 | 2.54    | 0.81    | 25.64                                          | 100             |

Reaction conditions: catalyst loading = 1.0 g; WHSV = 2.0 h<sup>-1</sup>;

Reaction pressure *P* = 2.0 MPa; *n*-C<sub>6</sub>:H<sub>2</sub> = 1:3;

Reaction temperature *T* = 230 °C; time on stream *t* = 480 min.

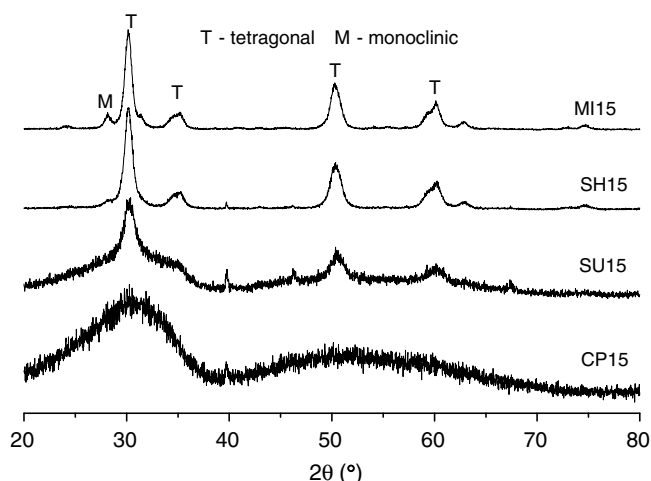


Fig. 2. XRD patterns of the samples.

phase has been formed although its crystallite size is rather small. It is clear that the tetragonal phase is a main compound in MI15 solid. As for the SH15 sample, the solid was well crystallized and only the tetragonal phase was detected. Kim [17] suggested that addition of alumina resulted in the formation of smaller crystallites of  $\text{ZrO}_2$  which stabilized the active tetragonal of  $\text{ZrO}_2$ . As shown in Fig. 2, tetragonal zirconia phase in SH15 by shaping method to introduce alumina was best stabilized in our experiment conditions.

Numbers of Lewis and Brønsted acid sites were determined by related amounts of adsorbed pyridine on FTIR spectroscopy under vacuum conditions at increasing temperatures of 50, 100, 200, 300 and 400 °C, respectively. Results were shown in Table 3. Unfortunately, the catalytic activity was not well correlated with the strong acid sites or total acidity according to Fig. 1 and Table 2. From published papers, it was clear that the explanations of the promotions of alumina were unanimous. Some researchers tried to use the effect of sulfate to correlate with catalytic

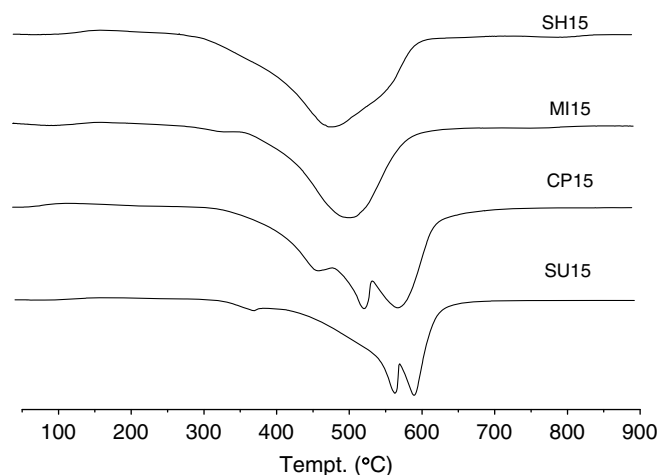
performance of SZA and PtSZA catalysts. In studies on the incorporation of  $\text{Al}_2\text{O}_3$  to SZ, Moreno believed that tetragonal zirconia and the sulfate densities (or coverage) would play an essential role in catalyst activity, whilst strong acidity was not a main condition [23]. Sun et al. considered that the catalytic activity of  $n\text{-C}_4$  hydroisomerization over SZA was correlated with sulfur content rather than catalyst surface area, sulfated density or the total number of Brønsted acid sites [24]. Our results also showed that strong acidity was not a key factor for  $n\text{-C}_6$  hydroisomerization over PtSZA.

We think that catalytic activity depends on various factors including the presence of tetragonal crystal phase, alumina introducing method, surface acidic properties and active surface sulfur species etc, whilst the number of the strong acid sites did not play the crucial factor. It was postulated that various alumina introduction methods would give impact on the active sulfur species and thus modify the catalytic activity. The more, the active surface sulfur species, the more dramatic, the cracking reactions presented at increasing temperatures. It might be used to explain why cracking was only observed over SH15 above a temperature of 230 °C, as shown in Fig. 1.

$\text{H}_2$ -TPR technique was used to examine the effect of  $\text{Al}_2\text{O}_3$  introduction methods on the reduction properties of PtSZA, shown in Fig. 3. According to the report by other researchers [26–28], unpromoted SZ showed a feature, peaking at 616 °C, which was attributed to reduction of the sulfate species, because no reduction of a pure zirconia sample took place in that temperature region. The peak maximum may lower to 516 °C for Pt.promoted SZ (Pt loading is 0.75%) [28]. Compared to that of the PtSZ catalyst, a stronger peak for SH15 sample which shifts towards lower temperatures with a maximum at about 475 °C was observed, showing an enhancement of sulfate reducibility of the PtSZA due to aluminum modification. From the TPR profiles in Fig. 3, the peak temperature maximum is raising in the following order: SH15 < MI15 < CP15 < SU15, which is well correlated with the catalytic activity of the samples.

Table 3  
Acidity measurements by pyridine adsorption at different temperatures

| Temperature °C | Acid amount/ $\mu\text{mol g}^{-1}$ | CP15 | SU15 | SH15 | MI15 |
|----------------|-------------------------------------|------|------|------|------|
| 50             | B acid                              | 132  | 238  | 156  | 74   |
|                | L acid                              | 705  | 282  | 491  | 1104 |
|                | Total acid                          | 837  | 520  | 647  | 1178 |
| 100            | B acid                              | 127  | 190  | 136  | 54   |
|                | L acid                              | 235  | 84   | 120  | 402  |
|                | Total acid                          | 362  | 274  | 256  | 456  |
| 200            | B acid                              | 126  | 130  | 74   | 24   |
|                | L acid                              | 109  | 57   | 77   | 227  |
|                | Total acid                          | 235  | 187  | 151  | 251  |
| 300            | B acid                              | 40   | 86   | 47   | 13   |
|                | L acid                              | 8    | 13   | 16   | 82   |
|                | Total acid                          | 48   | 99   | 63   | 95   |
| 400            | B acid                              | 19   | 16   | 16   | 5    |
|                | L acid                              | 2    | 5    | 0    | 48   |
|                | Total acid                          | 21   | 21   | 16   | 53   |

Fig. 3.  $\text{H}_2$ -TPR profiles of the samples.

For metal promoted SZ, the enhancement of sulfate reduction was observed in the two cases. One case is transition metals promoted SZ [29], such as, Fe, Mn etc., and gallium (Ga) promotion [30], another is Pt promoted SZ [26–28]. Cao et al. [30] reported that Ga in Ga-promoted SZ may lower the peak temperature on H<sub>2</sub>-TPR profile that was attributed to reduction of sulfate species; the incorporation of Ga also provides the red-ox properties so that it significantly improves the catalyst performance in *n*-hexane hydroisomerization. So a new bifunctional catalysis mechanism initiated by oxidation followed by acid catalysis was also proposed to explain the difference in catalytic activity between SZ and Fe–Mn promoted SZ. Davis [31] and Farcasiu [32] proposed that sulfated zirconia promoted by some transition metals as iron and manganese showed high catalytic activity in the *n*-butane isomerization owing to existing red-ox active metal sites in the catalyst. Sachtler et al. [29] reported that the enhancement of sulfate reduction is observed in H<sub>2</sub>-TPR analysis for transition metals promoted SZ, such as, Fe, and explained Fe promoted the dissociation of H<sub>2</sub> similar to that of Pt in PtSZ. However, alumina has no such red-ox ability, aluminum promotion must be different from transition metals [33]. On the other side, Loften and coworkers [28] reported that *n*-C<sub>6</sub> hydroisomerization on PtSZ still followed the classical bifunctional mechanism by his kinetic studies, although platinum in PtSZ also exhibited a shift of hydrogen consumption peak towards lower temperature range in TPR patterns. Therefore, the red-ox mechanism should also not be accepted to explain the activity behaviors of the PtSZA catalysts prepared by different alumina introduction methods in this study.

In our TPR results, an enhancement of sulfate reduction by PtSZA compared to PtSZ was observed, so we can guess different alumina introduction methods would give impact on the effect of platinum and thus modify the catalyst performance. Under the classical bifunctional mechanism, the catalytic performance is enhanced by facilitating dissociative chemisorption of hydrogen and promoting hydrogen spillover from Pt in the catalyst and acidic properties of the catalyst. The former was postulated to be the main factor, because the TPR peaking orders shown in Fig. 3 were well correlated with that of catalytic activities given in Fig. 1 and Table 2. In the scope of different methods to introduce alumina, the more significant impact to platinum seemed to be dehydrogenation–hydrogenation step compared to that of acidic properties. Of course, detailed survey of the effect of alumina on platinum by different introduction to prepare PtSZA catalysts should be addressed later on.

#### 4. Conclusion

Four Al-promoted PtSZA catalysts were prepared through different approaches to introduce alumina, the PtSZA catalyst through alumina SH introduction has the best catalytic performance. The alumina SH introduction is preferred to promote the H<sub>2</sub> dissociation role of Pt in

the PtSZA and stabilize the tetragonal zirconia and thus promote the catalytic performance. Aluminum introduction method is a crucial step to prepare a PtSZA catalyst for *n*-hexane isomerization. Shaping (Kneading) method would be the best option to introduce Al<sub>2</sub>O<sub>3</sub> in the preparation of the PtSZA catalyst.

#### Acknowledgements

We would like to thank the financial support from the key international cooperative research projects by the National Ministry of Science and Technology, PR China (No. 2004CB720603) and CONACyT (Mexco)-NSF (China) (No. J110.426/2005).

#### References

- [1] M. Hino, K. Arata, J. Chem. Soc. Chem. Commun. (1980) 851.
- [2] T. Yamaguchi, Appl. Catal. A 61 (1990) 1.
- [3] A. Corma, Chem. Rev. 95 (1995) 559.
- [4] X.M. Song, A. Sayari, Catal. Rev. Sci. Eng. 38 (1996) 320.
- [5] T.K. Cheung, B.C. Gates, Top. Catal. 6 (1998) 41.
- [6] M.A. Coelho, D.E. Resasco, E.C. Skabwe, R.L. White, Catal. Lett. 32 (1995) 256.
- [7] A. Játia, C. Chang, J.D. Macleod, T. Okubo, M.E. Davis, Catal. Lett. 25 (1994) 21.
- [8] V. Adeeva, J.W. Dehaan, J. Jänchen, G.D. Lei, V. Schunemann, L.J.M. Vandeven, W.M.H. Sachtler, R.A. Vansanten, J. Catal. 151 (1995) 364.
- [9] J.C. Yori, J.M. Parera, Appl. Catal. A 147 (1996) 145.
- [10] Z. Gao, Y.D. Xia, W.M. Hua, C.X. Miao, Top. Catal. 6 (1998) 101.
- [11] W.M. Hua, Y.D. Xia, Y.H. Yue, Z. Gao, J. Catal. 196 (2000) 104.
- [12] T. Kimura, Catal. Today 81 (2003) 57.
- [13] W.M. Hua, A. Goepfert, J. Sommer, J. Catal. 197 (2001) 406.
- [14] R. Olindo, A. Goepfert, D. Habermacher, J. Sommer, F. Pinna, J. Catal. 197 (2001) 344.
- [15] M. Haouas, S. Walspurger, J. Sommer, J. Catal. 215 (2003) 112.
- [16] M. Haouas, S. Walspurger, F. Taulelle, J. Sommer, J. Am. Chem. Soc. 126 (2004) 599.
- [17] S.Y. Kim, N. Lohitharn, J.G. Goodwin, R. Olindo, F. Pinna, P. Canton, Catal. Commun. 7 (2006) 209.
- [18] W.M. Hua, J. Sommer, Appl. Catal. A 227 (2002) 279.
- [19] Y.Y. Huang, B.Y. Zhao, Y.C. Xie, Appl. Catal. A 171 (1998) 65.
- [20] R. Olindo, F. Pinna, G. Strukul, G. Canton, Stud. Surf. Sci. Catal. 130 (2000) 2375.
- [21] W. Stichert, F. SchÜth, S. Kuba, H. KnÖzinger, J. Catal. 198 (2001) 277.
- [22] C. Morterra, G. Cerrato, F. Pinna, M. Signoretto, J. Catal. 157 (1995) 109.
- [23] J.A. Moreno, G. Poncelet, J. Catal. 203 (2001) 453.
- [24] Y. Sun, S. Walspurger, B. Louis, J. Sommer, Appl. Catal. A 292 (2005).
- [25] A. Sayari, A. Dicko, J. Catal. 145 (1994) 561.
- [26] B.Q. Xu, W.H. Sachtler, J. Catal. 167 (1997) 224.
- [27] T. Loften, E.A. Blekkan, Appl. Catal. A 299 (2006) 250.
- [28] J.D. Henao, B. Wen, W.M.H. Sachtler, J. Phys. Chem. B 109 (2005) 2055.
- [29] C.J. Cao, S. Han, C.L. Chen, N.P. Xu, C.Y. Mou, Catal. Comm. 4 (2003) 511.
- [30] K.T. Wan, C.B. Khouw, M.E. Davis, J. Catal. 158 (1996) 311.
- [31] D. Farcasiu, J.Q. Li, A. Kogelbauer, J. Mol. Catal. A: Chem. 124 (1997) 67.
- [32] W. Wang, J.H. Wang, C.L. Chen, N.P. Xu, C.Y. Mou, Catal. Today 97 (2004) 307.
- [33]