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Effects of calcination temperature and water-washing treatment on n-hexane hydroisomerization behavior of Pt-promoted sulfated zirconia based catalysts

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ABSTRACT

Synthesis of Pt-promoted sulfated zirconia catalyst $Pt/SO_4^{2-}/ZrO_2$ (designated as PSZ), $Pt/SO_4^{2-}/ZrO_2$-Al_2O_3 (designated as PSZA), and $Pt/SO_4^{2-}/ZrO_2$-Al_2O_3-Y_2O_3 (designated as PSZAY) was reported. These catalysts were characterized by N_2 adsorption–desorption, thermal gravimetric (TG) analysis, NH_3-temperature programmed desorption (NH_3-TPD), and H_2-temperature programmed reduction (H_2-TPR) techniques. Effects of calcination temperature of the catalysts on the n-hexane hydroisomerization behavior were investigated in details. The experiment results revealed that the addition of Al and Y or Al promoter alone could improve the thermal stability of the catalysts. PSZA and PSZAY exhibited higher isomerization activity than unmodified PSZ as the calcination temperature of sulfated $Zr(OH)_4$ was relatively high, for example, between 650 °C and 750 °C. For the first time, it was found that water-washing treatment of PSZA and PSZAY at different preparation stages had considerably different impacts on their catalytic activity. Water-washing after calcination of the sulfated $Zr(OH)_4$, the catalytic activity of PSZA and PSZAY was high, as indicated by approximately 80% of n-hexane conversion. However, water-washing before calcination of sulfated $Zr(OH)_4$ led to a significant decrease in the catalytic activity of PSZA and PSZAY, that is, the n-hexane conversion diminished to around 35%. It was proposed that the presence of excessive sulfur species over sample was favorable for keeping the active sulfur species in the catalyst surface.

1. Introduction

The transformation of n-alkanes into iso-alkanes through hydroisomerization process is of practical importance in petrochemical industry. For example, n-butane can be converted into iso-butane and the latter can be alkylated with butene to produce iso-octane, which is an environmentally friendly high-octane gasoline booster. In addition, n-pentane and n-hexane can also be isomerized into their isomers and directly acted as blending components of clean high-octane gasoline. The n-hexane isomerization process was commercialized; however, the used conventional bi-functional catalyst presented some shortcomings, such as small amount of high octane number components in the products and low catalytic activity at reaction temperature below 280 °C. Since sulfated zirconia (SZ) was found to possess super or strong acidity [1], it attracted much attention in acid-catalyzed field, especially in n-alkane isomerization reaction [2–6]. The isomerization activity of SZ or Pt-promoted SZ (PSZ) was greatly dependent on the preparation step or method. It is generally believed that the high isomerization activity of SZ and PSZ could be obtained only when amorphous zirconium hydroxide acted as the precursor of sulfation. In the preparing process of SZ and PSZ, the high calcination temperature was considered to be indispensable [7] and it strongly affected the catalytic activity of SZ and PSZ to a great extent [8–13]. The results from Arata et al. [12] and Sun et al. [13] indicated that the calcination temperature effect on the isomerization activity of SZ depended on the preparation method to some extent. Comelli et al. [8] examined the effect of calcination temperature on n-hexane isomerization catalytic performance of Pt-promoted SZ, and these authors considered that the isomerization activity reached maximum at the calcination temperature of 550–600 °C.

The influence of calcination temperature is usually related with different promoters. Hua and Sommer [9] once investigated the calcination temperature of sulfated $Zr(OH)_4$–$Al(OH)_3$ on n-butane isomerization activity over $Pt/SO_4^{2-}/ZrO_2$-Al_2O_3 (PSZA) and found that the optimized calcination temperature was 650 °C,

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in agreement with the previous investigation results from our groups [10]. Signoretto et al. [11] also reported the optimal calcination temperature of sulfated $Zr(OH)_4$ modified with Ga_2O_3 which depended on the content of Ga_2O_3 promoter. Our previous results confirmed the important role of rare earth Y promoter in PSZA in the isomerization activity and stability [14]. The investigation from Xia et al. [15] demonstrated that the introduction of Al to PSZ could not improve the isomerization activity, but was helpful to catalyst shaping. In fact, the effect of the calcination temperature of sulfated $Zr(OH)_4$ before and after the addition of Al or other promoters may be different, but there existed seldom systematic investigation about this aspect.

On the other hand, water-washing treatment usually plays an important role in the SZ catalyst preparation; it can partially remove sulfur species over catalyst, thus modify the surface acidity and catalytic activity [16]. However, for Pt-promoted SZ and SZA, update it is unclear whether or not only water soluble sulfur species over PSZ and PSZA are the catalytic active centers. According to the new isomerization reaction mechanism over PSZ suggested by Ebitani et al. and Manoli et al. [17,18] that the new strong acid sites could be created in the presence of gaseous hydrogen and acted as the catalytic active sites, after water washing, PSZ or PSZA may show certain catalytic activity in the hydroisomerization reaction.

The object of the present work is to further investigate the effect of calcination temperature of sulfated $Zr(OH)_4$ on the n-hexane isomerization activity of the Al or Al and Y promoted $Pt/SO_4{}^{2-}/ZrO_2$ catalysts. The role of water washing treatment at different preparing stages in the catalytic activities is also studied in detail.

2. Experimental

2.1. Catalyst preparation

A prepared 0.2 mol/L $ZrO(NO_3)_2$ solution was dropwise added into 5% ammonia solution with stirring. After precipitation, the slurry was stirred for additional 0.5 h and then aged statically at room temperature for 10 h. The obtained $Zr(OH)_4$ white precipitate was repeatedly washed with deionized water by evacuation filtration till the pH value of the filtrate was ca. 7 and then dried at 110 °C for 20 h. The dried sample was crushed to very fine powder. Part of the dry powder was mixed with boehmite powder. The mixture powder was extruded with dilute HNO_3 and dried again at 110 °C. Sulfating procedure was performed by impregnating separately the dry $Zr(OH)_4$ powder and the extrudate with 0.5 mol/L of H_2SO_4 solution (15 ml/g) at room temperature for 6 h. The sulfated samples were filtered without washing and dried overnight at 110 °C, denoted as SZ and SZA. Part of SZA sample was impregnated with yttrium nitrate solution to load Y and dried at 110 °C for 13 h, denoted as SZAY. Subsequently, the three dry sulfated solid samples were calcined at certain temperature for 3 h. Finally, the calcined samples were respectively impregnated in H_2PtCl_6 solution to load with 0.5 wt% Pt, dried at 110 °C and calcined at 500 °C for 3 h. Thus, the prepared $Pt/SO_4{}^{2-}/ZrO_2$, $Pt/SO_4{}^{2-}/ZrO_2\text{-}Al_2O_3$ and $Pt/SO_4{}^{2-}/ZrO_2\text{-}Al_2O_3\text{-}Y_2O_3$ catalysts were designated as PSZ, PSZA and PSZAY. The weight percentage of Al_2O_3 and Y_2O_3 in the support was 3%.

In order to investigate the water washing treatment, part of dry sulfated $Zr(OH)_4$ was washed with water three times (30 ml/g), denoted as WSZ. Part of calcined sulfated $Zr(OH)_4$ at 650 °C was washed with water three times (30 ml/g), denoted as SWZ. Then these samples were mixed with boehmite powder. The following preparation steps were the same as the above. The final catalysts were named as PWSZA and PSWZA.

2.2. Catalytic activity measurement

The n-hexane hydroisomerization reaction was carried out in a continuous flow-type fixed-bed stainless reactor (i.d. = 5 mm) loaded with 2.0 g of catalyst. The prepared catalyst was crushed and sieved to 40–60 mesh. Prior to the reaction, the catalyst sample was pretreated in flowing dry air (20 ml/min) at 400 °C for 3 h. The system was cooled to 250 °C and the catalyst was reduced with flowing hydrogen for 3 h at this temperature. After the reduction, the temperature of catalyst bed decreased to a set temperature. Hydrogen gas and n-hexane were simultaneously introduced into the reactor and the reaction pressure was controlled by hydrogen gas. The standard reaction conditions were as follows: the reaction total pressure = 2.0 MPa, n-hexane weight hourly space velocity (WHSV) = 1.0 h^{-1}, hydrogen/n-hexane molar ratio = 5, and the reaction temperature = 165 °C. Normal hexane feedstock was sent to the reactor by a double plunger micro pump and the hydrogen gas flow rate was controlled by a mass flow meter. The products were analyzed by on-line GC-920, equipped with an FID and an OV-101 capillary column. Since weight percentage of all kinds of isomers and the cracking products could be obtained by area normalization method in GC peaks, the conversion of n-hexane and the selectivity of iso-hexane were calculated according to the following formulas (1) and (2), respectively:

$$X\ \ (\text{n-hexane conversion}) = 100\% - \text{wt\% of n-hexane in product} \tag{1}$$

$$S\,(\text{iso-hexane selectivity}) = \frac{\text{wt\% of total iso-hexanes in products}}{X} \tag{2}$$

2.3. Catalyst characterization

2.3.1. X-ray diffraction (XRD)

XRD patterns were obtained with a Philips MagiX X-ray diffractometer, using Cu Kα_1 radiation and instrumental settings of 40 kV and 40 mA. The scanning was within a range of 2θ from 10° to 70° at a scanning rate of 6°/min.

2.3.2. NH_3-temperature programmed desorption (NH_3-TPD)

NH_3-TPD was carried out at a homemade equipment. The sample (0.14 g) was loaded into a stainless steel U-shaped microreactor (i.d. = 5 mm) and pretreated at 600 °C for 0.5 h in flowing He. After the pretreatment, the sample was cooled to 150 °C and was exposed to NH_3 atmosphere. As the catalyst was saturated with the adsorbed NH_3, helium was used as carrier to remove NH_3 physically adsorbed until the baseline was stable. NH_3-TPD was then carried out in a constant flow of He (20 ml/min) from 150 °C to 650 °C at a heating rate of 18 °C/min. The concentration of ammonia in the exit gas was monitored continuously by a gas chromatograph (Shimazu 8A) equipped with a thermal conductivity detector (TCD).

2.3.3. H_2-temperature programmed reduction (TPR)

TPR experiments were performed in a domestic apparatus. The sample (0.1 g) was loaded in a quartz tube and pretreated in helium for 0.5 h. After cooled to room temperature, a 5% H_2/He mixed gas passed through the sample with a flow rate of 30 ml/min. The sample began to be heated at a heating rate of 10 °C/min from room temperature to 800 °C. The hydrogen consumption was measured by using a thermal conductivity detector (TCD).

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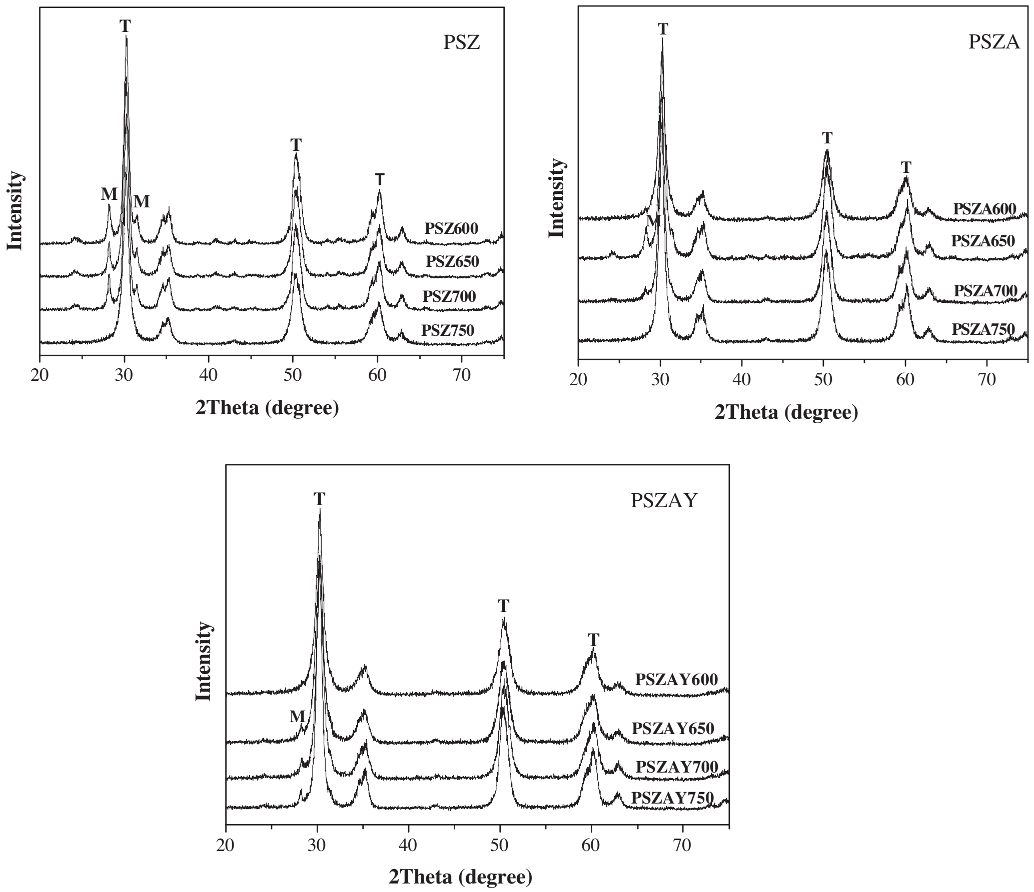

Fig. 1. XRD patterns of the samples at different calcinations temperatures (T – tetragonal zirconia; M – monoclinic zirconia).

2.3.4. *Thermal gravimetric analysis (TGA)*

TGA was carried out on SDT-Q600 TG analysis equipment (TA, USA). The catalyst sample (0.02 g) was heated from room temperature to 1000 °C in an air stream at a heating rate of 10 °C/min. In the recorded profiles, the weight loss before 600 °C was attributed to desorption of water. The decrease of weight from 600 °C to 1000 °C was caused by the removal of sulfur on the catalyst. Therefore, SO_4^{2-} content in the sample could be estimated according to the following formula:

$$SO_4^{2-}\ \text{amount}\,(\text{g/g cat}) = \frac{M_1 - M_2}{M_1} \qquad (3)$$

where M_1 represents the weight percent of catalyst after water desorption and M_2 represents the weight percent of the catalyst after the removal of sulfur.

3. Results and discussion

3.1. *Effect of calcination temperature*

3.1.1. *Effect on the crystalline phases*

The effects of calcination temperature of sulfated $Zr(OH)_4$ on the phase composition of PSZ, PSZA and PSZAY are shown in Fig. 1. It could be seen from Fig. 1a that in the temperature range 600 and 700 °C, PSZ mainly contained tetragonal zirconia with only few percentage of monoclinic zirconia. Further increasing the temperature led to monoclinic phase entirely disappearance. As for PSZA (Fig. 1b), when the calcination temperature was 750 °C, PSZA only contained tetragonal phase. In the Y promoted sample, PSZAY (Fig. 1c), even if the temperature was up to 750 °C, it still contained some monoclinic zirconia phase. The above phenomena allowed us to conclude that the crystalline structure of Pt-promoted SZ-based catalyst was related not only with the calcination temperature, but also with promoters, in agreement with the report from Signoretto et al. [11]. On the other hand, the effect of calcination temperature on the crystalline structure was complicated, because it also would influence sulfur content of the resultant catalyst [19]. Thus we will report the sulfur content in our catalyst in the following section.

3.1.2. *Effect on the sulfur content*

The variation of sulfur content over PSZ, PSZA and PSZAY with the calcination temperature is shown in Table 1. It could be seen that at the same calcination temperature, the sulfur content over PSZA and PSZAY was obviously higher than that over the unmodified PSZ sample. Even at higher calcination temperature, the Al and Y modified PSZ sample still contained relatively higher sulfur content than the unmodified PSZ sample. For example, at 750 °C, the sulfur content increased from 1.43% over PSZ, to 2.23% over PSZA, and to PSZAY over 2.59%. Obviously, the introduction of Al or rare

Table 1
Content of sulfated species over the samples calcined at different temperatures.

Sample	Sulfur content (wt%)	Sample	Sulfur content (wt%)	Sample	Sulfur content (wt%)
PSZ600	3.21	PSZA600	4.68	PSZAY600	4.77
PSZ650	2.87	PSZA650	3.46	PSZAY650	4.64
PSZ700	2.15	PSZA700	3.10	PSZAY700	3.28
PSZ750	1.43	PSZA750	2.23	PSZAY750	2.59

"600" in PSZ600 represented the calcination temperature of sulfated $Zr(OH)_4$.

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Table 2
Textural structures of PSZA catalysts calcined at different temperatures.

Sample	S_{BET} (m^2/g)	Pore diameter (nm)	Total volume (cm^3/g)
PSZA600	135.05	3.821	0.142
PSZA650	118.29	5.585	0.152
PSZA700	108.13	6.504	0.147
PSZA750	101.75	4.325	0.132

earth promoter could increase the sulfur content over PSZ and the thermal stability of sulfur species.

3.1.3. Effect on the textural property

Besides, the specific surface area also changed with the calcination temperature, as shown in Table 2. As for PSZA, the BET surface area of PSZA600 was up to ca. 135 m^2/g. And the increase in the calcination temperature only led to a slight decrease in the area. As the calcination temperature increased up to 750 °C, the surface area decreased to 101 m^2/g. The pore diameter and pore volume reached maximum (ca. 6 nm and 0.15 m^3/g) as the calcination temperature was intermediate, i.e. 650–700 °C.

3.1.4. Effect on the catalytic behavior

The dependence of isomerization activity of PSZ, PSZA and PSZAY on the calcination temperature is shown in Fig. 2. When the calcination temperature was relatively low, i.e. 600 °C, the conversion of n-hexane on PSZ600 was about 63%, which was higher than that over PSZA600 and PSZAY600. As the calcination temperature increased to 650 °C, the conversion over the three samples greatly increased, for example, n-hexane conversion over PSZAY catalyst almost doubly increased from approximately 36% to 74%. Further increasing the calcination temperature to 700 °C resulted in a great decrease in n-hexane conversion over PSZ, and in a slight decrease over PSZA. While over PSZAY, n-hexane conversion was almost unchanged at 700 °C. When the calcination temperature reached 750 °C, the n-hexane conversion over PSZ750 significantly reduced to ca. 5%, which was much lower than that was achieved over PSZA and PSZAY. At this temperature, the n-hexane conversion over PSZAY750 was the highest, i.e. 40%, which was similar to the conversion over PSZ700. Obviously, the calcination at low temperature was favorable to the isomerization reaction over PSZ; while, high calcination temperature was favorable to the reaction over PSZA and PSZAY.

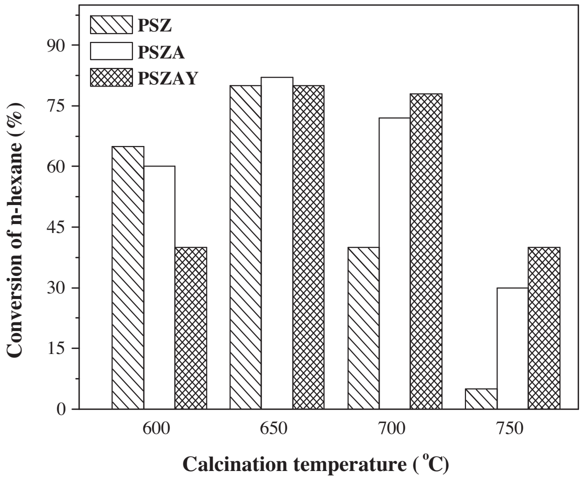

Fig. 2. n-Hexane conversion over PSZ and modified PSZ catalysts calcined at different temperatures (WHSV = 1.0 h^{-1}, P = 2.0 MPa, $n(H2)/n(n\text{-}C6)$ = 5:1, reaction temperature = 165 °C, TOS = 3 h).

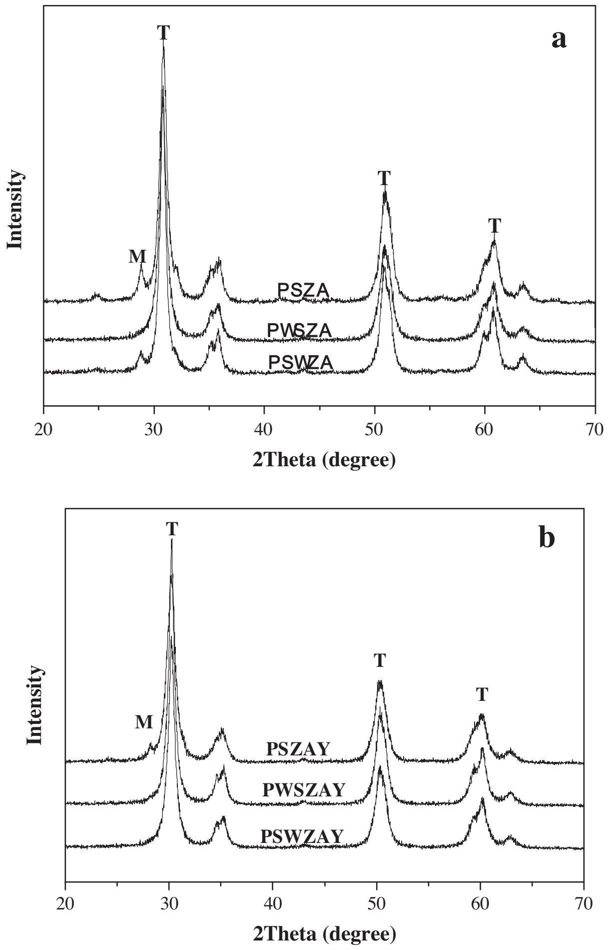

Fig. 3. XRD patterns of the catalyst samples washed with water at different steps (T – tetragonal zirconia; M – monoclinic zirconia).

3.2. Effect of water washing treatment

3.2.1. Effect on the phase composition

Li et al. [16] found that some water-soluble sulfur species existed over the SZ sample, which was considered to be catalytic active centers for the isomerization reaction of n-alkane. Similar results were also reported by Manoilova et al. [20]. In the present work, since both PSZA and PSZAY catalysts at 650 °C show better thermal stability, as evidenced by the above experimental results, in the following section, the two samples PSZA650 and PSZAY650 were chosen for investigating the influence of water-washing on the crystalline structure and hydroisomerization activity.

The effect of water-washing on the crystalline phase of PSZA650 is shown in Fig. 3. It could be clearly seen from Fig. 3a that PWSZA sample which corresponds to water washing treatment before the calcination, contained only tetragonal phase; while the crystalline structure of PSWZA which corresponds to water-washing after the calcination, was similar to that of the unwashed sample PSZA as it contained a large amount of tetragonal phase with very few monoclinic phase. This indicates that water-washing treatment before calcination led to the formation of complete tetragonal phase in PSZA, and after calcination, the water-washing treatment could not alter the crystalline structure.

However, for PZAY sample, no matter the water-washing treatment was operated before or after calcination, both the resulted PWZAY and PZWAY catalysts contain pure tetragonal phase, as shown in Fig. 3b. This result indicates that water-washing treatment is insensitive to the Y modified catalyst. Therefore, the

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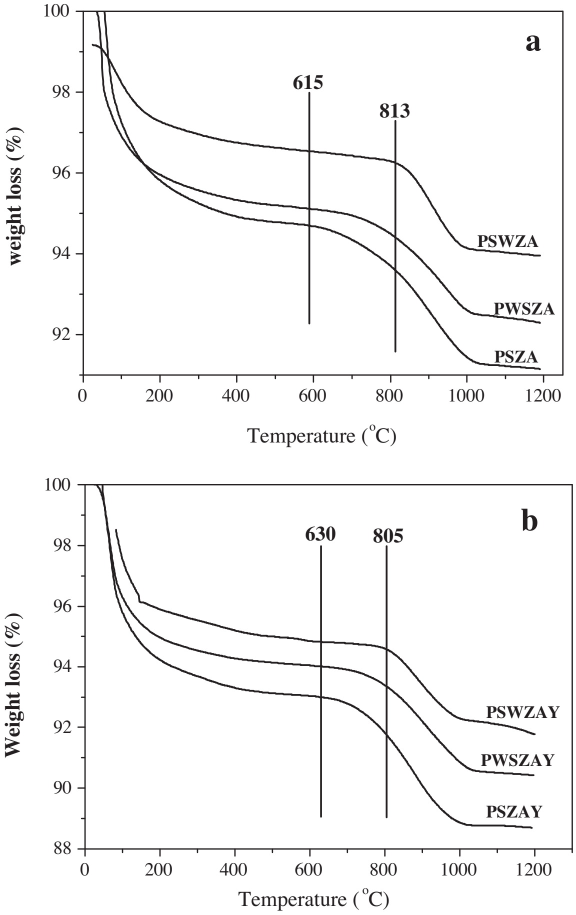

Fig. 4. TG curves of the (a) PSZA and (b) PSZAY samples before and after water-washing.

influence of water washing treatment on the phase composition is also affected by the different promoters.

3.2.2. Effect on the sulfur content

The variations in the sulfur content over PSZA and PSZAY before and after water-washing were determined by TG technology, as shown in Fig. 4 and Table 3. It could be clearly seen that the water-washing treatment before and after calcination of sulfated $Zr(OH)_4$ removed partial sulfur species over PSZA and PSZAY, as evidenced by the decrease in the sulfur content (in Table 3). This suggests that there exists some water-soluble sulfur species over the PSZA and PSZAY samples even after calcination, in agreement with the suggestion from Li et al. [16]. Moreover, the water-washing at different stages resulted in similar sulfur content for PSZA or PSZAY.

In TG curves, the weight loss occurring above 600 °C is generally attributed to the loss of sulfur species. It could be seen that the weight decrease of PSWZA and PSWZAY in TG curves due to the sulfur loss (in Fig. 4) occurred at temperature above ca. 800 °C, which was higher than that for other samples, demonstrating that after calcination, the water-washing treatment mainly removed the sulfur species with thermal instability. In another word, the water-soluble sulfur species over the calcined catalyst was thermal instable ones.

Table 3
Sulfur contents of PSZA sample before and after water-washing.

Sample	Sulfur content (wt%)	Sample	Sulfur content (wt%)
PSZA	3.41	PSZAY	4.77
PWSZA	2.60	PWSZAY	3.11
PSWZA	2.67	PSWZAY	2.97

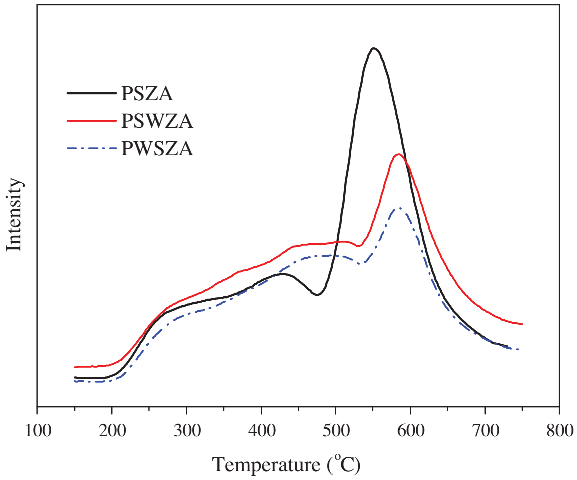

Fig. 5. NH_3-TPD profiles of PSZA catalysts before and after water-washing.

3.2.3. Effect on the surface acidity

The effect of water-washing on the surface acidity of PSZA before and after water-washing is characterized by NH_3-TPD, as shown in Fig. 5. Compared with PSZA, the water-washed samples (PSWZA and PWSZA), no matter after or before calcination, the NH_3 desorption peak area recorded at high temperature greatly decreased; while the low temperature peak area only exhibited slightly decrease. This implies that the water-washing treatment led to a great decrease in the strong acid sites, which should be attributed to the drop of sulfur content, in line with the suggestion from Manoilova et al. [20].

3.2.4. Effect on the H_2 reduction behavior

The reduction property of PSZA, PWSZA and PSWZA characterized by H_2-TPR is shown in Fig. 6. There appeared two reduction peaks for all the three samples. In the TPR profile of the PSZA sample, one high temperature peak was centered at 550 °C and another low temperature peak at 450 °C. After water-washing treatment, the peak area of the samples (PWSZA and PSWZA) obviously lowered.

3.2.5. Effect on the textural property

Table 4 listed the textural data of the PSZA catalyst before and after water-washing. Water-washing of the calcined SWZA650

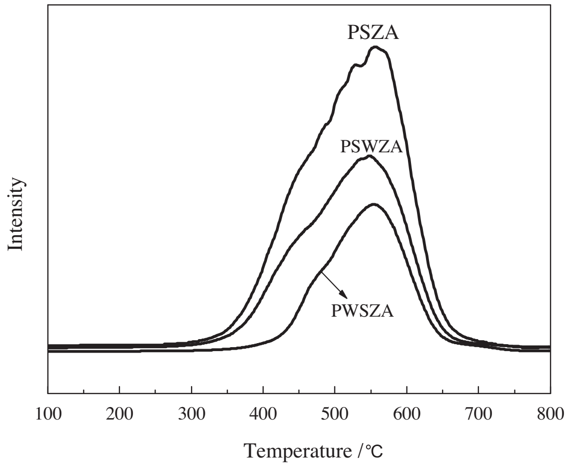

Fig. 6. H_2-TPR profiles of PSZA catalysts before and after water-washing.

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Table 4
The textural data of PSZA sample before and after water-washing.

Sample	S_{BET} (m^2/g)	Pore diameter (nm)	Total volume (cm^3/g)
PSZA	118	5.59	0.152
PWSZA	94	5.59	0.136
PSWAZ	116	5.58	0.158

sample had no influence on the surface area, pore diameter and pore volume. However, washing uncalcined sample, WSZA650, led to an appreciable decrease in the surface area and pore volume. It was inferred that after the calcination at high temperature, the relatively stable textural structures of the catalyst were formed and water-washing the calcined sample could not change these properties. On the contrast, water-washing sulfated $Zr(OH)_4$ caused the removal of partial sulfur species, and during calcination the sintering phenomenon may occur due to the decrease in the sulfur content, and thus, the textural structure of the resulting sample would change to some extent.

3.2.6. Effect on the catalytic activity

The effects of water-washing before and after calcination on the isomerization performances of PSZA650 are shown in Fig. 7. The n-hexane conversion over PSZA650 was similar to that over PSWZA650, varied between 80% and 85%, depending on the time on stream. It was much higher than the value of ca. 37% achieved over PWSZA 650 (in Fig. 7). Similar results were achieved on the PZAY650 sample.

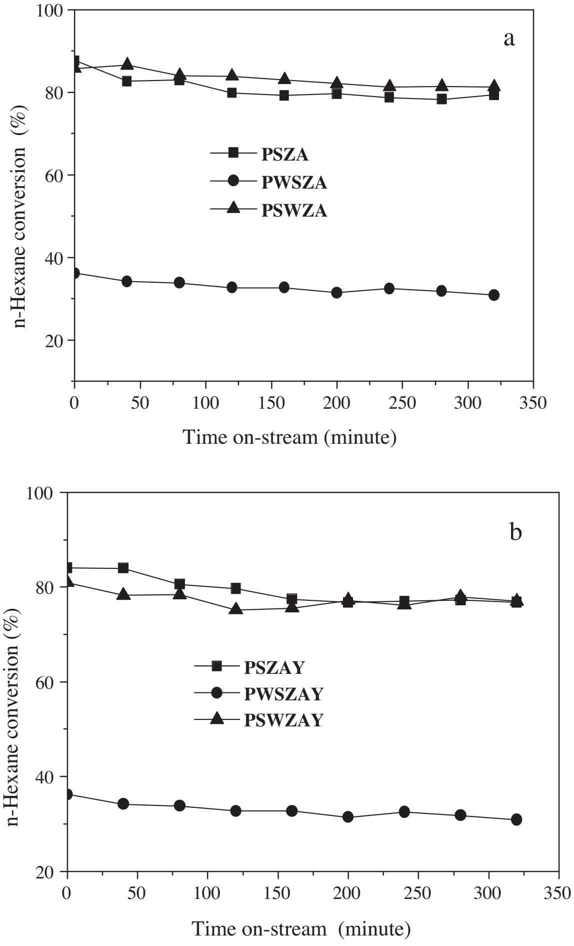

Fig. 7. Comparison in iso-hexanes yield over the catalysts before and after water-washing (WHSV = 1.0 h^{-1}, P = 2.0 MPa, $n(\mathrm{H2})/n(\mathrm{n\text{-}C6})$ = 5:1, reaction temperature = 165 °C).

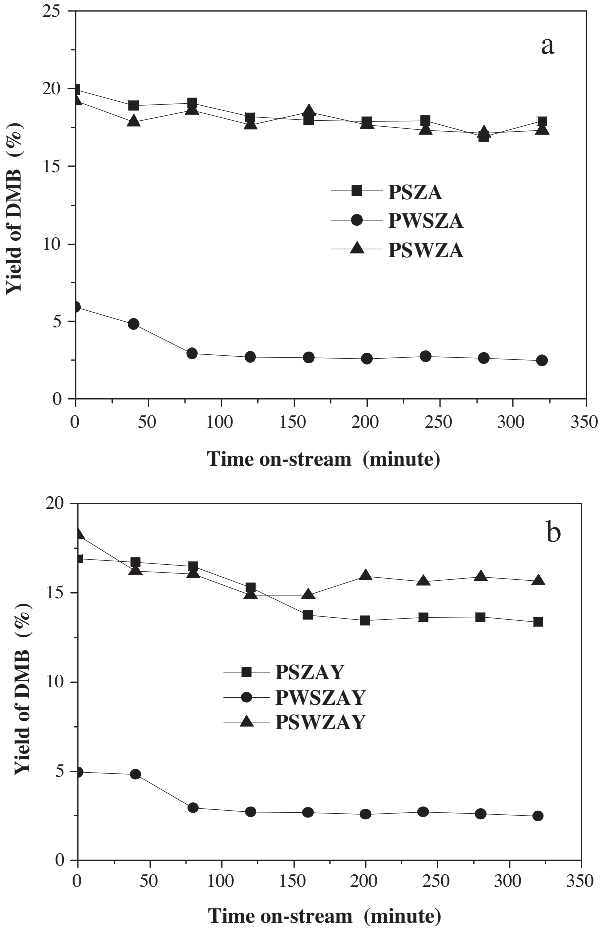

Fig. 8. Comparison in DMB yield over the catalysts before and after water-washing (DMB – dimethyl butanes).

The influence of water-washing on the isomers distribution was similar to that on the isomerization activity. The yield of di-methyl butanes (DMB) over PSZA and PSZAY was 15–20%, very close to the value over PSWZA and PSWZAY; while the yield over PWSZA and PWSZAY was extremely low, below 5%, as shown in Fig. 8. This indicates that after calcination of sulfated $Zr(OH)_4$, water-washing treatment does not affect on the isomerization behavior of PSZA and PSZAY. However, before calcination, the water-washing treatment seriously deteriorates the isomerization performance of the catalysts, by lowering the activity and altering the isomers distribution.

3.3. Discussion

The effect of calcination temperature of sulfated $Zr(OH)_4$ or sulfated $Zr(OH)_4$ modified with Al on catalytic activity in hydroisomerization of n-alkane has been reported in previous investigation [8–10]. However, comparison between the effect of calcination temperature on the isomerization catalytic activity of PSZ, PSZA and PSZAY is rarely reported up to now. The previous investigation from our group showed that the optimized calcination temperature for PSZA was 650 °C [10]. The present experiment results also indicate that PSZ and PSZ modified with Al and rare earth Y exhibited relatively higher catalytic activity when the calcination temperature was 650 °C. However, the further increase in the temperature had greater effect on the catalytic activity of PSZ

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than that of PSZA and PSZAY. The catalytic activity of the latter two was much higher than that of the former at higher calcination temperature. This indicated that the promoted PSZ possessed better thermal stability. As evidenced by TG in Table 1, PSZ possessed lower sulfur content than the modified PSZ (i.e. PSAZ and PSZAY). Especially PSZ750 had very lower sulfur content, which may be the main factor leading to the very low catalytic activity.

The effect of water-washing of SZ on the n-alkane hydroisomerization activity has been reported by Li et al. [16] and they found that the water-washing treatment for calcined sulfated $Zr(OH)_4$ led to an almost complete loss of isomerization activity. In contrast to their results, in the present work, water-washing treatment after calcination had no distinct effect on the catalytic activity. The distinct discrepancy between the catalytic activity of the water-washed PSWZA in the present investigation and that of water-washed SZ in the report from Li et al. [16,20] may be related with the addition of Pt. For SZ or SZA unpromoted with Pt, the original acidity or/and re-dox played the key role in the isomerization reaction. Water-washing led to a great decrease in the strong Brønsted acid sites, as confirmed by Manoilova et al. [20], which resulted in the significant reduction of catalytic activity. In the case of Pt-promoted SZ or SZA and in the presence of hydrogen gas, Pt could dissociate hydrogen molecules into hydrogen atoms and hydrogen atoms spilt over SZ to create new strong Brønsted acid sites [17]. These newly created acid centers may act as the catalytic active centers. Therefore, even if partial sulfur species was removed during the water-washing, the newly created active centers could still catalyze the isomerization reaction.

It was noteworthy that the water-washing before calcination of sulfated $Zr(OH)_4$–$Al(OH)_3$ resulted in the drastic decrease in the isomerization activity. Water-washing treatment at different stages of catalyst preparation brought about the partial removal of sulfur species, but the catalysts water-washed at different stages showed different catalytic activity although the final sulfated species contents over PWSZA and PSWZA or PWSZAY and PSWZAY were very similar (Table 3). Obviously, the difference between the catalytic activities of PWSZA and PSWZA or PWSZAY and PWSZA should be not attributed to the sulfur content. The role of hydrogen spillover was reported in the improvement of catalytic activity over PSZ [18,21], but the amount of hydrogen spillover was seldom taken into account in explanation their catalytic performance. Kusakari et al. [22] found that the support would influence the hydrogen spillover amount. Another investigation demonstrated that the spiltover hydrogen was stored in the cationic defects of zirconia [23]. Over sulfated $Zr(OH)_4$, some H_2SO_4 strongly interacted with hydroxyl groups and others were only weakly attached on $Zr(OH)_4$. Water-washing of sulfated $Zr(OH)_4$ may lead to the removal of H_2SO_4 only weakly linked to $Zr(OH)_4$. For the unwashed sulfated $Zr(OH)_4$, surplus sulfur may protect other sulfated species interacting with $Zr(OH)_4$ in the process of calcination. However, for the water-washing sulfated $Zr(OH)_4$, some sulfur species could not be protected due to partial removal of sulfur species. Therefore, it could be inferred that SZA (or SZAY) after water-washing at different stages may possessed different properties, which would lead to the different hydrogen spillover behavior, thus showing very different isomerization activities.

4. Conclusions

The introduction of promoters (Al or Al and Y) greatly improved the thermal stability of the $Pt/SO_4^{2-}/ZrO_2$ catalyst. High calcination temperature of the sulfated $Zr(OH)_4$ was more favorable to the isomerization reaction over PSZ modified with Al or Al and Y in comparison with the unmodified PSZ. For the first time, it was found that the resultant catalysts showed very different isomerization behaviors if the water-washing treatment was operated at different preparation stages. When water-washing was done after calcination of the sulfated Zr(OH), the PSZA or PSZAY exhibited high catalytic activity. In contrast, if the water-washing was performed before calcination of the sulfated $Zr(OH)_4$, the catalytic activity of the catalysts drastically decreased to approximately 50% of that achieved on the catalysts with water-washing after calcination. It was proposed that the presence of the excessive sulfur species over the catalyst surface was indispensable to prepare PSZA or PSZ with high catalytic activity.

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