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Effect of the properties of hydrous zirconia prepared under various hydrothermal conditions on the isomerization activity of Pt/WO_3-ZrO_2

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ABSTRACT

A series of hydrous zirconia samples were prepared by hydrothermal method and the effects of the properties of hydrous zirconia on the catalytic activity of Pt/WO_3-ZrO_2 in the hexane isomerization were investigated. The catalysts were characterized by X-ray diffraction (XRD), thermal gravimetric analysis (TGA) and differential thermal analysis (TDA), H_2-temperature programmed reduction (H_2-TPR) and NH_3-temperature programmed desorption (NH_3-TPD). The results showed that the hydrothermal treatment under different times and pH values led to remarkable changes in the properties (such as hydroxyl group, ordering degree and thermal stability) of hydrous zirconia. Moreover, the isomerization activity of Pt/WO_3-ZrO_2 varied distinctly with the hydrothermal treatment condition of hydrous zirconia. The correlation between the properties of hydrous zirconia and the isomerization activity of the catalyst was primarily established. It was proposed that the isomerization activity was strongly dependent on the stability and ordering degree of hydrous zirconia, while it was irrelevant to the amount of hydroxyl groups in hydrous zirconia.

1. Introduction

Since Arata and Hino found that amorphous $Zr(OH)_4$ promoted with W (denoted as WO_3-ZrO_2) after calcination at high temperatures possessed the properties of super-acidity and high *n*-alkane isomerization activity [1], tungstated zirconia catalysts, especially using amorphous $Zr(OH)_4$ as support attracted numerous attentions in the hydro-isomerization of the *n*-alkanes into iso-alkanes [2–11]. The strong acidity and high isomerization activity of WO_3-ZrO_2 were attributed to the interaction between tungstate ions and larger number of hydroxyl groups of $Zr(OH)_4$ as suggested by Vartuli et al. [12]. The crystallization of $Zr(OH)_4$ led to a nearly complete depletion of surface hydroxyl groups [13]. Therefore, it could be inferred that the very low isomerization activity of tungstated crystalline zirconia may be related to the lack of surface hydroxyl groups of crystallized zirconia.

As a matter of fact, the properties (such as the stability, hydroxyl groups and ordering degree) of hydrous zirconia varied with the preparation method and condition even if the obtained hydrous zirconia was amorphous [14,15]. The effects of the properties of amorphous hydrous zirconia on the isomerization performances of the sulfated zirconia system have been reported in several literatures [13,16]. However, little work has been carried out to investigate the effect of the properties of amorphous hydrous zirconia on the isomerization activity of Pt/WO_3-ZrO_2 catalyst. The hydrothermal treatment of $Zr(OH)_4$ is a widely used and effective method to control the properties of the amorphous hydrous zirconia [16–18]. In the present work, we synthesized the amorphous hydrous zirconia with different properties by the hydrothermal method under different conditions and investigated the effects of the properties of hydrous zirconia on the isomerization performances of Pt/WO_3-ZrO_2. And some interesting results were primarily obtained.

2. Experimental

2.1. Catalyst preparation

Amorphous hydrous zirconia was prepared by direct precipitation method and hydrothermal method, respectively. $ZrO(NO_3)_2$ aqueous solution of 0.17 M was added drop-wise into NH_3 solution of 5 wt.% with vigorously stirring and the final pH value of the slurry was about 13–14. The formed white precipitate of $Zr(OH)_4$ was aged at room temperature for 10 h. The precipitate in mother liquor was divided into two parts. One part was filtered and washed thoroughly with deionized water till the pH value of the

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filtered liquid was 7 and the obtained hydro-gel was re-split into two parts. One was directly dried at 110 °C for 12 h, denoted as Zr-D. The other was evenly mixed with distilled water with vigorous stirring and then the formed slurry (pH 7) was transferred into a stainless Teflon-lined 100 ml capacity autoclave. Another part of the unwashed precipitate together with the mother liquor (pH 14) was directly transferred into a stainless Teflon-lined 100 ml capacity autoclave. The two autoclaves were subjected to hydrothermal treatment at 110 °C for given time. The products after the hydrothermal treatment at pH 7 and pH 14 were washed and dried at 110 °C, named as Zr-H7(*t*) and Zr-H14(*t*), respectively, where "*t*" represented the hydrothermal time. The tungstated zirconia was prepared by impregnating the hydrous zirconia with ammonium meta-tungstated and calcinated at 700 °C in air for 3 h unless illustrated additionally. The calcined samples were denoted as WZr-D, WZr-H7(*t*) and WZr-H14(*t*). Pt was added to the calcined tungstated zirconia by impregnation with hexachloroplatinic acid solution and then calcined in air at 500 °C for 3 h. The content of tungsten oxide and Pt in Pt/WO_3-ZrO_2 was 15 wt.% and 0.5 wt.%, respectively.

2.2. Catalytic testing for *n*-hexane isomerization

The isomerization reaction of *n*-hexane was performed in a continuous flow fixed-bed stainless steel reactor (i.d. = 5 mm). Before the reaction, the catalyst was pretreated in dry air flow at 450 °C for 3 h. Then, the catalyst was cooled down to 280 °C and reduced in a flow of pure hydrogen at a rate of 20 ml/min for 2 h. After that, hydrogen and *n*-hexane were simultaneously introduced into the reactor at a given temperature. The molar ratio of H_2 to *n*-hexane was 30, reaction pressure 2 MPa, and weight hourly space velocity (WHSV) was 1 h^{-1}. The products were analyzed on-line by GC-920, equipped with an FID and an OV-101 capillary column.

2.3. Catalyst characterization

X-ray diffraction (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.

NH_3-teperature programmed desorption (NH_3-TPD) was carried out at a home-made 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 down to 150 °C and was exposed to NH_3 atmosphere. As the catalyst is saturated with the adsorbed NH_3, Helium was used as carrier to remove NH_3 physically adsorbed until the base-line 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 TCD.

H_2-temperature programmed reduction (H_2-TPR) was carried out on a TP5000 multi-functional adsorption equipment. The sample (0.1 g) was first pretreated in a flow of He at 200 °C for 30 min and then cooled down to room temperature. Subsequently, under a flowing 5% H_2/N_2 flow (30 ml/min), the sample was again heated from ambient temperature to 800 °C at a heating rate of 10 °C/min. The consumption of H_2 was determined by a TCD.

Thermal gravimetric (TG) and differential scanning (DSC) analysis was carried out on an SDT-Q600 instrument (TA, USA). The catalyst sample (0.03 g) was heated from room temperature to 800 °C in an air stream at a heating rate of 10 °C/min.

3. Results and discussion

3.1. Crystalline structure

The XRD patterns of the different tungstated zirconia samples are presented in Fig. 1. All the hydrous zirconia samples prepared by different methods were amorphous (not shown here). It could be obviously seen from Fig. 1a that the diffraction patterns of tungstated zirconia samples prepared by different methods calcined at 700 °C were almost the same. Zirconia in the samples existed mainly in the form of tetragonal phase and only very few percentage of monoclinic zirconia was detected. No WO_3 phase was observed, implying that tungsten oxide was well dispersed on zirconia. As tungstated zirconia samples were calcined at 800 °C, there appeared distinct diffraction peaks of WO_3 (in Fig. 1b). Moreover, the diffraction peaks of WO_3 in WZr-D were stronger and sharper than those in WZr-H7(48) and WZr-H14(48), which suggested that WO_3 crystals in the former were more and larger than those in the latter. In addition, the samples mainly contained tetragonal zirconia.

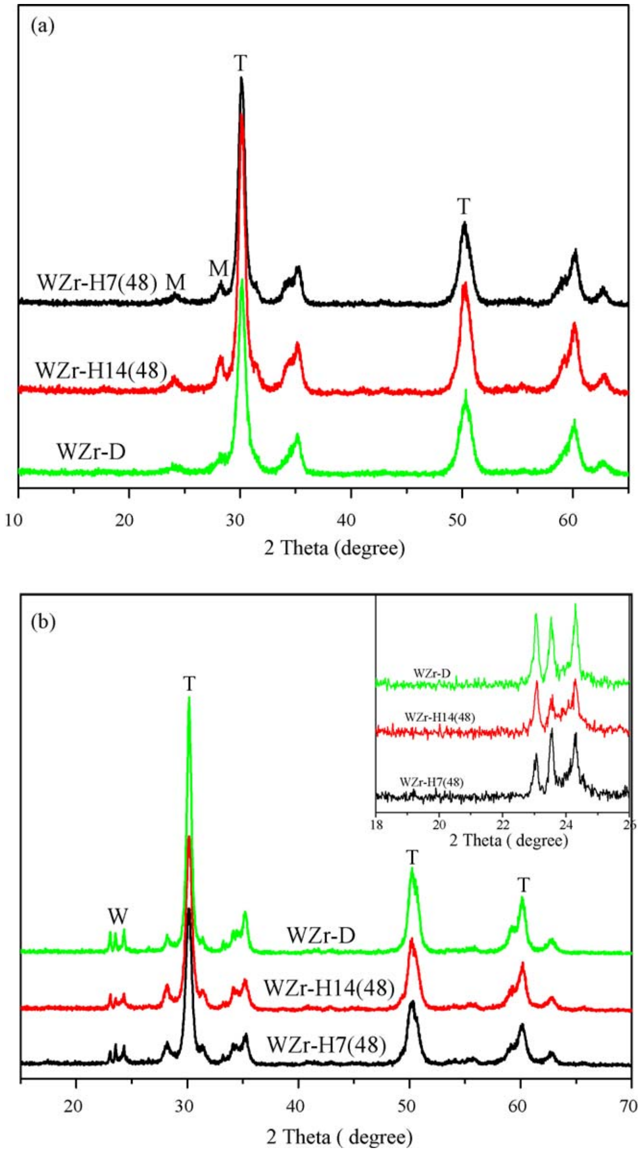

Fig. 1. XRD patterns of WZr-D, WZr-H7(48) and WZr-H14(48) samples (1a and 1b represents the samples calcined at 700 °C and 800 °C, respectively; T-tetragonal zirconia, M-monoclinic zirconia, W-WO_3).

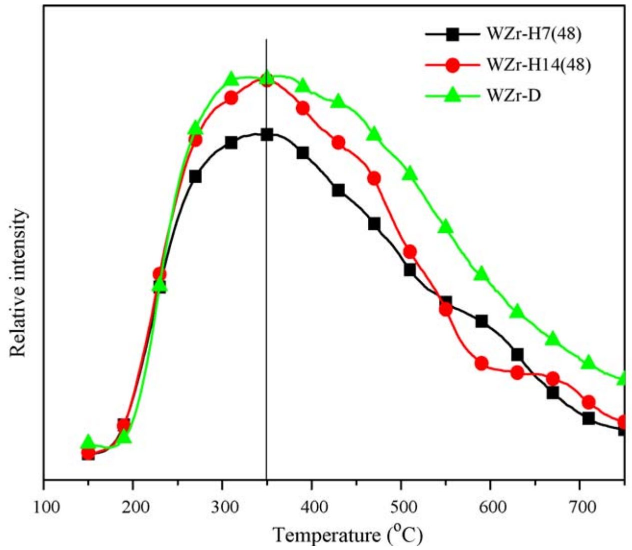

Fig. 2. NH-TPD profiles of WZr-D and WZr-H samples calcined at 700 °C.

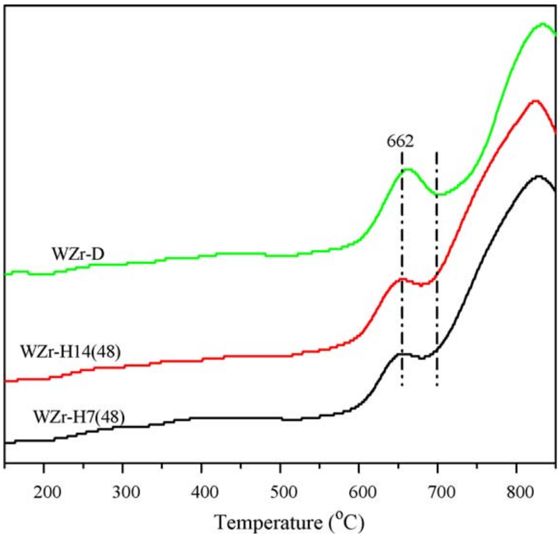

Fig. 3. H_2-TPR profiles of WZr-D and WZr-H samples calcined at 700 °C.

3.2. Acidity and reduction properties

The acidity of the different samples was determined by NH_3-TPD technology, as shown in Fig. 2. The desorption peak area represents the amount of acid sites and the peak temperature represents the acid strength. Here, the peak at temperature lower than 350 °C was related to the weak acid sites and that higher than 350 °C to the strong acid sites. It could be seen that the acidity of tungstated zirconia prepared by different routes exhibited distinct difference. The amount of the strong acid sites over WZr-D was larger than that over WZr-H7(48) and WZr-H14(48). This indicated that the hydrothermal treatment of $Zr(OH)_4$ for long period led to the reduction of the strong acid sites over the tungstated zirconia although the treatment did not resulted in crystallization of the hydrous zirconia.

The reduction property of different tungstated zirconia samples was determined by H_2-TPR, as shown in Fig. 3. It seemed that the reduction behaviors of different samples were very similar. In fact, there existed appreciable difference. The starting reduction temperature of different samples was almost the same, but the temperature of the first reduction peak of WZr-D was slightly higher than that of WZr-H7(48) and WZr-H14(48). Moreover, the starting temperature of the second peak of the former was still higher than that of the latter. Generally speaking, the reduction temperature is related to the strength of the interaction between W and Zr, and the higher reduction temperature is indicative of the stronger interaction [19]. Thus, it could be inferred that the interaction between W and Zr in WZr-D was stronger than that in WZr-H7(48) and WZr-H14(48), which should be responsible for the large amount of the strong acid sites over the former [20].

3.3. Thermal analysis of hydrous zirconia

Fig. 4 gives the TG curves of hydrous zirconia samples prepared by different methods. Obviously, the weight loss of different samples existed great difference. The percentage of weight loss decreased in the order: Zr-D (22.9%) > Zr-H14(48) (18.2%) > Zr-H7(48) (13.5%). The observed weight loss was entirely due to the dehydration of hydrous zirconia [21]. Therefore, it could be inferred that the hydrothermal treatment led to the dehydration of hydrous zirconia. Moreover, Zr-H7(48) treated at a very weak base condition contained smaller amount of hydroxyl groups than Zr-H14(48) treated at a high basic concentration. More interesting was that the final temperatures of weight loss for the hydrous zirconia prepared by different methods also showed marked difference. Weight loss hardly occurred for Zr-D and Zr-H14(48) as the temperature exceeded 450 °C, while very distinct weight loss could be still observed for Zr-H7(48) till the temperature was up to 500 °C. This indicated that the hydroxyl groups in Zr-H7(48) from hydrothermal treatment in very weak basic medium were more stable, while hydroxyl groups in the Zr-D without aging and Zr-H14(48) from hydrothermal treatment under high base concentration were relative active and easy to be removed. The above information indicated that the hydrothermal treatment of $Zr(OH)_4$ not only led to the removal of the hydroxyl groups, but enhanced the stability of hydroxyl groups in hydrous zirconia under certain condition.

In order to more clearly observe the weight loss behaviors of the different hydrous zirconia samples, the TG curves were differentiated and the obtained DTG curves are shown in Fig. 5. There appeared two distinct peaks in DTG curves of Zr-D and Zr-H14(48), centering at ca. 100 °C and 200 °C. This suggested that the maximum loss rate of weight occurred at ca. 100 °C and 200 °C for the above samples. Different from Zr-D and Zr-H14(48), there appeared a peak at a higher temperature of ca. 460 °C for Zr-H7(48)

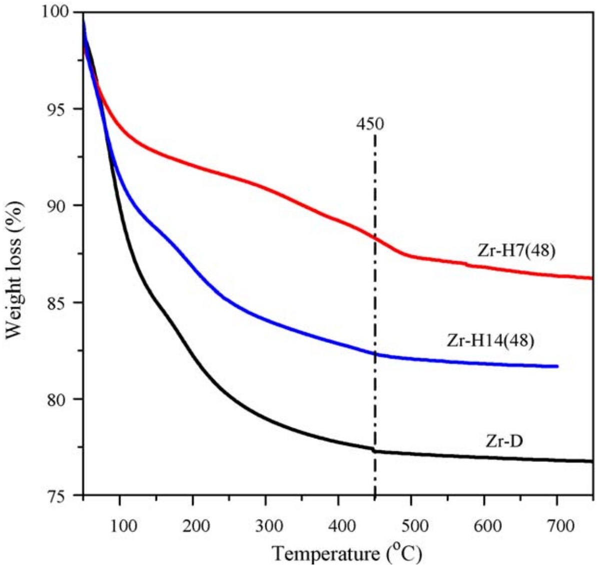

Fig. 4. TG curves of hydrous zirconia prepared by different methods.

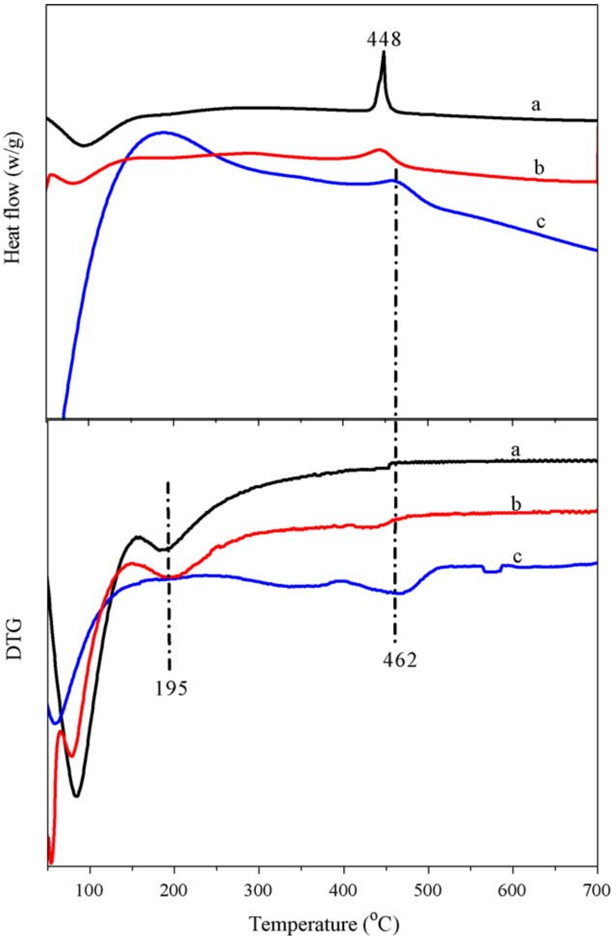

Fig. 5. DTA and DTG curves of hydrous zirconia prepared by different methods (a–c represents the sample Zr-D, Zr-H7(48) and Zr-H14(48), respectively).

except for a distinct peak at ca. 100 °C. This further confirmed that the longer-period hydrothermal treatment under the very weak basic condition was favorable to stabilize some hydroxyl groups except for the dehydration. This was in agreement with the proposal by Pan et. al. [16] that the elimination of some hydroxyl groups in $Zr(OH)_4$ was favorable to stabilize the other hydroxyl groups.

The heat changes in weight loss of different hydrous zirconia samples are also presented in Fig. 5. Firstly, the endotherm peak appeared for every sample at temperatures lower than 400 °C. This is due to the water loss from hydrous zirconia [22]. A distinct exotherm peak for Zr-D and Zr-H14(48) appeared at ca. 450 °C as the weight loss hardly occurred. This exotherm was attributed to the transformation of amorphous hydrous zirconia into crystalline zirconia. However, the peak maximum for Zr-H7(48) shifted toward a higher temperature of 462 °C and the dehydration was still underway at this temperature. This suggested that it was hard to crystallize for Zr-H7(48), which may be related to the existence of the stable hydroxyl groups. In addition, it was worth noting that the exotherm peak for Zr-D was much stronger than that for Zr-H7(48) and Zr-H14(48). Thus, the exotherm in the crystallization of the former was much more than that of the latter. The appearance of exotherm is indicative of a change from short-range ordering to long-range ordering of atoms [14]. Since the final state is essentially at the same energy, the large exotherm implied a more disordered precursor. Consequently, it could be inferred that Zr-H7(48) and Zr-H14(48) was much more ordered than Zr-D. The above information told us that the longer-period hydrothermal treatment led to the removal of hydroxyl groups and the enhancement of the ordering degree in hydrous zirconia, as well as to the increasing stability of the hydrous zirconia as the hydrothermal treatment was carried out at pH 7.

Not only the hydrothermal medium could influence the properties of hydrous zirconia, but the hydrothermal time would also influence the properties. And the influence of the hydrothermal time was also investigated by TG and DTA technology and the results are shown in Figs. 6 and 7. It could be seen that the hydrothermal treatment time obviously influenced the weight loss and the weight loss decreased in the order: Zr-H7(12) > Zr-H7(5) ≫ Zr-H7(48) (Fig. 6), and Zr-H14(12) > Zr-H14(48) > Zr-H14(5) (Fig. 7). Obviously, the weight loss in hydrous zirconia did not reduce with the prolonging hydrothermal time. That is, the amount of hydroxyl groups did not change with the hydrothermal time. In addition, the exotherm of the different samples in the DTA curves was related to the hydrothermal time and basicity of medium. For the samples prepared under weak basic condition, the exothermic peak for Zr-H7(12) appeared at lower temperature, compared with Zr-H7(48) and Zr-H7(5), (shown in Fig. 6), implying that the latter was more stable than the former. Additionally, it was also observed that the intensity of the exothermic peak for Zr-H7(5) and Zr-H7(12) was similar and much higher than that for Zr-H7(48). According to the proposal from Chuah et. al. [14] that the exotherm in crystallization for more disordered precursor was more, it could be concluded that the prolonging hydrothermal treatment time would increase the ordering degree of hydrous zirconia. However, for the Zr-H14(*t*) samples treated with high basic concentration, the exotherm peak became weak with the prolonging hydrothermal time although the exothermic peak for different samples appeared at the same temperature (in Fig. 7). This implied that the ordering degree of hydrous zirconia increased with hydrothermal time. These changes in the properties of

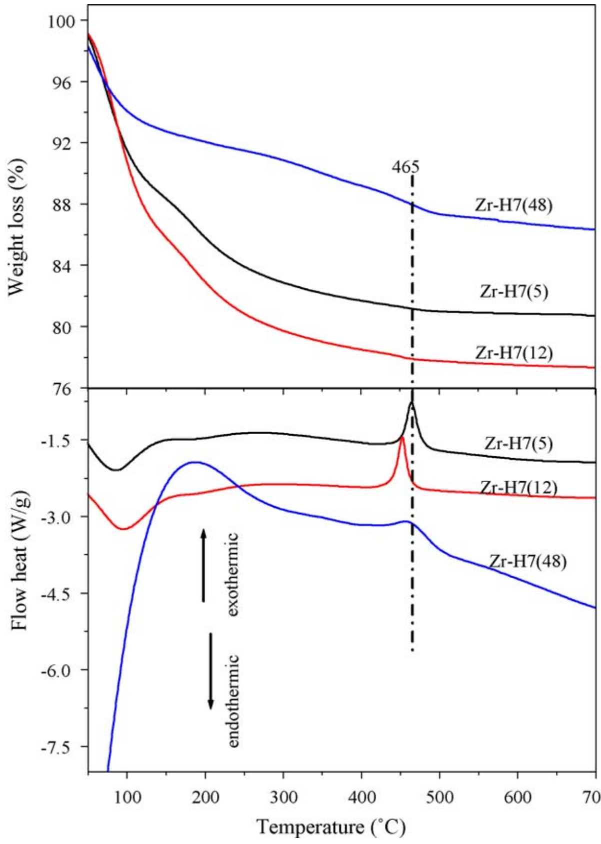

Fig. 6. TG and DTA curves of Zr-H7(*t*) prepared from different hydrothermal treatment time.

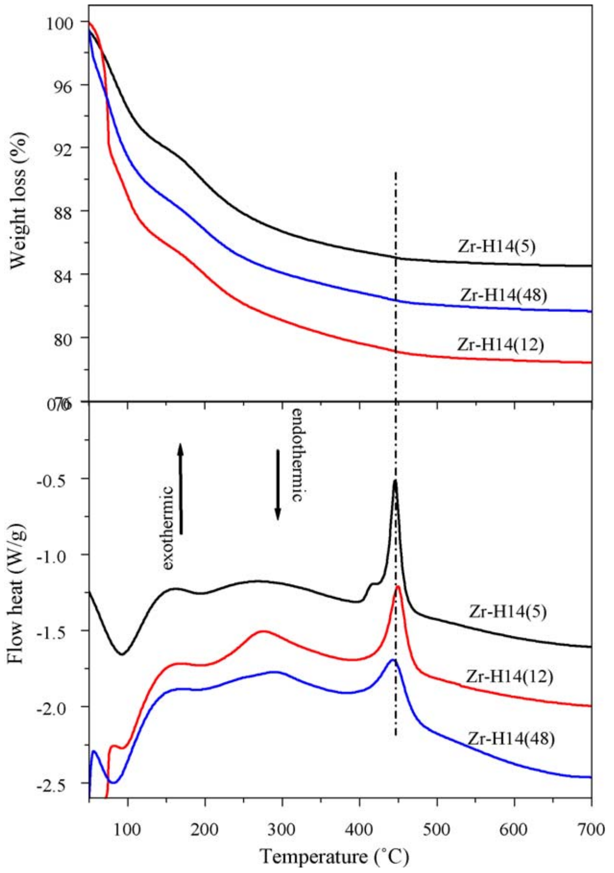

Fig. 7. TG and DTA curves of Zr-H714(*t*) prepared from hydrothermal treatment times.

hydrous zirconia resulting from hydrothermal treatment may influence the catalytic performance of Pt/WO_3-ZrO_2.

3.4. Effect of hydrothermal treatment of $Zr(OH)_4$ on the catalytic activity

3.4.1. Effect of hydrothermal treatment and calcination temperature

The isomerization performances of the catalysts prepared by different methods are shown in Fig. 8. It could be seen obviously from Fig. 8 that the preparation method of hydrous zirconia support had great effect on the isomerization activity. The conversion of *n*-hexane over Pt/WZr-D was much higher than that over Pt/WZr-H7(48) and Pt/WZr-H14(48) (Fig. 8a). At the same conversion of *n*-hexane, the isomerization selectivity of Pt/WZr-H14(48) was much lower than that of Pt/WZr-H7(48) (Fig. 8b). Pt/WZr-H7(48) showed a relatively stable isomerization selectivity, similar to Pt/WZr-D. Specifically, the selectivity of isomers reduced only from 100% to 95% when *n*-hexane conversion increased from 5% to 70%. But, the value decreased drastically from 100% to 65% as *n*-hexane conversion increased from 5% to 60% for Pt/WZr-H14(48). Apparently, the hydrothermal treatment of $Zr(OH)_4$, especially under a basic condition reduced significantly both the catalytic activity and the isomerization selectivity of the catalyst.

Fig. 9 gives the catalytic performances of different catalysts, in which the calcination temperature of hydrous zirconia after loading tungsten was increased up to 800 °C. Differing from results in Fig. 8, the conversion of *n*-hexane over Pt/WZr-H7(48) was the highest and the lowest over Pt/WZr-H14(48). And the selectivity of iso-hexane over Pt/WZr-H7(48) at the same conversion of *n*-hexane was much higher than that over Pt/WZr-D and Pt/WZr-H14(48). This indicated that the hydrothermal treatment at the condition of pH 7–8 enhanced the activity of the catalyst as the tungstated zirconia was calciniated at 800 °C. The above results showed that the effect of the hydrothermal treatment on the isomerization activity of the catalyst was strongly dependent on the calcination temperature of tungstated zirconia and perhaps the high calcination would increase the interaction between W and Zr and change the isomerization performances of the catalysts.

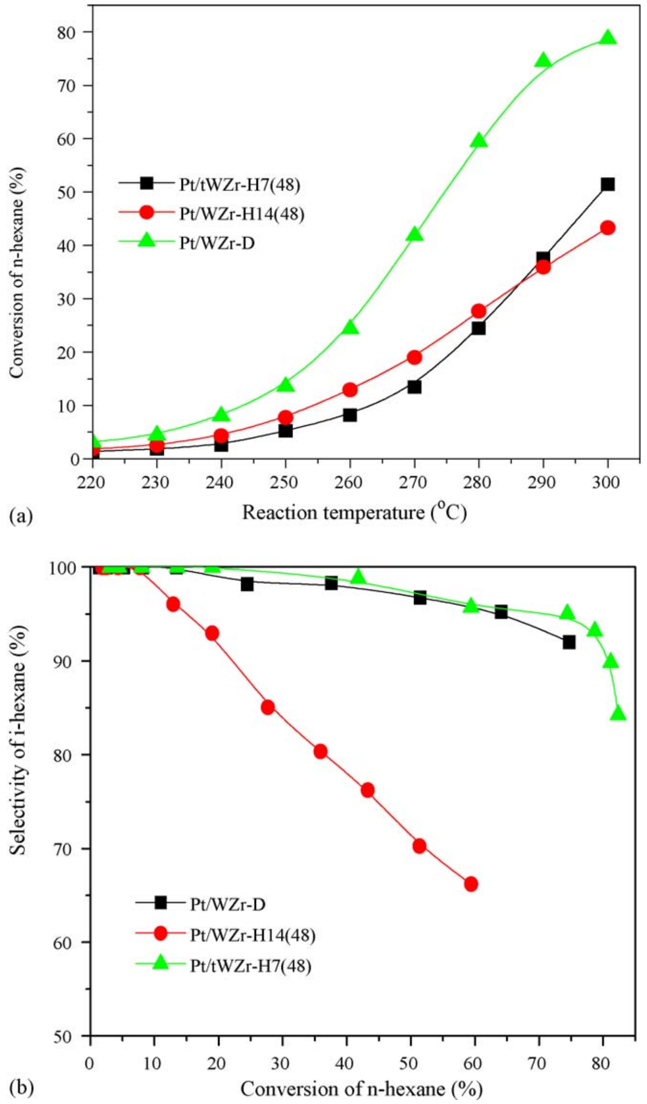

Fig. 8. *n*-Hexane isomerization performances of Pt/WO_3-ZrO_2 (tungstated zirconia calcined at 700 °C).

3.4.2. Effect of hydrothermal time

As stated above, the properties of hydrous zirconia varied with the hydrothermal time, which also led to the change in the isomerization activity (expressing as yield of iso-hexane) of the catalyst, as shown in Fig. 10. The isomerization activity increased significantly with the shortening hydrothermal treatment time regardless whether the treatment was carried out at pH 7 or pH 14. Even the isomerization activity of the catalyst prepared by the hydrothermal route under the conditions of pH 14 for 5 h exceeded that of the catalyst from zirconium hydroxide without hydrothermal treatment. The above results indicated that the hydrothermal treatment under the suitable condition could enhance the isomerization activity of the catalyst.

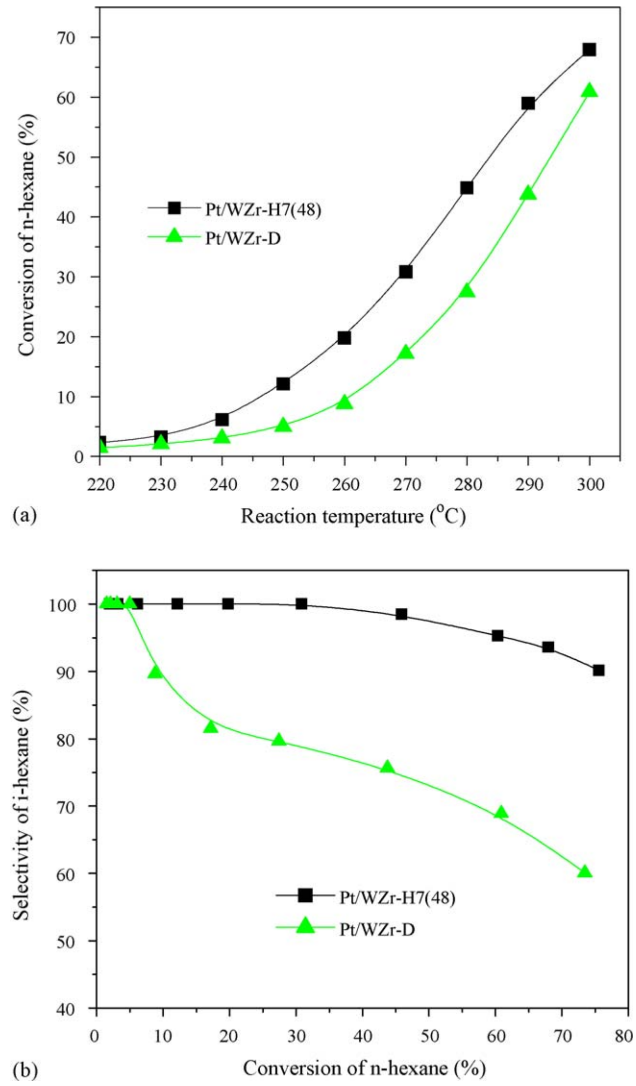

Fig. 9. *n*-Hexane isomerization performances of Pt/WO_3-ZrO_2 (tungstated zirconia calcined at 800 °C).

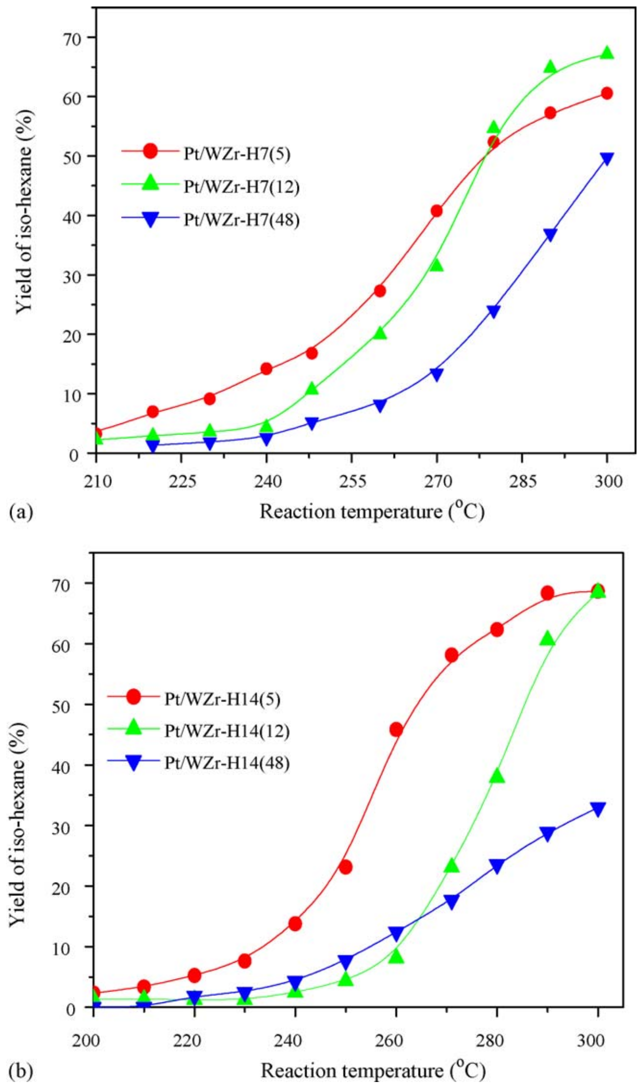

Fig. 10. Effect of hydrothermal time on the isomerization activity (tungstated zirconia calcined at 700 °C).

3.5. Correlation between isomerization activity and the properties of hydrous zirconia

It has been accepted that Pt/WO_3-ZrO_2 has high isomerization activity as amorphous hydrous zirconia promoted with tungsten is calcinated at high temperature. The amorphous hydrous zirconia prepared by different methods in fact possessed "different properties", i.e. hydroxyl amount, atomic-ordering and stability [14,15,23]. At present, it was unclear whether the properties of the amorphous hydrous zirconia would influence the catalytic performances of tungstated zirconia. The present results demonstrated that the hydrothermal treatment of $Zr(OH)_4$ for long time resulted in the distinct changes in the property of amorphous hydrous zirconia and the reduction in the strong acid sites on the catalyst, which may be the main reason for the drastic decrease in the isomerization activity. This implied that the isomerization activity of the catalyst was closely related to the properties of hydrous zirconia. Firstly, the longer-period of hydrothermal treatment of $Zr(OH)_4$ led to the serious dehydration and an enhancement in the ordering of hydrous zirconia although the hydrous zirconia was still amorphous measured by XRD. Moreover, the stability of hydrous zirconia was also improved as the hydrothermal process was carried out at pH 7 for 48 h. Our previous investigation indicated that the enhancement in the calcination temperature of tungstated zirconia could improve the isomerization activity as the support was more stable [24]. Here, in order to clarify the effect of the stability of hydrous zirconia on the isomerization performance, Zr-H7(48) with relatively high stability after loading tungsten was calcined at an elevated temperature (800 °C). Compared with Pt/WZr-H7(48) calcined at 700 °C, the isomerization activity of the catalyst in which tungstated zirconia was calcined at 800 °C, greatly increased. The enhancement in the calcination temperature of tungstated zirconia may lead to an increase in the interaction between W and Zr in the catalyst, which should be related to the improved isomerization activity. This, in turn indicated that the effect of stability of the hydrous zirconia on the isomerization activity of the catalyst should be attributed to the effect on the interaction between W and Zr in the catalyst.

In addition, it was noteworthy that the hydrothermal treatment led to the dehydration and long-range ordering of hydrous zirconia. In order to investigate the effect of the removal of hydroxyl groups and the ordering degree of hydrous zirconia on the isomerization behaviors of the catalyst, a series of hydrous zirconia samples were prepared under different hydrothermal conditions. The hydrous zirconia Zr-H7(12) contained more hydroxyl groups than Zr-H7(5) (Fig. 6), while Pt/WZr-H7(12) exhibited the lower isomerization activity than Pt/WZr-H7(5) (Fig. 10a). The ordering of Zr-H7(5) and Zr-H7(12) was very similar, as confirmed by the same exotherm for the two samples in the crystallization. This implied that the dehydration of hydrous zirconia may not be the main reason for the reduced catalytic activity. However, Santiesteban et. al. [25] claimed that the high acid site density and isomerization activity of WO_3-ZrO_2 derived from the interaction between tungstate ions and large amount of hydroxyl groups of $Zr(OH)_4$.

For the sake of further investigating the effect of hydroxyl and ordering of hydrous zirconia on the isomerization activity, the isomerization activity of the different catalysts using hydrous zirconia prepared at pH 14 was compared. The amount of the hydroxyl groups in Zr-H14(5) was much smaller than Zr-H14(12) according to the results of TG in Fig. 7, while Pt/WZr-H14(5) possessed much higher isomerization activity than Pt/WZr-H14(12) (Fig. 10b). This further confirmed that the reduction of hydroxyl groups in hydrous zirconia from hydrothermal treatment could not lead to the reduction of the catalytic activity. Additionally, the ordering degree of the hydrous zirconia samples increased in the order: Zr-H14(5) < Zr-H14(12) < Zr-H14(48), as evidenced by the reduction of the exotherm in the DTA curves (Fig. 7). And the isomerization activity of the different catalysts increased in the order: Pt/WZr-H14(48) < Pt/WZr-H14(12) < Pt/WZr-H14(5), which was opposite to the ordering degree of the corresponding hydrous zirconia support. The above results showed that the increase in the ordering degree of atoms in hydrous zirconia, rather than the removal of the hydroxyl groups in hydrous zirconia reduced significantly the isomerization activity of the catalyst. In addition, the investigation by Guo et. al. [15] indicated that the existence of large amount of OH^- ions in the hydrothermal medium would result in the formation of the more defection structures, while a low pH value would result in a more ordered structure. Hence, it could be inferred that Zr-H7(5) had higher degree of structural regularity than that Zr-H14(5). The catalytic evaluation showed that the isomerization activity of Pt/WZr-H7(5) was lower than that of Pt/WZr-H14(5) (Fig. 10a and b) although Zr-H14(5) was drier than Zr-H7(5). This further confirmed the above proposal that the ordered degree of atoms in hydrous zircona had greater effect on the catalytic activity, in comparison with the effect of the amount of the hydroxyl groups in hydrous zirconia. To sum up, the structural ordering degree and stability of hydrous zirconia support played an important role in determining the isomerization activity of the catalyst.

However, there was still a lack of the information in the literature regarding the effect of the hydrous zirconia properties on the isomerization performances of Pt promoted tungstated zirconia catalyst although several literatures reported the isomerization activity of sulfated zirconia catalyst prepared by the hydrous zirconia with different properties [16,26]. The present investigation only obtained some primary results. The effect of the properties of hydrous zirconia on the physico-chemical properties and isomerization performances of the catalyst was to be investigated in detail and deeply in later work.

4. Conclusions

The hydrothermal treatment of $Zr(OH)_4$ not only led to the elimination of the hydroxyl groups in the hydrous zirconia, but also to the variation in the stability and the ordering degree of hydrous zirconia. The isomerization activity of Pt/WO_3-ZrO_2 varied with the properties of hydrous zirconia. The enhancement in the stability and the ordering degree of hydrous zirconia lowered greatly the isomerization activity of the catalyst. However, the reduction in the amount of the hydroxyl groups in hydrous zirconia had no distinct effect on the isomerization activity.

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