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Highly active and stable *n*-pentane isomerization catalysts without noble metal containing: Al- or Ga-promoted tungstated zirconia

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This paper reports on the isomerization of *n*-pentane over Al- or Ga-promoted tungstated zirconia (WZ) in the presence of hydrogen. The catalytic activity was significantly improved with the addition of Al or Ga to WZ (AWZ or GWZ). It was found that both AWZ and GWZ catalysts have higher activities for the isomerization of *n*-pentane: conversion is over 70% and the selectivity to iso-pentane reaches ~92% at 215 °C. These catalysts exhibit excellent stability and the deactivation is undetected for 1000 h operation. The promoted-WZ catalyst is a mixed oxide solid acid catalyst without noble metal. Furthermore, the alkanes isomerization catalyst is halogen-free, which is environmentally friendly. The promoted-WZ was characterized by Fourier-transformed infrared spectroscopy (FT-IR), NH_3 adsorption microcalorimetry and X-ray photoelectron spectroscopy (XPS). The remarkable activity and selectivity for *n*-pentane isomerization are due to enhanced strong acid sites and redox properties in the promoted-WZ.

KEY WORDS: tungstated zirconia; aluminum; gallium; *n*-pentane isomerization.

1. Introduction

Isomerization of light *n*-alkanes (*n*-pentane and *n*-hexane) is important for the production of clean and high-octane number fuels. The major commercial catalysts for light *n*-alkanes isomerization are Pt on chlorinated alumina or Pt/H-mordenite [1,2]. Pt on chlorinated alumina has high catalytic activity at low temperature (115–150 °C) where the production of branched isomers is favored in the equilibrium of production distribution [3]. However, this catalyst suffers from chlorine loss during the isomerization process and requires constant addition of chlorine-containing compounds. This chlorine-containing catalyst is also subjected to stringent environmental control. While Pt/H-mordenite does not have these disadvantages, but it requires higher reaction temperature (~260 °C) which is thermodynamically unfavorable for the formation of branched isomers.

Extensive researches have been devoted to the search for an environmentally friendly catalyst that can operate at low temperature. It has been known that modified zirconia catalysts offer as a replacement for halogen-containing catalysts since they exhibit good potential for *n*-alkanes isomerization. Sulfated zirconias (SZ) have been found to be a strong solid acid for $C_4/C_S/C6$ isomerization at low temperature [4–7]. SZ system, however, has the disadvantages of deactivation and sulfur loss during reaction and regeneration [8]. Tungstated zirconia (WZ) catalysts, first reported by Hino and Arata [9] for *n*-butane isomerization, are sought as a nice alternative to SZ system and have been studied extensively [10–12]. WZ catalysts appear to be more suitable for practical application because of their superior stability under reducing and oxidizing conditions and thus regenerability. Whereas, the non-promoted WZ is less active, its catalytic properties can be greatly improved by promotion with noble metals (Pt or Pd) and some metal oxides [13–15]. $A1_2O_3$-doped WZ (AWZ) catalyst has been claimed as an efficient catalyst for the skeletal isomerization of *n*-butane [16]. Previously, we have reported Ga-promoted WZ (GWZ) greatly improved the catalytic properties for *n*-butane isomerization [17]. At present, there has been no report yet on the *n*-pentane isomerization over Al- or Ga-promoted WZ catalysts. Compared to the major commercial catalysts, Al- or Ga-promoted WZ catalysts are composed of mixed oxides without noble metal and are halogen-free catalysts. So the cost of Al- or Ga-promoted WZ catalysts is low and isomerization of *n*-pentane over this catalyst is a green process. In this paper, we report the *n*-pentane isomerization over Al- or Ga-promoted WZ catalysts. The stability of AWZ and GWZ catalysts is also investigated for extended time-on-stream, up to 1000 h test.

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2. Experimental

2.1. Catalyst preparation

AWZ and GWZ catalysts synthesis procedures were described in our previous report [18]. $Zr(OH)_4$ was prepared from zirconia nitrate solution by adding dropwise ammonium hydroxide solution up to pH 9–10 and then refluxed for 24 h. The precipitated hydrogel was filtered and washed repeatedly until the filtered solution is neutral. The gel was dried and impregnated with aqueous ammonium tungstate (Acoros). In the synthesis of Al or Ga-promoted WZ catalyst, appropriate amount of $Al(NO)_3$ or $Ga(NO)_3$ was added to the WZ slurry. The resultant suspension was refluxed, dried and calcined at 800 °C. The W loading was 15 wt%, unless otherwise noted. Al content for all AWZ catalysts was 0.5 wt% and Ga content in GWZ was 1.0 wt%.

2.2. Catalyst characterization

Pyridine-adsorbed Fourier-transformed infrared (FT-IR) spectra were conducted on a Nicolet 550 Spectrometer instrument. Samples were treated at 400 °C for 1 h under a vacuum of 10^3 Pa and introduced pyridine at room temperature. The system was then evacuated and the FT-IR spectra were recorded at 300 °C. Microcalorimetric studies of the adsorption of NH_3 were performed on a heat-flow microcalorimeter of the Tian–Valven type. A known amount of the probe molecular (1–10 μmol) was exposed stepwise to saturated adsorption at 150 °C. X-ray photoelectron spectroscopic analyses of samples was performed on VG Scientific SCALAB 250 fitted with a monochromatic AlK_α radiation X-ray resource, under a residual pressure of 10^{-9}–10^{-10} Torr.

2.3. Catalytic test

The isomerization of *n*-pentane was carried out in a fixed-bed flow reactor. Two gram of 40-mesh catalyst was charged into the reactor and activated at 450 °C under flowing dry air for 3 h. After catalyst pretreatment, the reactor was cooled to reaction temperature, and then pressurized with H_2 at 2.0 MPa or other setting pressure. *n*-Pentane was fed into the reactor and hydrogen and *n*-pentane flows was adjusted to give a 3 $H_2/n\text{-}C_5$ molar ratio at *n*-pentane weight hour space velocity (WHSV) of 1.0 h^{-1}. An on-line gas chromatograph equipped with FID was used to analyze the reaction products.

3. Results and discussion

3.1. Catalyst characterization

3.1.1. FT-IR spectra

The nature of acid sites in the catalyst was determined by pyridine-adsorbed FT-IR. Figure 1 compares the FT-IR spectra of WZ, AWZ and GWZ after pyridine adsorption at 300 °C. Brönsted and Lewis acid sites were found on all samples. For WZ and GWZ, there is no obvious difference in the intensity of band at 1540 cm^{-1} (Brönsted acid sites) or 1450 cm^{-1} (Lewis acid sites). In the case of AWZ, the intensity of band of Lewis acid sites is enhanced. These spectra indicate that the addition of Al to WZ caused an increase of Lewis acid sites.

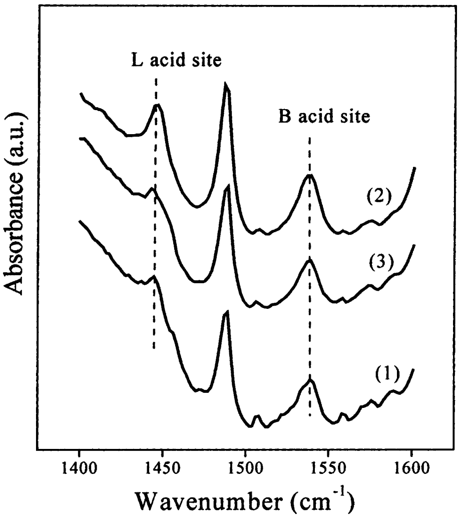

Figure 1. Pyridine adsorption FT-IR spectra of samples: (1) WZ, (2) AWZ and (3) GWZ.

3.1.2. NH_3 adsorption microcalorimetry

NH_3 adsorption microcalorimetry was used to investigate the effect of Al or Ga on the surface acidities of WZ. The adsorption microcalorimetry results are summarized in table 1. The total number of acid sits for WZ and AWZ is about the same, but adding Al to WZ increases the initial heat of adsorption from 199 to 237 kJ mol^{-1}. The numbers of weak acid sites (different heat < 100 kJ mol^{-1}) and moderate acid sites (different heat between 100 and 170 kJ mol^{-1}) show no obvious difference between WZ and AWZ. Although there are few strong acid sites (different heat > 170 kJ mol^{-1}) for WZ and AWZ, the number of strong acid sites is increased from 9.1 to 14.9 μmol g^{-1} after adding Al to WZ. For Ga-promoted WZ, both the total number of acid sits and the initial heat of adsorption are increased. Adding Ga to WZ also appears to generate more strong acid sites than those on AWZ and WZ. It was reported that the catalytic activity of zirconia-based catalysts for alkane isomerization is related to the strength of the acid sites. Hua and Sommer [19] suggested the strong acid sites are active sites for alkane isomerization. The calorimetric results suggest a correlation of the activity difference between promoted and non-prompted WZ to the number of strong acid sites. The addition of small amounts of Al or Ga to WZ increases the acid site

Table 1
NH_3 adsorption microcalorimetry results of distribution of acid site strength

Catalyst	Initial heat/kJ mol^{-1}	Acid sites/μmol g^{-1}			
		Total	< 100 kJ mol^{-1}	100–170 kJ mol^{-1}	> 170 kJ mol^{-1}
WZ	199	252.7	205.1	38.5	9.1
AWZ	237	259.3	205.2	39.2	14.9
GWZ	214	275.6	210.7	47.3	17.6

strength and thus produces a more active alkanes isomerization catalyst.

3.1.3. X-ray photoelectron spectroscopy

The W 4*f* XPS spectra of WZ, AWZ and GWZ are shown in figure 2 and the fitting results of the XPS are compiled in table 2. The W 4*f* XPS spectra of WZ can be deconvoluted into three doublet at 35.6, 34.5 and 33.5 eV, assigned to W^{6+}, $W^{5+}$and W^{4+} [20]. The relative concentrations of W^{6+}, W^{5+} and W^{4+} in WZ are 28, 42 and 30%, respectively. Compared to WZ, the W 4*f* spectra of AWZ and GWZ could not be fitted to reveal the presence of W^{4+}, which resulted in the relative concentration of W^{6+} and W^{5+} increased. The W 4*f* XPS measurement showed that the tungsten species are more reducible in AWZ and GWZ than in WZ because of the enrichment of w^{6+}. We have also found that Al or Ga-doped WZ is more easily reduced than WZ as using H_2-TPR technique [18]. The enrichment of W^{6+} density can also influence the electronic properties of WO_x. It involves the dissociation of H_2 and the migration of H atom to WO_x, domain, which stabilize protons ($H^{\delta+}$) to form Brönsted acid sites by delocalizing the compensating electron density among the W^{6+} Lewis acid centers [21].

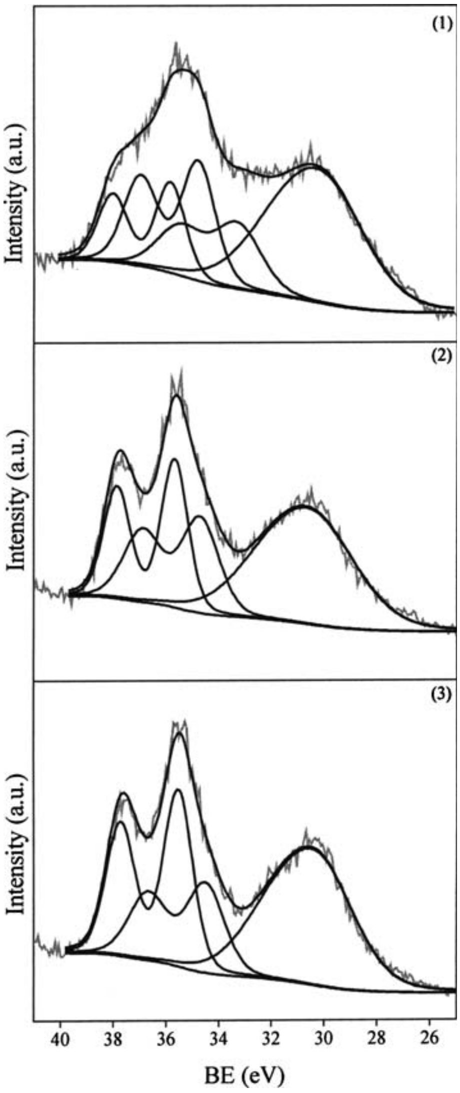

Figure 2. W 4*f* XPS spectra of (1) WZ, (2) AWZ and (3) GWZ.

The surface W/Zr ratios of samples are also listed in table 2. The surface W/Zr is calculated from the ratio of the integrated area of W 4*f* XPS peaks to the integrated area of Zr 3*d* XPS peaks (not shown) and consideration of the atomic sensitivity factor of W and Zr. The surface W/Zr ratio in WZ is 0.23. Conversely, the surface W/Zr ratios in AWZ and GWZ decrease to 0.086 and 0.084. The results showed that Al and Ga facilitate the dispersion of WO_x on the surface of zirconia.

3.2. Catalytic reaction performance

3.2.1. Catalytic activity and product distribution

Isomerization reaction of *n*-pentane was carried out at 215 °C in the presence of H_2. Figure 3 shows the conversion with time on stream over the promoted and non-promoted catalysts. Catalyst deactivation was not observed during the test period of 6 h. The promoted catalysts exhibit higher *n*-pentane conversion than WZ. Under the identical reaction condition, the catalytic

Table 2
W 4*f* XPS fitting results

Sample	BE (eV)	Assignment	W (%)	W/Zr
WZ	35.8	W^{6+}	28	0.23
	34.8	W^{5+}	42	
	33.4	W^{4+}	30	
AWZ	35.7	W^{6+}	53	0.086
	34.7	W^{5+}	47	
GWZ	35.5	W^{6+}	61	0.084
	34.5	W^{5+}	39	

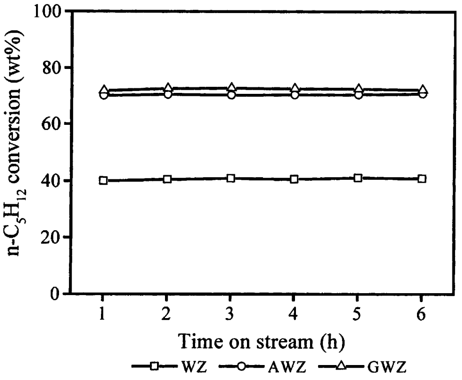

Figure 3. Catalytic activity of WZ, AWZ and GWZ catalysts for *n*-pentane isomerization as a function of time. P = 2 MPa, T = 215 °C, $H_2/n\text{-}C_5$ = 3 and WHSV = 1 h^{-1}.

activity of WZ is low; *n*-pentane conversion is only 41%. The catalytic conversions of pentane for AWZ and GWZ are greatly improved to 71 and 72%, respectively. The product distributions of *n*-pentane isomerization over WZ, AWZ and GWZ catalysts are compared in table 3. In contrast to WZ, AWZ and GWZ catalysts not only display much higher catalytic activity, but also favor the formation of iso-pentane. The yield of iso-pentane over AWZ and GWZ reaches 65 and 66%, much more than that over WZ. The higher catalytic activity of AWZ and GWZ is also reflected in the formation of a little higher amount of cracking products, C_{4-}. The cracking products are negligible over WZ because of its lower catalytic activity.

For comparison with the major commercial catalysts for *n*-pentane isomerization, the results of Pt–C1/A1$_2$O$_3$ and Pt/HM are also listed in table 3. Pt/HM shows the highest reaction temperature of 250 °C for *n*-pentane isomerization where thermodynamic constrains give the lowest yield of iso-pentane. AWZ and GWZ show the lower reaction temperature of 215 °C and improved *n*-pentane conversion and the yield of iso-pentane. Although the reaction temperature over AWZ and GWZ is higher than Pt–Cl/A1$_2$O$_3$, AWZ and GWZ have *n*-pentane isomerization activities approaching that of Pt–Cl/A1$_2$O$_3$. However, chloride is corrosive to the facility and harmful to the environment. AWZ and GWZ catalysts are novel halogen-free and Pt-free solid acid catalysts that give a green process for *n*-pentane isomerization. Both Pt–Cl/A1$_2$O$_3$ and Pt/HM require noble metal Pt to maintain the catalytic activities and stabilities. AWZ and GWZ, composed of mixed metal oxides without using noble metal, may be cheaper and sulfur-tolerant.

3.2.2. *Effect of reaction pressure on the catalytic activity*

The reaction pressure has a great effect on the catalytic activities of AWZ and GWZ for *n*-pentane isomerization. Figure 4 shows *n*-pentane conversion greatly depends on the reaction pressure. For both AWZ and GWZ, *n*-pentane conversion and the cracking products, C_{4-}, show the similar trend, they pass through a maximum at a reaction pressure of approximate 2.0 MPa and slightly decreased as the reaction pressure was further increased to 2.5 MPa. Because of the highest cracking products at the reaction pressure of 2.0 MPa, the selectivity to iso-pentane is ~92%, slightly lower than those at other setting pressure. Pentane isomerization is an equimolecular reaction. The change of reaction pressure has no effect on pentane isomerization theoretically. Actually, the side reaction, such as the cracking of pentane or its oligomer, can increase the number of molecules. It is suggested that increasing reaction pressure can suppress the side hydrogenolysis reaction. However, Kuba *et al.* [22] suggested the reaction pathway in *n*-pentane isomerization over WZ catalysts by two modes: monomolecular and bimolecular. For both modes, iso-pentane is formed from isomerization intermediate and isomerization intermediate is originally derived from the dehydrogenation of *n*-pentane. Too high the reaction pressure is a disadvantage in the dehydrogenation of *n*-pentane. It seems 2.0 MPa is the optimum reaction pressure.

3.2.3. *Effect of tungsten content on the catalytic activity*

Figure 5 shows the effect of W content on the catalytic activity for *n*-pentane isomerization over AWZ. At the same calcination temperature of 850 °C, the activity of AWZ catalyst depends strongly on W content. AWZ

Table 3

Comparison of the catalytic performance of WZ, AWZ, GWZ and some commercial catalysts

Catalyst	WZ	AWZ	GWZ	Pt–Cl/Al$_2$O$_3$	Pt/HM
T/°C	215	215	215	< 160	250
P/MPa	2	2	2	3	3
Space velocity	1 g g^{-1} h^{-1}	1 g g^{-1} h^{-1}	1 g g^{-1} h^{-1}	2 v v^{-1} h^{-1}	1 g g^{-1} h^{-1}
$H_2/n\text{-}C_5H_{12}$	3	3	3	–	2.5
$n\text{-}C_5H_{12}$ conversion (wt%)	41	71	72	77[a]	63
Total cracking C_{4-} (wt%)	0.5	2.6	3.0	–	0.5
$i\text{-}C_5H_{12}$ (wt%)	40	65	66	76[a]	61
Selectivity to $i\text{-}C_5H_{12}$ (wt%)	98	92	92	90*	97
Reference	This study	This study	This study	1	2

[a] The feedstock contained 7 wt% iso-pentane.

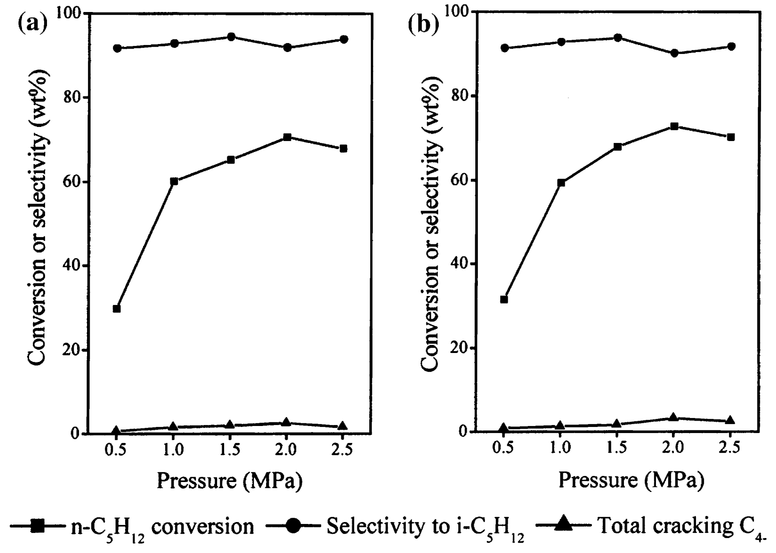

Figure 4. Effect of reaction pressure on catalytic performance of (a) AWZ and (b) GWZ. Data obtained after 6 h on feed. T = 215°C, $H_2/n\text{-}C_5$ = 3 and WHSV = 1 h^{-1}.

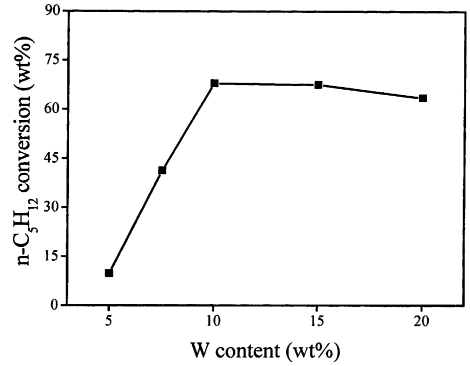

Figure 5. Effect of W content on catalytic performance of AWZ. Data obtained after 6 h on feed. P = 2 MPa, T = 215 °C, $H_2/n\text{-}C_5$ = 3 and WHSV = 1 h^{-1}.

catalyst is almost inactive below 5 wt% W content; *n*-pentane conversion is only ~10%. Increasing W content leads to a large improvement in catalytic activity. The maximum conversion is found at 10–15 wt% W loading. Further increasing W content, the catalytic activity of AWZ shows a small decline. It was reported that the maximum catalytic activity of WZ for *o*-xylene isomerization occurred at the WO_x surface density higher than the theoretical monolayer capacity of WZ catalysts [23]. Baertsch [24] suggested the acidity and number of Brönsted acid sites presented on WZ increased with the loading of WO_x to monolayer coverage.

3.2.4. *Effect of calcination temperature on the catalytic activity*

The effect of calcination temperature of AWZ on the catalytic activity for n-pentane conversion is shown in figure 6. AWZ catalysts with 10 and 15 wt% W content show the higher catalytic acidity from figure 5. So, two samples of AWZ with 10 and 15 wt% W content respectively were used to investigate the effect of calcination temperature. From figure 6, the optimum calcination temperature is 850 °C for AWZ of 10 wt% W content; and the optimum calcination temperature is 800 °C for AWZ of 15 wt% W content. At the calcination temperature of 850 °C, the catalytic activity of AWZ of 10 wt% W content is slightly higher than that of AWZ of 15 wt% W content. As the calcination temperature decreased to 800 °C, the catalytic activity of AWZ of 10 wt% W content sharply decreases to a much lower level than that of AWZ of 15 wt% W content. The results are qualitatively in accord with the conclusions that increasing WO_x surface concentration resulted in the lowering of optimum calcination temperature of WZ catalysts for *o*-xylene isomerization [24].

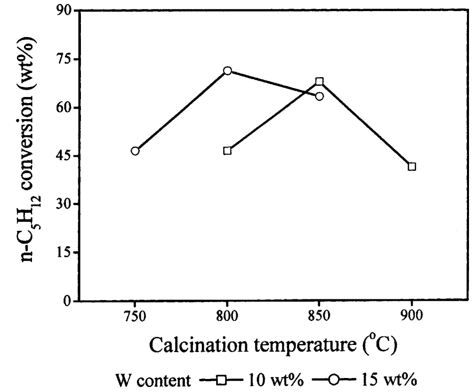

Figure 6. Effect of calcination temperture on catalytic performance of AWZ. Data obtained after 6 h on feed. P = 2 MPa, T = 215°C, $H_2/n\text{-}C_5$ = 3 and WHSV = 1 h^{-1}.

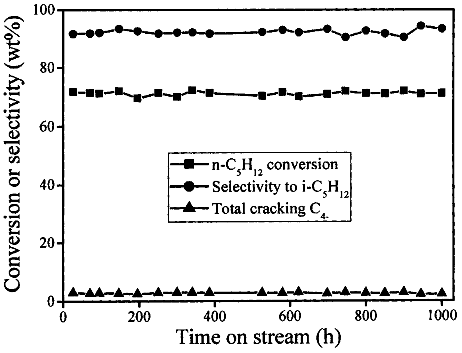

Figure 7. Thousand hours stability test of *n*-pentane isomerization over GWZ. P = 2 MPa, T = 220 °C, $H_2/n\text{-}C_5 = 4$ and WHSV = 1 h^{-1}.

3.2.5. *Stability of the catalysis*

In order to evaluate the application potential of AWZ and GWZ catalysts, it is necessary to investigate their stability. The result of stability test of GWZ for 1000 h is shown in figure 7. No catalyst deactivation was observed during the entire test period of 1000 h. *n*-Pentane conversion is stable at ~71%, the selectivity to iso-pentane reaches ~92% and the cracking products, C_{4-}, is less than 3%. Figure 8 gives the stability of AWZ for a 200 h test. Deactivation was not observed during the test period for AWZ catalyst. *n*-Pentane conversion is stable at ~72%, the selectivity to iso-pentane reaches ~93% and the cracking products, C_{4-}, is less than 3%.

3.2.6. *The nature of promotional effect*

The promotion of catalytic activities of Al and Ga are through two different effects: (a) the formation of stronger acid sites (b) the increased redox activity of W. Both are important for the catalytic isomerization of alkanes. The pentane molecules are activated by dehydrogenation on well-dispersed polyoxotungstate *via* a redox process. Then the resulting alkenes are protonated on the acidic sites. A stable and active catalyst for alkane isomerization requires the balanced action of the above two functions. It seems Al and Ga play promotional roles in both the redox and acidic properties. The strengths of the acid sites in AWZ and GWZ are found to be stronger than those originally present on WZ. Al and Ga favor the dispersion of WO_x on the surface of zirconia. In our previous work [18], the crystal WO_3 was observed on WZ and disappeared on AWZ and GWZ by UV–visible diffuse reflectance spectra. It is known that the crystal WO_3 is an inactive phase. The well-dispersed WO_x can affect the acid sites distribution and cause more active sites in catalysis.

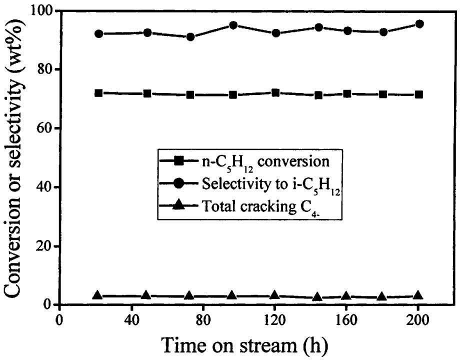

Figure 8. Two hundred hours stability test of *n*-pentane isomerization over AWZ. P = 2 MPa, T = 215 °C, $H_2/n\text{-}C_5 = 3$ and WHSV = 1 h^{-1}.

Addition of Al or Ga to WZ also improves the redox properties of W^{6+}. The redox properties of W^{6+} in WO_x/ZrO_2 play a crucial role as a redox initiator in activation of alkanes. Kuba *et al.* [25] suggested that in tungstated zirconia alkane activation proceeds *via* a hemolytic C–H bond breaking by electron transfer to W^{6+} forming W^{5+}. Occhiuzzi *et al.* [26] further found that in a reducing environment W^{5+} forms on small WO_x clusters or polyoxotungstates. In. $W0_3$, the inactive W^{4+} would form. Our investigation by XPS technique found that the Al or Ga addition do help the dispersion of tungstated on zirconia and lead to the more active W^{5+} species. The improved redox pair of W^{6+}/W^{5+} in promoted WZ is accompanied by the easier activation of alkanes. With both improved initiation of alkane dehydrogenation and acidity in forming carbenium ion, the isomerization activities in promoted WZ are thus increased and more importantly well-balanced.

4. Conclusion

In this paper, we have shown that Al- and Ga-promoted WZ catalyze isomerization of *n*-pentane with high catalytic activity and selectivity. Their high catalytic activities remain very stable over a long period. For both AWZ and GWZ, the catalytic activity is greatly dependent on W content, calcination temperature and reaction pressure. Compared to the commercial catalysts, Al- or Ga-promoted WZ catalysts show *n*-pentane isomerization activities approaching that of Pt on chlorinated aluminum catalyst, and much higher than that of Pt/H-mordenite. AWZ and GWZ catalysts are a new kind of halogen-free solid acid catalysts that are friendly to the environment. Another notable characteristic of AWZ and GWZ catalysts is that they are composed of mixed oxides without noble metal.

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