

Ga-promoted tungstated zirconia catalyst for *n*-butane isomerization

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Ga-promoted tungstated zirconia (GWZ) was prepared by a slurry impregnation method. The textural properties as well as the acidities of the Ga-promoted catalysts were characterized by X-ray powder diffraction (XRD), N₂ adsorption, NH₃ temperature-programmed desorption (NH₃ TPD), microcalorimetry and H₂ temperature-programmed reduction (H₂ TPR). The catalytic behavior of GWZ for *n*-butane isomerization was studied in the presence of hydrogen. In comparison to tungstated zirconia (WZ), the catalytic activity of the Ga-promoted catalyst was greatly improved. The reason proposed for the higher activity of the Ga-promoted catalysts was that Ga enhances the oxidizing ability of the catalysts.

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

1. Introduction

Strong solid acids as catalysts for hydrocarbon isomerization reactions are sought because they have the potential to offer key advantages over liquid acids such as much easier handling and storage, less corrosion and more friendly to the environment [1]. For example, there is a worldwide need for removing aromatics in gasoline because of their toxicity. The loss of octane number as a result of the removal of aromatics could be mitigated by the addition of other high-octane compounds such as multi-branched hydrocarbons [2]. Since the discovery of its strong solid acidity by Hino and Arata [3,4], tungstated zirconia (WZ) has attracted much attention as a potential petrochemical process catalyst. The strong acidity and high activity of WZ made it attractive as a catalyst in the isomerization of hydrocarbons. WZ was demonstrated by several authors to be active in the isomerization of normal alkanes such as *n*-butane [5], *n*-pentane [6,7] and *n*-hexane [8,9].

Similar environmental concerns also arise regarding the use of sulfated zirconia (SZ), the well-known solid super-acid first discovered by Tanabe and Hattori [10]. Although high catalytic activity and product selectivity can be achieved in skeletal isomerization reactions, serious concerns remain about the long-term stability of zirconia-supported sulfate species in reducing and oxidizing environments that are typical of hydrocarbon reactions and catalyst regeneration. This may lead to the generation of hazardous SO_x and H₂S [11,12]. This situation raises many doubts about their possible industrial application.

Although WZ is less active than SZ and the catalytic activity of WZ for *n*-butane isomerization is low, tungstated zirconia (WZ) has become increasingly important as an alternative to SZ. The stable and inorganic nature of these types of mixed metal oxide catalysts (WO₃/ZrO₂) ensures that they are environmentally friendly in both oxidizing and reducing environments, even at high reaction temperature.

Recently, Al and Ga introduced to SZ have shown good activity and selectivity for *n*-butane isomerization [13–15]. Moreno and Poncelet [14] reported that Ga shows better catalytic performances than Al. Hua and Sommer [16] reported alumina-doped Pt/WO_x/ZrO₂ catalysts for *n*-heptane isomerization.

In this paper we are interested in the study of the promotion of WZ with Ga and its potential as a catalyst for the isomerization of *n*-butane. Isomerization of *n*-butane on a series of Ga-promoted tungstated zirconia catalysts was studied in a fixed-bed flow reactor. A large increase in the catalytic activity can be observed on the Ga-promoted WZ catalysts. Pt addition improved further the stability, activity and the selectivity of Ga-promoted WZ in the isomerization of *n*-butane. The reasons for the improvement in activity and stability of the Ga-promoted catalysts are discussed.

2. Experimental

2.1. Catalyst preparation

Zr(OH)₄ was prepared from zirconia nitrate solution by adding dropwise ammonium hydroxide solution up to pH 9–10. The precipitated hydrogel was filtered and

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washed repeatedly until the filtrate liquid showed a pH of 7. The gel was dried at 105 °C. The dried particles were impregnated with aqueous ammonium tungstate ($\text{H}_8\text{N}_2\text{O}_4\text{W}$, Acros) in order to obtain a W content of 10 wt% in the final catalyst. In the synthesis of Ga-promoted WZ catalyst, the appropriate amount of $\text{Ga}(\text{NO}_3)_3$ was added to a WZ slurry. The resultant suspension was refluxed overnight at 120 °C, dried at 110 °C, and then calcined at final temperature in static air for 3 h.

Pt-impregnated GWZ catalyst was prepared by impregnating 1.0GWZ850 (the first digits indicate the Ga weight percent in the final catalyst, the final digits the calcination temperature in °C) with hydrogen hexachloroplatinate (Acros, 40% Pt) solution overnight. The concentration of the solution was adjusted in order to obtain 0.3% Pt in the final catalyst. Then it was dried at 110 °C and calcined at 450 °C in an air stream for 3 h.

2.2. Catalyst characterization

XRD patterns of the samples were obtained using a Bruker D8 Advance instrument with $\text{CuK}\alpha$ radiation at 40 kV and 30 mA. BET surface areas of the samples were acquired using a Micromeritics ASAP 2010 automatic adsorption instrument using N_2 as the adsorbent. The temperature-programmed desorption of ammonia (NH_3 TPD) was carried out using a Micromeritics Auto-Chem 2910 instrument. An amount of 150 mg of sample was pretreated at 500 °C under pure He (50 ml/min) for 1 h and then cooled to 120 °C. After introducing 3% NH_3 in He at 120 °C for 0.5 h, the sample was flushed with He for 1.5 h. The TPD profile of NH_3 was obtained from 120 to 800 °C at a heating rate of 10 °C/min. The desorption process was monitored by a quadrupole mass spectrometer (Thermo ONIX, ProLab) connected on-line through a heated capillary interface. The mass number 16 was followed to obtain TPD profiles of NH_3 because the mass intensity is relatively strong and the interference from H_2O is negligible. Microcalorimetric studies of the adsorption of NH_3 were carried out at 150 °C using a self-assembled differential calorimeter. H_2 temperature-programmed reduction (H_2 TPR) of samples was performed using a self-assembled instrument equipped with a thermal conductivity detector (TCD). Samples were pretreated in a flow of air at 400 °C for 1 h, cooled to room temperature in N_2 , and then heated to 800 °C at a rate of 10 °C/min in a gas stream of 5% H_2 in N_2 .

2.3. Catalytic experiments

The isomerization of *n*-butane was performed in a fixed-bed flow reactor. Prior to reaction, the catalyst was pretreated at 450 °C for 3 h under air conditions, and then contacted with flowing hydrogen at the reaction

temperature for 1 h. The following reaction conditions were used: reaction temperature, 300 °C; pressure, 101.3 kPa; catalyst mass, 1.0 g; feed flow rate (at NTP), 3 ml/min of *n*-butane mixed with 12 ml/min of H_2 at *n*-butane WHSV of 0.47/h. An on-line SP6800A gas chromatograph equipped with a FID was used to analyze the reaction products.

3. Results and discussion

3.1. X-ray diffraction

The XRD patterns of WZ and GWZ were recorded for investigating the effect of calcination temperature on the zirconia crystal structure. The results are presented in figure 1. All samples calcined at 750 °C, 800 °C contained zirconia primarily in the tetragonal phase and no WO_3 crystallite was observed for these samples. The emergence of WO_3 crystallite ($2\theta = 23\text{--}25^\circ$) on the zirconia surface was found with an increase of the calcination temperature. Two small peaks of monoclinic zirconia ($2\theta = 28.5^\circ, 31.5^\circ$) were observed from WZ850 while WZ900 showed a mixture of a monoclinic phase and a tetragonal phase. When Ga is incorporated, it suppresses the monoclinic zirconia. No monoclinic zirconia was present on the XRD patterns of 1.0GWZ850 and 1.0GWZ900. Huang *et al.* [17] reported that the tetragonal structure was essential in highly active acid catalysts and a monoclinic phase would result in a material of distinctly lower acidity. This suggested that Ga influenced catalytic activity through the crystallization behavior. It favored the formation of the tetragonal phase and stabilized tetragonal zirconia crystallites even at higher calcination temperature. Previously, we have also found that Al suppressed the formation of monoclinic zirconia in sulfated zirconia [18].

3.2. BET surface area

The BET surface areas of all promoted and non-promoted WZ catalysts calcined at 850 °C are around 50–60 m^2/g , shown in table 1. Ga addition to WZ had less effect on the surface area of WZ. The surface area of the 1.0 wt% Ga-doped WZ catalysts decreased with increasing calcination temperature.

3.3. Acidity measurements

We used the NH_3 TPD technique to compare the acidic characteristic of the same set of WZ850 and 1.0GWZ850 catalysts. Figure 2 shows there is no obvious difference in the NH_3 TPD profiles between WZ850 and 1.0GWZ850.

The surface acidities of WZ850 and 1.0GWZ850 were measured by microcalorimetry using ammonia as a basic

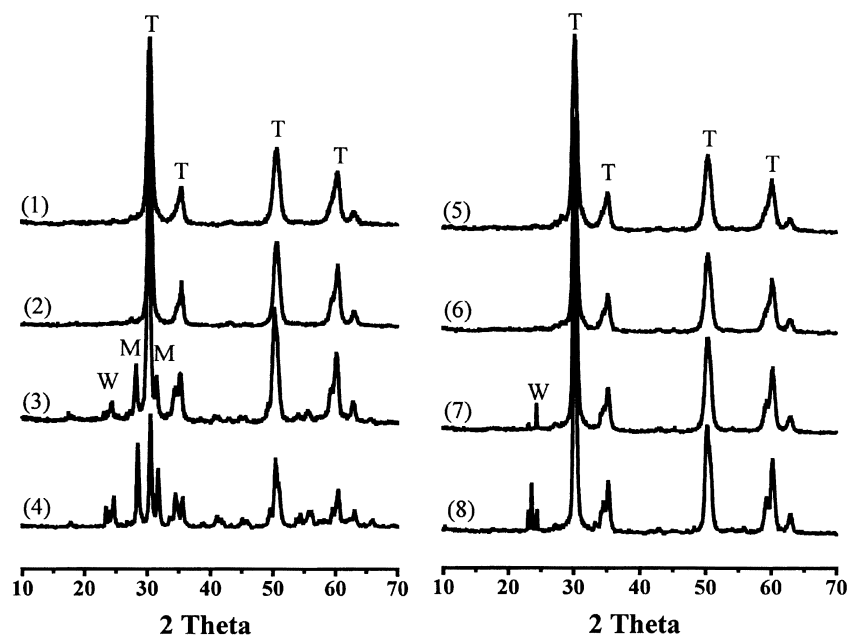


Figure 1. XRD patterns of samples: (1) WZ750; (2) WZ800; (3) WZ850; (4) WZ900; (5) 1.0GWZ750; (6) 1.0GWZ800; (7) 1.0GWZ850; (8) 1.0GWZ900. T, tetragonal zirconia; M, monoclinic zirconia; W, tetragonal WO_3 .

probe molecule. The results are shown in figure 3. The differential heat of adsorption decreases with NH_3 coverage, indicating a distribution of acid site strengths in the catalysts. The calorimetric data provided parallel results which give the initial adsorption heat of WZ850 and 1.0GWZ850 to be 136 and 135 kJ/mol. The total acid sites of WZ850 and 1.0GWZ850 are 195 and 182 $\mu\text{mol/g}$, respectively.

3.4. H_2 TPR of WZ and GWZ

To understand the promotion effect of Ga, we used the H_2 TPR technique to compare the characteristics of WZ850 and 1.0GWZ850. As shown in figure 4, the H_2 TPR profile of WZ850 presents a peak of hydrogen consumption at 505 $^\circ\text{C}$ while 1.0GWZ850 shows a peak at 440 $^\circ\text{C}$. Addition of Ga to WZ decreased the

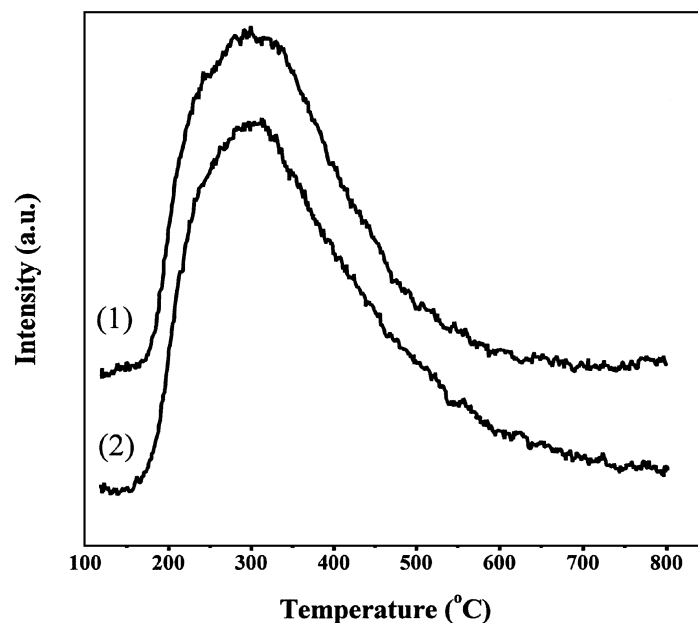
reduction temperature of WZ. The redox properties of WZ had been observed and related to the activation of *n*-alkane [19,20]. Kuba *et al.* [19] reported that the redox properties of W^{6+} in WO_x/ZrO_2 played a crucial role as a redox initiator in the activation of alkanes. It was suggested that Ga addition improved the redox properties of W^{6+} . We can infer that GWZ might be bifunctional, exhibiting both acidic and redox properties, and that alkane isomerization might be initiated by oxidation of the alkane. The decreased reduction temperature of GWZ may make *n*-butane isomerization easier.

3.5. Catalytic activity in *n*-butane isomerization

Rossi *et al.* [21] reported that the reaction temperature influences the activity and selectivity of *n*-butane isomerization and reaction at 300 $^\circ\text{C}$ shows good performances. The isomerization reaction of *n*-butane was carried out at 300 $^\circ\text{C}$. The performances of WZ catalysts with different Ga content and GWZ calcined at differential temperature are listed in table 2. We can see that the *n*-butane initial activity increased with Ga content up to 1.0 wt%, and decreased again as the Ga content was further increased. For 1.0GWZ calcined at different temperatures, a maximum catalytic performance occurred of about 37.3% at 850 $^\circ\text{C}$. The catalysts calcined at 750 and 800 $^\circ\text{C}$ showed low initial activities. On increasing the calcination temperature to 900 $^\circ\text{C}$, the initial activity decreased. Except for the low selectivity to *i*- C_4 of WZ850 catalyst, not much difference was observed in selectivity to *i*- C_4 for Ga-promoted

Table 1
Surface area of various catalysts

Catalyst	Calcination temperature ($^\circ\text{C}$)	Ga content (wt%)	Surface area (m^2/g)
GWZ	750	1.0	77.6
	800	1.0	58.6
	850	1.0	58.1
	900	1.0	31.0
	850	0.5	53.4
	850	1.5	57.6
	850	2.0	53.0
WZ	850	0	53.3

Figure 2. NH_3 TPD profiles: (1) WZ850; (2) 1.0GWZ850.

catalysts. It is concluded that the best conversion is achieved when the catalyst is promoted by 1.0 wt% Ga addition and calcination at 850 °C.

The Ga-promotion effect of *n*-butane conversion versus time-on-stream (TOS) in the flow reactor is shown in figure 5. The influence of platinum addition was also considered. The conversion over WZ850 was much lower and attained a stable conversion of 3.9% after 180 min; its selectivity was less than 80%. The initial activity of 1.0GWZ850 showed a tremendous

improvement compared with WZ850, reaching 37.3%, slightly decreased with TOS and reached a stable conversion of 23.7% while the initial selectivity of 1.0GWZ850 was less than 80% and attained a stable selectivity of 85.5%. In contrast, Pt/1.0GWZ850 immediately attained a stable conversion of 42% and selectivity of 94%. Although deactivation of 1.0GWZ850 in the initial stage was observed, the deactivated catalyst 1.0GWZ850 can be completely regenerated in air at 450 °C.

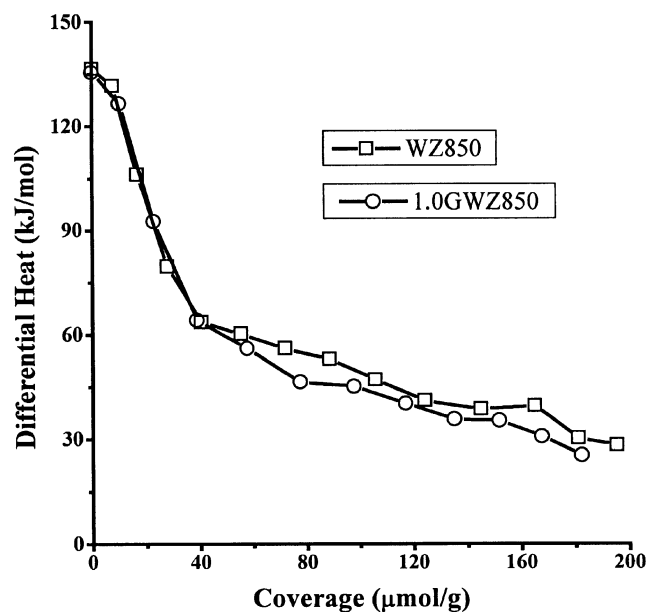


Figure 3. Microcalorimetry results of WZ850 and 1.0GWZ850.

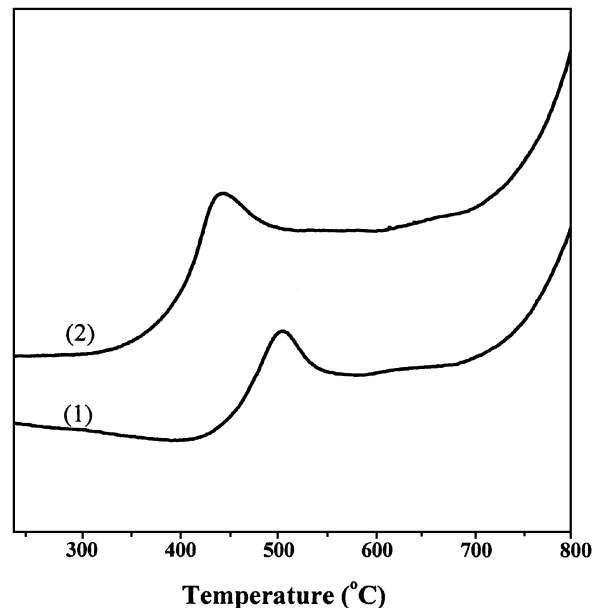
Figure 4. H_2 TPR profiles: (1) WZ850; (2) 1.0GWZ850.

Table 2
Catalytic performances over various catalysts

Catalyst	<i>n</i> -C ₄ conversion (%)			Selectivity to <i>i</i> -C ₄ (%)		
	10 min	60 min	300 min	10 min	60 min	300 min
WZ850	5.1	4.1	3.9	78.9	78.6	78.7
1.0GWZ750	11.9	8.7	7.5	81.8	81.3	81.5
1.0GWZ800	26.2	21.3	16.3	81.5	83.9	85.9
1.0GWZ850	37.3	31.1	23.7	79.2	82.8	85.5
1.0GWZ900	29.4	24.2	18.5	81.1	83.9	85.1
0.5GWZ850	12.8	11.7	10.4	83.9	84.1	84.1
1.5GWZ850	29.1	25.2	20.1	82.4	84.1	84.9
2.0GWZ850	19.5	16.5	13.9	84.5	85.8	85.1

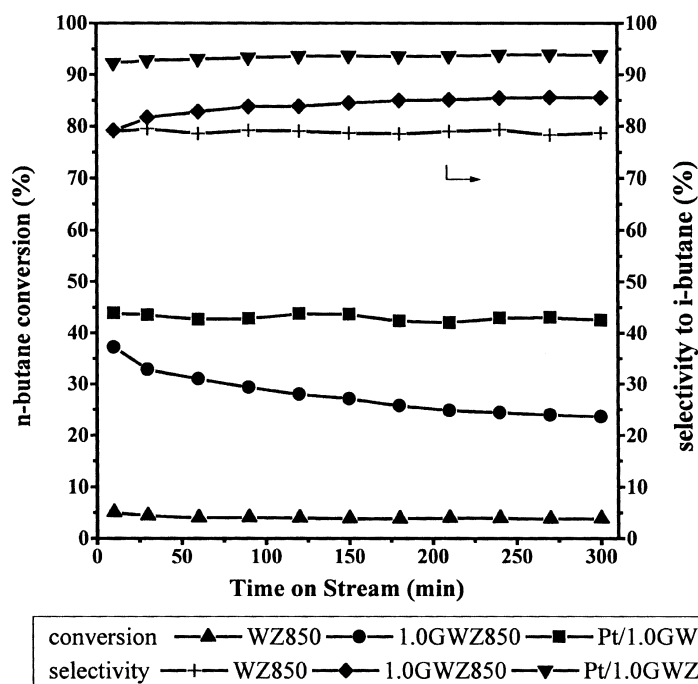


Figure 5. Catalytic performances versus TOS over WZ850, 1.0GWZ850 and Pt/1.0GWZ850.

4. Conclusions

From the results of this study it can be concluded that the best Ga loading in these catalysts is around 1.0 wt% and calcination should be at 850 °C. The high isomerization activity of the catalysts promoted by the addition of Ga in the presence of H₂ can be explained by assuming that Ga suppresses the monoclinic zirconia, and favors and stabilizes tetragonal zirconia. In contrast to WZ, Ga-promoted WZ showed less difference in acidity characteristics, but had lower reduction temperature, which improved the redox properties of W⁶⁺. As a redox initiator, W⁶⁺ plays an important role in the oxidation of the alkane. The decreased reduction temperature of GWZ made *n*-butane isomerization easier.

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