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Al- and Ga-promoted WO_3/ZrO_2 strong solid acid catalysts and their catalytic activities in *n*-butane isomerization

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Abstract

A series of Al- and Ga-promoted tungstated zirconia strong solid acid catalysts were prepared. The effect of Al_2O_3 and Ga_2O_3 on the structural, acidic and redox features of WO_3/ZrO_2 (WZ) has been characterized by means of X-ray powder diffraction (XRD), N_2 adsorption (BET), UV–visible diffuse reflectance spectra (UV–vis), infrared spectra (IR), NH_3 temperature-programmed desorption (NH_3-TPD) and H_2 temperature-programmed reduction (H_2-TPR). With respect to tungstated zirconia, the promoted catalysts stabilized the zirconia tetragonal phase, prevented crystalline WO_3 growth. Al or Ga addition to WZ had less effect on the strength of the acid sites, but effected reduction temperature of WZ. The isomerization of *n*-butane was investigated at 300 °C over tungstated zirconia and promoted catalysts. The promoted catalysts improved the isomerization conversion and stability in the presence of hydrogen. The best Al and Ga loading in these catalysts is around 0.5 and 1.0%, respectively, and the optimal calcination temperature is ∼850 °C. The experiment results showed that Ga was a more efficient promoter than Al. Pt addition to promoted catalysts showed great improvement on the performance of selectivity and stability.

Keywords: WO_3/ZrO_2; $Al_2O_3/WO_3/ZrO_2$; $Ga_2O_3/WO_3/ZrO_2$; Strong solid acid; Butane isomerization

1. Introduction

Strong solid acids based on supported metal oxides are potential replacements for liquid acids and halide-containing solid acids with the need for reformulated high-octane gasoline not containing aromatics and the stringent environment regulation. Among the strong solid acids, sulfated zirconia (SZ) catalysts have attracted significant attention because of their ability to isomerize light alkanes at low temperature [1,2]. Yet, SZ catalysts suffer from the disadvantages of deactivation and possibly from sulfur loss during reaction and regeneration, which limit their applicability in isomerization and alkylation processes. Recently, many literatures reported that the stability, activity and selectivity of SZ catalysts could be improved by addition some promoters [3–6].

As an alternative to SZ, tungstated zirconia (WZ) has become increasingly important since its discovery by Arata and Hino [7]. Although WZ catalysts are less active than SZ, they have superior stability under both reducing and oxidizing conditions and appear to be more suitable for industrial applications. The catalytic activity of WZ, like that of SZ, can be improved by promotion with platinum and some metal oxides [8,9]. Moreno and Poncelet [10] found that the addition of small amounts of Al_2O_3 or Ga_2O_3 to SZ system enhance the catalytic and the stability for *n*-butane isomerization at 250 °C in the presence of H_2. The promoting effect of Al or Ga on SZ was later confirmed by other researchers [6,11]. Al_2O_3-doped WO_x/ZrO_2 catalysts and Pt-impregnated forms were claimed as efficient catalysts for the skeletal isomerization of *n*-butane and other alkanes [12,13]. Previously, we have reported Ga-promoted WZ greatly improved the catalytic activity for *n*-butane isomerization [14].

In this paper, *n*-buatne isomerization has been investigated over Al- and Ga-promoted tungstated zirconias and compared with tungstated zirconia. The aim was to investigate the nature of the promoters on the catalytic performances. The influence of platinum addition was also considered.

2. Experimental

$Zr(OH)_4$ was prepared from zirconia nitrate solution by adding dropwise ammonium hydroxide solution up to

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pH 9–10 and refluxed for 24 h. The precipitated hydrogel was filtered and washed repeatedly until the filtrate liquid showed pH 7. The gel was dried at 105 °C. The dried particles were impregnated with aqueous ammonium tungstate (H8N2O4W, Acoros, 99.999%) in order to obtain W content 10 wt.% in the final catalyst. For all catalysts studied in this work, the W content was 10 wt.%. In the synthesis of Al- or Ga-promoted WZ catalyst, the appropriated amount of $Al(NO)_3$ or $Ga(NO)_3$ was added to 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/WZ, Pt/AWZ or Pt/GWZ catalyst was prepared by impregnating hydrogen hexachloroplatinate (Acoros, 40% Pt) solution with WZ850, 0.5AWZ850 or 1.0GWZ850 (the former letters mean the promoter weight percent in the final catalyst, the latter letters mean the calcination temperature in °C) 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. The contents of Pt, W, Al, Ga in the final catalysts are the nominal contents.

XRD patterns of the samples were obtained on a Bruker D8 ADVANCE instrument with Cu Kα radiation at 40 kV and 30 mA. BET surface areas of the samples were acquired on a CHEMBET-3000 instrument using N_2 as the adsorbent. UV–visible diffuse reflectance spectra (UV–vis) were investigated on a Hitachi U-3010. Infrared spectra (IR) were recorded on a Nicolet 550 spectrometer using a KBr pellet. NH_3 temperature-programmed desorption (NH_3-TPD) of samples was carried out on a Micromeritics AutoChem 2910 instrument. 0.2 g calcined sample was used for each experiment. Prior to NH_3 adsorption, sample was pretreated at 450 °C in flowing air for 1 h in order to clean the surface from adsorbed species, and then cooled down in He. The NH_3 adsorption was carried out at 100 °C. After the saturation adsorption of NH_3, the carrier gas He was allowed to flow over the sample at 100 °C for 0.5 h. The desorption of NH_3 was started at 100 °C and continued until 800 °C at 10 °C/min. The desorption process was monitored by a Quadruple 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. H_2 temperature-programmed reduction (H_2-TPR) of samples was performed on a CHEMBET-3000 instrument equipped with a thermal conductivity detector (TCD). About 0.2 g sample was pretreated in a flowing 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 20 ml gas stream of 10% H_2 in Ar.

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 condition, and then contacted with flowing hydrogen at reaction temperature for 1 h. The following reaction condition was 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. An on-line GC-14C gas chromatograph equipped with FID was used to analyze the reaction products.

3. Results and discussion

3.1. BET surface area

The BET surface areas of the AWZ and GWZ samples with different Al, Ga content and calcinations temperature were measured, and the data are presented in Table 1. The addition of Al or Ga does not change the specific surface areas of WZ samples. Samples calcined at 850 °C have nearly same surface areas about 55 m^2/g, and the higher the calcinations temperature, the smaller the surface areas.

3.2. X-ray diffraction

Fig. 1 shows the XRD patterns of samples calcined at different temperature. All samples calcined at 800 and 850 °C show peaks characteristic of the tetragonal phase zirconia, the main peak appearing at $2\theta = 30.2^\circ$ and no WO_3 crystallite was observed. As temperature increased to 900 °C, WZ900 presents a mixture of a monoclinic phase and a tetragonal phase of zirconia, 0.5AWZ900 shows two small peaks of monoclinic zirconia ($2\theta = 28.5^\circ, 31.5^\circ$), but no monoclinic phase is observed from 1.0GWZ900. The diffraction peak of WO_3 crystallite ($2\theta = 23$–25°) on the zirconia surface can be detected with an increase of the calcination temperature to 900 °C. The intensity of crystalline WO_3 in 0.5AWZ900 and 1.0GWZ900 was weaker than that in WZ900. The stabilization of tetragonal zirconia by various metal-oxide dopants and sulfate is well-known phenomenon in the materials fields [11,13,15–17]. It can be explained that aluminum and gallium retard the growth of crystalline WO_3 on the surface of zirconia and suppress the monoclinic zirconia. As the specific surface area dropped and the crystallinity of ZrO_2 increased during calcinations

Table 1
Surface area of various catalysts

Samples	Promoter content (%)	Surface area (m^2/g)
WZ850	0	53.3
AWZ800	0.5	72.0
AWZ850	0.3	51.2
AWZ850	0.5	52.0
AWZ850	0.7	55.0
AWZ900	0.5	31.8
GWZ800	1.0	77.6
GWZ850	0.5	53.3
GWZ850	1.0	58.1
GWZ850	1.5	57.6
GWZ900	1.0	31.0

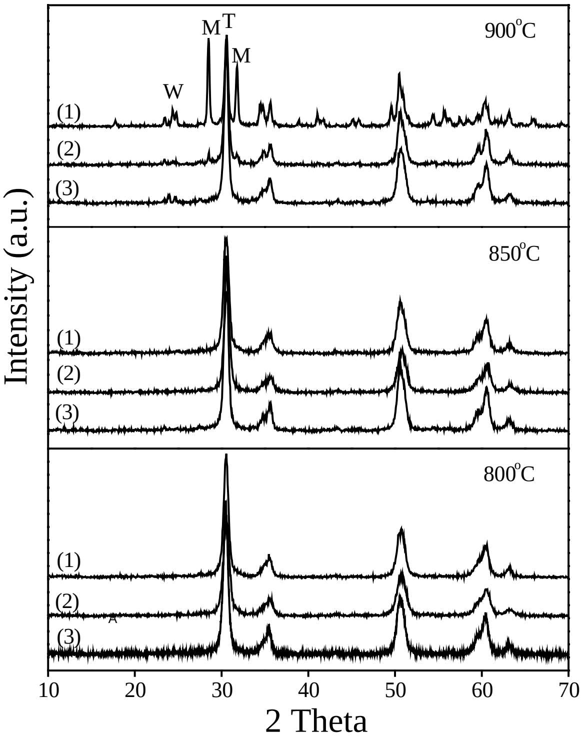

Fig. 1. XRD patterns of samples: (1) WZ, (2) 0.5AWZ and (3) 1.0GWZ. T—tetragonal zirconia; M—monoclinic zirconia; W—crystalline WO_3.

at high temperature, these resulted in the formation of microcrystalline WO_3 observed. It was known [18,19] that the tetragonal structure was essential in highly active acid catalysts and monoclinic phase was poorly efficient in *n*-butane isomerization. This suggested that aluminum and gallium influence catalytic activity through the crystallization behavior. It favored the formation of the tetragonal phase and stabilized tetragonal zirconia crystallites even at higher calcination temperature.

3.3. UV–visible diffuse reflectance spectra

UV–visible diffuse reflectance spectroscopy was used to probe tungsten oxide species dispersed on zirconia surface (showed in Fig. 2). The size effect can be reflected from the shift of the absorption edge [20]. Because pure WO_3 has a large size of crystallization, it gave the highest absorption edge near 450 nm that is the characteristic edge of crystalline WO_3 among the samples examined. To WZ850, with WO_x well dispersed on zirconia surface, one obtained small size of crystalline WO_3, so WZ850 showed weak absorption intensity near 450 nm. The size of crystalline WO_3 became smaller after Al or Ga introduced to WZ. No absorption edge of crystalline WO_3 on 0.5AWZ850 and 1.0GWZ850 near 450 nm was detected. It indicated that Al and Ga efficiently suppressed the growing of crystalline WO_3. The results are qualitatively in accord with the conclusions obtained from X-ray diffraction.

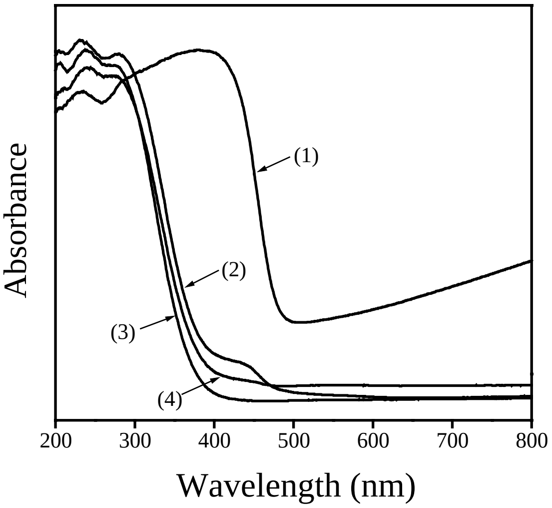

Fig. 2. UV–visible diffuse reflectance spectra of (1) WO_3, (2) WZ850, (3) 0.5AWZ850 and (4) 1.0GWZ850.

3.4. Infrared spectra

Fig. 3 illustrated the IR spectra of WZ850, 0.5AWZ850 and 1.0GWZ850. The band at 750 cm^{-1} is the characteristic of monoclinic zirconia. For Al- and Ga-promoted samples, the intensity of the band at 750 cm^{-1} was weaker than WZ850. 1.0GWZ850 sample exhibited the weakest intensity at 750 cm^{-1} among the three samples. This further confirms that the monoclinic phase was restrained when Al or Ga introduced to WZ. Promotion by Al or Ga enhanced the stability of the tetragonal structure with respect to tungstated zirconia and the fractions of tetragonal structure are found to play an essential role in the catalytic activity. It was also confirmed that Ga was a more efficient promoter than Al.

3.5. Acidity measurements

We used NH_3-TPD technique to compare the acidic characteristic of the same set of WZ850, 0.5AWZ850 and

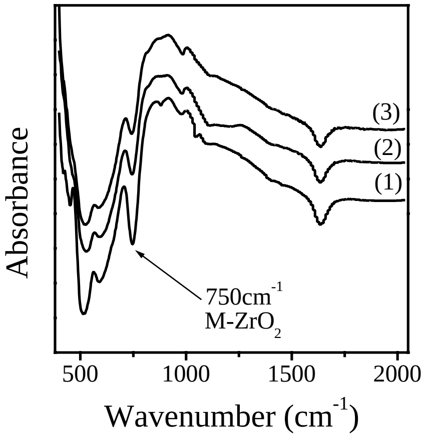

Fig. 3. Infrared spectra of (1) WZ850, (2) 0.5AWZ850 and (3) 1.0GWZ850.

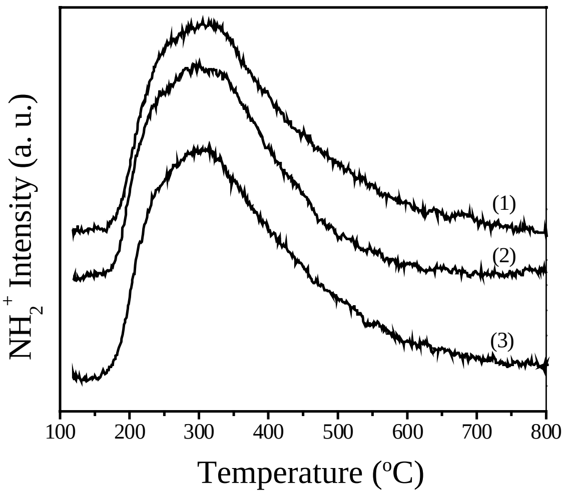

Fig. 4. NH_3-TPD profiles of (1) WZ850, (2) 0.5AWZ850 and (3) 1.0GWZ850.

1.0GWZ850 catalysts. Fig. 4 shows that there is no obvious difference in the strength of the acid sites among these three samples. This suggested that the promoter of Al or Ga does not affect the acidity of WZ.

3.6. H_2-TPR of WZ, AWZ and GWZ

To understand the promotion effect of Al and Ga, we used H_2 temperature-programmed reduction (H_2-TPR) technique to compare the characteristic of WZ850, 0.5AWZ850 and 1.0GWZ850. It has been suggested that reduction of tungstated zirconia with H_2 at elevated temperatures leads to the formation of new OH groups associated with W^{5+} and that those OH groups or the W^{5+} sites may play a crucial role in the mechanism of the isomerization of small alkanes [21–23]. According to the literature [24], pure WO_3 exhibits three reduction peaks, namely a shoulder 540 °C ($WO_3 \rightarrow W_{20}O_{58}$), a sharp peak at 775 °C ($W_{20}O_{58} \rightarrow WO_2$) and a peak at higher temperature ($WO_2 \rightarrow W$). Pure ZrO_2 does not show any detectable TPR peak at temperature below 1000 °C. So the reduction peaks observed from Fig. 5 can be attributed to the reduction of WO_x. The H_2-TPR profile of WZ850 presents a peak of hydrogen consumption at 450 °C. 0.5AWZ850 shows two peaks at 450 and 650 °C, respectively, and 1.0GWZ850 shows a peak at 375 °C. The profiles indicate that the first reduction temperature of WZ and AWZ was the same. The second reduction temperature of WZ was not detected until the reduction temperature increased to ∼800 °C, but it was decreased after addition Al to WZ. Addition of Ga to WZ decreased the first reduction temperature of WZ and undetected the second reduction temperature in the testing range. It was suggested that Al or Ga addition improved the redox properties of W^{6+} and Ga is a more efficient promoter to the redox properties of W^{6+}. The redox properties of WZ had been observed and related to the activation of *n*-alkane [25,26]. Recently, many literatures [25–27] reported that the redox properties of W^{6+} in WO_x/ZrO_2 played a crucial role as a redox initiator in activation of alkanes. In our study, the catalysts show the catalytic activity in the order 1.0GWZ850 > 0.5AWZ850 > WZ850 in correspondence with the H_2-TPR results. We can infer that 1.0AWZ850 and 1.0GWZ850 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 0.5AWZ850 and 1.0GWZ850 may make *n*-butane isomerization easier.

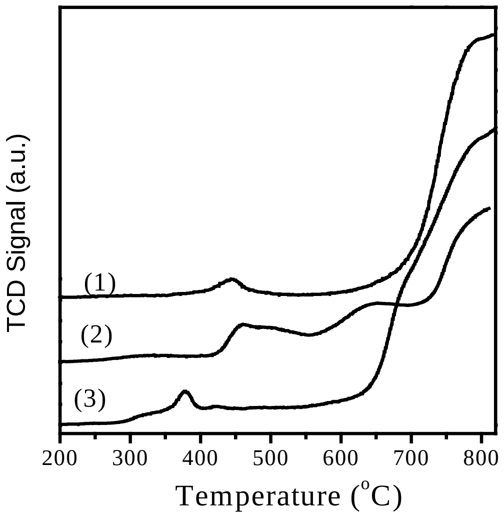

Fig. 5. H_2-TPR profiles of (1) WZ850, (2) 0.5AWZ850 and (3) 1.0GWZ850.

3.7. Catalytic activity in n-butane isomerization

The dependence of initial catalytic activity of promoted catalysts calcined at 850 °C on promoter content is shown in Fig. 6. The conversion of *n*-butane at 10 min is as the initial activity. All promoted catalysts exhibited higher initial conversion than WZ850. For Ga-promoted catalysts, the *n*-butane conversion increased with the Ga content up to

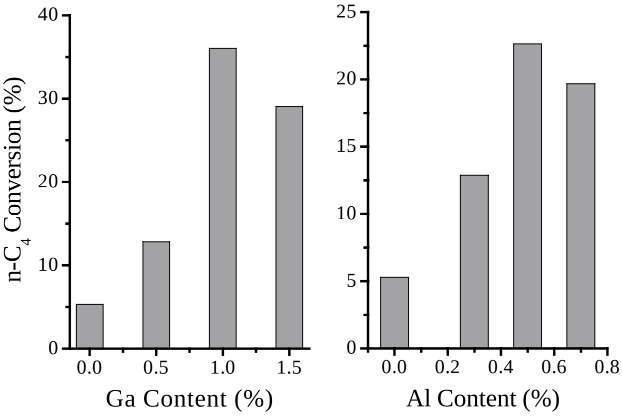

Fig. 6. The effect of promoter content in WZ catalysts on *n*-butane isomerization. All samples are calcined at 850 °C. Reaction temperature: 300 °C; WHSV: 0.47 h^{-1}; $H_2/n\text{-}C_4 = 4$.

Table 2
Calcination temperature effect on initial activity

Samples	1.0AWZ			0.5GWZ		
Calcination temperature(°C)	800	850	900	800	850	900
Initial conversion (%)	16.4	22.6	12.9	26.2	36.0	29.4

1.0 wt.%, and then decreased, as the Ga content was further increased. We also obtained the optimal Al loading in WZ is 0.5 wt.%. Compared to the low initial activity of WZ850 about 5.7%, the initial conversion of *n*-butane over WZ850 with the best Ga and Al loading reaches 37.3 and 22.6%, respectively. It was observed that gallium is a better promoter than aluminum under comparable condition.

Table 2 shows the dependence of *n*-butane conversion on calcination temperature. We investigated the catalytic activity of 0.5AWZ and 1.0GWZ samples over the range of 800–900 °C. It was found that calcination at 850 °C for both 0.5AWZ and 1.0GWZ was more effective than at 800 or 900 °C. A possible explanation is that tungstated zirconia catalysts must be calcined at high temperature to develop the catalytic activity toward alkanes isomerization [28]. However, high calcination temperature favors monoclinic zirconia formation, which would result in a material of distinctly lower acidity. Furthermore, the higher the calcination temperature, the lower the surface area one obtains, which results in lower catalytic activity. So calcination at 850 °C seems to be an optimum temperature for tungstated zirconia catalysts.

The conversions and selectivity to i-C_4 versus time curves obtained at 300 °C over the Pt-impregnated and Pt-free catalysts are compared in Fig. 7. Promotion with Al or Ga greatly enhanced the catalytic properties and stability relative to pure tungstated zirconia. Although 1.0GWZ850 showed higher *n*-butane conversion than 0.5AWZ850, the stable selectivity to i-C_4 of 1.0GWZ850 was ~85%, the same as 0.5AWZ850. Pt impregnation further increased the catalytic performances with respect to the Pt-free forms. The addition of Pt to WZ850 does improve in activity of the catalyst for *n*-butane isomerization at 300 °C, but does not improve the selectivity to i-C_4. The selectivity to i-C_4 over Pt/WZ850 was ~40%, much lower than WZ850, in accordance with previous literatures [29,30]. Pt/1.0GWZ850 immediately attained a stable conversion of 42% and selectivity of 94%. The initial activity of Pt/0.5AWZ850 was very high, reaching 50%, but the initial selectivity was much low because the cracking productions were rich. With time-on-stream, the cracking productions decreased. Pt/0.5AWZ850 attained a stable conversion of 40% and selectivity of 91.5%. At steady conversion, Pt/1.0GWZ850 was more active than Pt/0.5AWZ850.

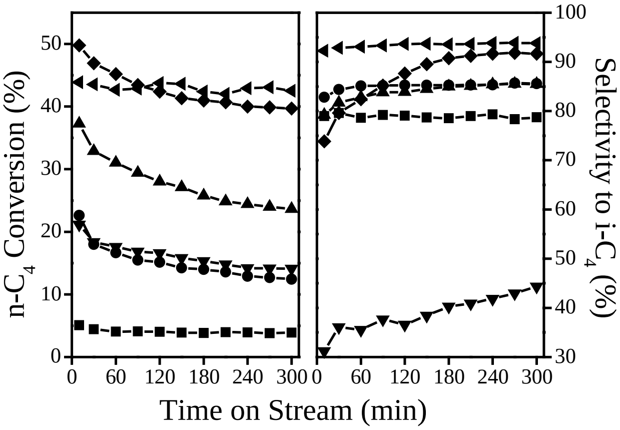

Fig. 7. The catalytic performances vs. time-on-stream over the catalysts. WZ850 (■), 0.5AWZ850 (●), 1.0GWZ850 (▲), Pt/WZ850 (▼), Pt/0.5AWZ850 (◆), Pt/1.0GWZ850 (◀).

4. Conclusions

Promotion of tungstated zirconia with Al and Ga improved the efficiency and stability of tungstated zirconia in *n*-butane isomerization. The optimal promoter loading in AWZ or GWZ calcination at 850 °C is 0.5 or 1.0%, respectively. From the results obtained from this study, Ga was a more efficient promoter than Al. Platinum addition significantly increased the overall *n*-butane conversion and the selectivity to i-butane of all promoted catalysts. These catalysts show the catalytic activity in the order Pt/1.0GWZ850 > Pt/0.5AWZ850 > 1.0GWZ850 > 0.5AWZ850 > WZ850 under the identical reaction condition.

In contrast to WZ, Al- and Ga-promoted WZ showed less difference in acidity characteristic, but had lower reduction temperature, which improved the redox properties of W^{6+}. The promoting effect of Al or Ga is suggested to be a combination of several possible factors, such as (1) enhancing the stability of the tetragonal structure; (2) affecting the crystallite size of WO_3 on the surface of WZ; (3) improving the redox properties of W^{6+}.

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