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Influence of preparative method on Al₂O₃-doped Pt/WO₃-ZrO₂ catalyst for *n*-heptane isomerization

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ABSTRACT

Alumina-doped Pt/WO₃/ZrO₂ catalysts were prepared using either a constant or variable pH method. The obtained catalyst samples were characterized using N₂ adsorption, X-ray diffraction, ultra-violet-visible diffuse reflectance, CO chemisorption, X-ray photoelectron spectroscopy, ²⁷Al magic-angle spinning nuclear magnetic resonance, and infrared spectroscopy of adsorbed pyridine. Compared to the catalyst prepared using the variable pH method, the catalyst prepared using the constant pH method had a higher surface area and Pt dispersion. More Brønsted acid sites were generated in the presence of H₂ on the latter catalyst, and this was responsible for its higher catalytic activity in *n*-heptane hydroisomerization. When the reaction temperature was 200 °C and the weight hourly space velocity of *n*-heptane was 0.9 h⁻¹, the Pt/WO₃/Al₂O₃-ZrO₂ catalyst prepared using the constant pH method gave 70.0% conversion of *n*-heptane, which was significantly greater than the conversion obtained using the corresponding catalyst prepared using the variable pH method (43.5%).

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1. Introduction

In order to improve the quality of gasoline and enable it to better meet environmental protection regulations, there has been a sharp rise in the demand for processes that can produce clean fuels with non-aromatic hydrocarbons and high octane numbers [1,2]. One potential solution is to isomerize C₇₊ *n*-alkanes (C₇ and higher paraffins), which are a major constituent of some crude oil fractions, to their high-octane-number branched isomers as octane-enhancing components. Unlike the case of isomerization of C₄–C₆ light *n*-paraffins, during the isomerization of long-chain C₇₊ *n*-alkanes, cracking caused by β-scission occurs easily, resulting in lower selectivity for branched isomers, especially at high conversion.

Various catalysts have been investigated for the isomeriza-

tion of *n*-heptane, mainly based on Pt or Pd catalysts loaded on SAPO molecular sieves [3], zeolites [4], heteropolyacids [5], SO₄²⁻/ZrO₂ [6], and WO₃/ZrO₂ [7–9]. Among the catalysts studied, Pt/WO₃/ZrO₂ displayed superior catalytic performance. Compared with traditional Pt/zeolite catalysts, Pt/WO₃/ZrO₂ exhibits higher activities at lower temperatures because of its stronger acidity [10–12]. The Pt/WO₃/ZrO₂ catalyst displays much higher isomerization selectivity and longer stability than does Pt/SO₄²⁻/ZrO₂ [7,10,13]. Pt/WO₃/ZrO₂ has therefore recently received more attention. Hua et al. [14] found that incorporating small amounts of Al₂O₃ into the Pt/WO₃/ZrO₂ system enhanced the catalytic activity in *n*-heptane isomerization. This promoting effect of Al₂O₃ in Pt/WO₃/ZrO₂ was later confirmed by Xu et al. [15]. Liu et al. [16] reported that the addition of an appropriate amount of ZnO to Pt/WO₃/ZrO₂ led to a

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moderate increase in the selectivity and yield of C₇ isomers in *n*-heptane isomerization. In our previous work [17,18], we also observed that adding small amounts of Ga₂O₃ or In₂O₃ to Pt/WO₃/ZrO₂ improved the conversion and selectivity in *n*-heptane isomerization. However, there has been no report on the influence of the preparative method on Pt/WO₃/ZrO₂-based catalysts for *n*-heptane isomerization.

In the present work, Al₂O₃-doped Pt/WO₃/ZrO₂ catalysts prepared by constant and variable pH methods, respectively, were tested in *n*-heptane isomerization. The reasons for the effect of the preparative method on the catalytic activity were explored, based on characterization results.

2. Experimental

2.1. Catalyst preparation

ZrO(NO₃)₂·7H₂O (Zibo Rongruida Powder Material Factory, 35 g) and the required amount of Al(NO₃)₃·9H₂O (Sinopharm Chemical Reagent Co. Ltd.) were dissolved in water (400 ml). This solution and an ammonia aqueous solution (Sinopharm Chemical Reagent Co. Ltd., 6 mol/L) were simultaneously added dropwise to 200 ml of ammonia aqueous solution of pH = 9 under vigorous stirring. During coprecipitation, the pH was kept constant at 9. The hydroxide suspension was aged for 24 h at room temperature. The precipitate was then filtered, washed, and dried overnight. WO₃/Al₂O₃-ZrO₂ (denoted by WAZ-C) was prepared by incipient wetness impregnation of Al(OH)₃-Zr(OH)₄ with an aqueous solution of ammonium metatungstate (Aldrich), followed by drying and then calcination in static air at 800 °C for 3 h. WO₃/Al₂O₃-ZrO₂ prepared by another method was denoted WAZ-V. In this case, ammonia solution (6 mol/L) was added dropwise to a mixed aqueous solution of ZrO(NO₃)₂·7H₂O and Al(NO₃)₃·9H₂O until the final pH was 9. The subsequent preparation steps were the same as those for WAZ-C. In both the WAZ-C and WAZ-V samples, the WO₃ loading was 18% and the Al/Zr molar ratio was 0.02. Pt/WAZ-C and Pt/WAZ-V catalysts were prepared by incipient wetness impregnation of WAZ-C or WAZ-V with an aqueous solution of [Pt(NH₃)₄](NO₃)₂ (Aldrich), followed by drying and then calcination in an air flow at 450 °C for 3 h. The Pt content of each catalyst was 1%.

2.2. Catalyst characterization

X-ray diffraction (XRD) measurements were performed using a Bruker D8 Advance diffractometer (Cu K_α tube potential 40 kV, tube current 40 mA, 2θ = 20°–70°, 4°/min). The Brunauer-Emmett-Teller (BET) surface areas were analyzed using N₂ adsorption at –196 °C with a Micromeritics ASAP 2010 instrument. Before measurements, each sample was degassed at 300 °C for 3 h. Diffuse reflectance ultraviolet-visible (UV-Vis) spectra were collected on a Shimadzu UV-2450 spectrometer equipped with an integrating sphere attachment using BaSO₄ as the reference. The Pt dispersions on the WAZ-C and WAZ-V supports were determined using a pulsed CO chemisorption technique with a Micromeritics AutoChem II apparatus loaded

with 0.3 g of catalyst. The catalyst was activated at 450 °C in an air flow for 2 h, reduced in an H₂ flow at 250 °C for 2 h, and then swept under the He flow at 250 °C for 1 h. The catalyst was then cooled to room temperature and a pulse of 5%CO-95%He mixture was repeatedly injected into the reactor until the CO signals from the thermal conductivity detector remained constant. He was used as the carrier gas. The volume of CO chemisorbed was determined by summing the fractions of CO consumed in each pulse. Toluene hydrogenation was carried out at 160 °C in a pulsed microreactor loaded with 50 mg of catalyst. The carrier gas was H₂ at a flow rate of 40 ml/min. The amount of toluene injected for each test was 1 μl. Prior to the reaction, the catalyst was first activated at 450 °C in an air flow for 2 h, and then reduced at 250 °C in an H₂ flow for 2 h. ²⁷Al magic-angle spinning nuclear magnetic resonance (MAS NMR) measurements were performed using a Bruker DSX-300 spectrometer. A resonance frequency of 78.2 MHz, a recycle delay of 0.2 s, and short 0.3 μs pulses were applied. X-ray photoelectron spectroscopy (XPS) measurements were carried out using a Perkin-Elmer PHI 5000C spectrometer with Mg K_α radiation as the excitation source. All binding energy values were referenced to the C 1s peak at 284.6 eV. Prior to the measurements, the catalyst was first activated at 450 °C in an air flow for 2 h, and then reduced at 250 °C in an H₂ flow for 2 h. Infrared (IR) spectra of adsorbed pyridine were recorded on a Nicolet Nexus 470 FT-IR spectrometer, which was furnished with an in-situ sample cell. A self-supporting disk of the sample was first degassed at 300 °C for 4 h, and then cooled to 100 °C to adsorb pyridine. After evacuation at 150 °C, the IR spectra were recorded. Cumene cracking was carried out at 250 °C in a pulsed microreactor loaded with 50 mg of catalyst. The amount of cumene injected for each test was 1 μl. The flow rate of the carrier gas was 40 ml/min. Prior to the reaction, the catalyst was first activated at 450 °C in an air flow for 2 h, and then reduced at 250 °C in an H₂ flow for 2 h when H₂ was used as the carrier gas. When He was used as the carrier gas, the catalyst was activated at 450 °C in an air flow for 2 h.

2.3. Activity evaluation

The hydroisomerization of *n*-heptane was performed at 200 °C in a flow fixed-bed reactor at atmospheric pressure. The catalyst loading was 0.3 g. *n*-Heptane was introduced to the reactor using H₂ as a carrier gas (30 ml/min), flowing through a saturator maintained at 15 °C, which gave an H₂/*n*-heptane molar ratio of 27:1. The weight hourly space velocity (WHSV) of *n*-heptane was 0.9 h^{–1}. Prior to the reaction, the catalyst was first activated at 450 °C in an air flow for 2 h, and then reduced at 250 °C in an H₂ flow for 2 h. The products were analyzed using an on-line gas chromatograph equipped with a flame ionization detector and an HP-PONA capillary column (50 m × 0.2 mm × 0.5 μm). The oven temperature was kept at 70 °C.

3. Results and discussion

3.1. Phase structure and surface area

Fig. 1. XRD patterns of Pt/WAZ-C (1) and Pt/WAZ-V (2) catalysts.

Figure 1 shows the XRD patterns of the Pt/WAZ-C and Pt/WAZ-V catalysts prepared using different methods. Both catalysts displayed a mixture of the tetragonal and monoclinic phases of zirconia, but primarily the tetragonal phase. The Pt/WAZ-C catalyst exhibited stronger diffraction peaks characteristic of tetragonal ZrO_2 than Pt/WAZ-V did, whereas the peaks attributed to monoclinic ZrO_2 were weaker for the former catalyst. These results suggested that the constant pH method helped to stabilize the tetragonal phase of zirconia in the catalyst and inhibited the transformation from the metastable tetragonal phase to the monoclinic phase at the high calcination temperature. This was related to the fact that a higher number of Al^{3+} ions were incorporated into the ZrO_2 lattice in the Pt/WAZ-C catalyst prepared using the constant pH method. The characteristic peaks of crystalline WO_3 appeared in both catalysts, but the diffraction intensities for Pt/WAZ-C were weaker than those for Pt/WAZ-V. This indicated that WO_3 was better dispersed in Pt/WAZ-C, and this was associated with its higher surface area. The surface areas of the Pt/WAZ-C and Pt/WAZ-V catalysts were 45 and 30 m^2/g , respectively (Table 1).

3.2. UV-Vis diffuse reflectance and Pt dispersion

Figure 2 shows the diffuse reflectance UV-Vis spectra of WAZ-C and WAZ-V samples. The absorption edge energies are listed in Table 1. The absorption edge energy was slightly greater for WAZ-C (3.32 eV) than for WAZ-V (3.19 eV), reflecting a smaller WO_3 domain size in the former sample [19], i.e., better dispersion of WO_3 . This was consistent with the XRD observations.

The Pt dispersions on the Pt/WAZ-C and Pt/WAZ-V cata-

Fig. 2. Diffuse reflectance UV-Vis spectra of WAZ-C (1) and WAZ-V (2) samples.

lysts were estimated from CO chemisorption. The results are listed in Table 1. The Pt dispersion on the Pt/WAZ-C catalyst was 23%, which was higher than that in Pt/WAZ-V (18%). This was probably related to the greater surface area of the former catalyst. The metallic properties of Pt in the catalysts were further investigated using toluene hydrogenation. As shown in Table 1, the Pt/WAZ-C catalyst gave 41.8% conversion in hydrogenation of toluene, which was greater than the conversion obtained using Pt/WAZ-V (34.7%). This demonstrated that Pt exhibited better metallic properties in Pt/WAZ-C, which was in agreement with the higher Pt dispersion on this catalyst.

3.3. ^{27}Al MAS NMR and XPS

To investigate the coordination environments of Al in the Pt/WAZ-C and Pt/WAZ-V catalysts prepared using different methods, ^{27}Al MAS NMR spectroscopic measurements were carried out. The results are shown in Fig. 3. Both catalysts displayed an intense peak at $\delta = 0.4$, assigned to six-coordinated Al. The narrower resonance signal observed for Pt/WAZ-C than for Pt/WAZ-V implied that the chemical environment of the octahedral Al species in the former catalyst, which was prepared using the constant pH method, was more uniform. An additional weak peak that appeared at around $\delta = 25$ was attributed to Al species in a disordered state. This was probably associated with Al species incorporated into the ZrO_2 lattice [20]. After peak deconvolution, the ratio of this Al species to octahedral Al species was 0.51 in Pt/WAZ-C and 0.40 in

Fig. 3. ^{27}Al MAS NMR spectra of Pt/WAZ-C (1) and Pt/WAZ-V (2) catalysts.

Table 1

Physico-chemical characteristics and activities for toluene hydrogenation of catalysts.

Catalyst	$A_{\text{BET}}/$ (m^2/g)	$E_0^a/$ (eV)	$D_{\text{Pt}}^b/$ (%)	Conver- sion ^c (%)	E_b of W 4f _{7/2} (eV)	$n(\text{W}^{5+})/$ $n(\text{W}^{6+})$	
Pt/WAZ-C	45	3.32	23	41.8	34.7	35.7	0.77
Pt/WAZ-V	30	3.19	18	34.7	34.5	35.6	0.52

^aAbsorption edge energy for WAZ-C and WAZ-V samples. ^bPt dispersion obtained by CO chemisorption. ^cHydrogenation of toluene.

Fig. 4. W 4f XPS spectra of Pt/WAZ-C (1) and Pt/WAZ-V (2) catalysts after reduction in flowing H_2 at 250 °C for 2 h.

Pt/WAZ-V, suggesting that more Al^{3+} ions were incorporated into the ZrO_2 lattice in the Pt/WAZ-C catalyst prepared using the constant pH method. This can be understood as follows. During preparation using the variable pH method, Al^{3+} and Zr^{4+} were precipitated at different pH values, resulting in relatively poor dispersion of Al^{3+} . In contrast, during preparation using the constant pH method, Al^{3+} and Zr^{4+} were simultaneously precipitated, leading to better dispersion of Al^{3+} . A higher level of Al^{3+} substitution in the ZrO_2 lattice was therefore achieved in the calcined catalyst.

Figure 4 displays the W 4f XPS spectra of the catalysts after reduction in flowing H_2 at 250 °C for 2 h. The XPS data obtained using a peak-fitting program are listed in Table 1. The W 4f transition can be deconvoluted into two doublet peaks with binding energies of ca. 35.5 and 34.5 eV ($W 4f_{7/2}$), assigned to W^{6+} and W^{5+} , respectively [11]. As can be seen from Table 1, the ratio of W^{5+} to W^{6+} was higher for Pt/WAZ-C (0.77) than for Pt/WAZ-V (0.52), showing that more surface W^{6+} species in the Pt/WAZ-C catalyst were reduced to W^{5+} species.

3.4. Surface acidity

The acidic properties of the WAZ-C and WAZ-V supports were investigated using IR spectra of adsorbed pyridine. After calibration of the sample weight, the relative numbers of Brönsted (B) and Lewis (L) acid sites were expressed in terms of the integrated areas of the absorbance peaks at 1540 and 1450 cm^{-1} , respectively [21]. The results are given in Fig. 5. The WAZ-C sample had B acidity equivalent to that of WAZ-V, but the former sample had more L acid sites. Taking the ^{27}Al MAS NMR results (Fig. 3) into account, the presence of more L acid sites on the WAZ-C support was probably related to the fact that more Al^{3+} ions were incorporated into the ZrO_2 lattice in this sample.

Cumene cracking is a typical reaction catalyzed only by B acid sites [22]. Figure 6 shows the catalytic activities of the Pt/WAZ-C and Pt/WAZ-V catalysts for cumene cracking in H_2 and He, respectively. In an He carrier, cumene conversion decreased with increasing pulse number, indicative of catalyst deactivation. The catalysts had the same initial activities for cumene cracking (ca. 20%), suggesting that the inherent B

Fig. 5. Acidities of WAZ-C and WAZ-V samples measured from IR spectra of adsorbed pyridine. B: Brönsted acidity; L: Lewis acidity.

acidity was equivalent in the catalysts. In an H_2 carrier, cumene conversion was almost unchanged after four consecutive doses. The Pt/WAZ-C catalyst exhibited significantly higher activity in cumene cracking than Pt/WAZ-V did (~76% vs ~47%), indicating that there were more B acid sites on the former catalyst than on the latter one in the presence of H_2 . A comparison of the activities for cumene cracking in H_2 and He atmospheres revealed that more new B acid sites were generated on the Pt/WAZ-C catalyst in H_2 . Triwahyono et al. [23] proposed that the generation of B acid sites on Pt/ WO_3/ZrO_2 in H_2 involved the following steps. Hydrogen molecules were adsorbed on Pt sites to form hydrogen atoms, which underwent spillover onto the surface of the WO_3/ZrO_2 support, and reached L acid sites, where each hydrogen atom donated an electron to the L acid site and became a B acid site (H^+). Meanwhile, a second spillover hydrogen atom reacted with the electron trapped by the L acid site to form a hydride (H^-). Ebitani et al. [24] directly confirmed the formation of B acid sites in a Pt/ SO_4^{2-}/ZrO_2 catalyst during H_2 treatment, using IR spectra of adsorbed pyridine. Hence, according to the mechanism of B acid site generation proposed by Ebitani et al., the formation of more B acid sites on Pt/WAZ-C than on Pt/WAZ-V in H_2 was caused by the higher Pt dispersion on the former catalyst and the presence of more L acid sites on the WAZ-C support than on the WAZ-V support.

Fig. 6. Cumene cracking activities of Pt/WAZ-C and Pt/WAZ-V catalysts at 250 °C in an H_2 stream (filled symbols) or in an He stream (open symbols).

Table 2

Reaction data for Pt/WAZ-C and Pt/WAZ-V catalysts in *n*-heptane hydroisomerization.

Catalyst	Conversion (%)	Selectivity (%)	Isomer distribution (%)		
			MB	DB	TB
Pt/WAZ-C	70.0	97.5	72.2	27.0	0.8
Pt/WAZ-V	43.5	98.9	82.8	16.9	0.3

MB: monobranched *C*₇ isomers; DB: dibranched *C*₇ isomers; TB: tribranched *C*₇ isomer.

Reaction conditions: 200 °C, *n*(H₂):*n*(heptane) = 27:1, WHSV = 0.9 h⁻¹, 3 h.

3.5. Catalytic activity

The catalytic performances of the catalysts for *n*-heptane hydroisomerization were investigated at 200 °C. The catalytic activities remained almost stable for 3 h. The reaction data after 3 h on stream are listed in Table 2. The conversion of *n*-heptane was obviously higher on Pt/WAZ-C (70.0%) than on Pt/WAZ-V (43.5%), demonstrating that the method used to prepare the Al₂O₃-doped Pt/WO₃/ZrO₂ catalyst had a significant influence on the activity in *n*-heptane isomerization. The catalyst prepared using the constant pH method exhibited significantly higher activity than that shown by the catalyst prepared using the variable pH method. The isomerization selectivity was a little lower on Pt/WAZ-C (97.5%) than on Pt/WAZ-V (98.9%). In terms of isomer distribution, the Pt/WAZ-C catalyst gave more dibranched and tribranched *C*₇ isomers than Pt/WAZ-V did (27.8% vs 17.2%). The isomerization of *n*-heptane in the presence of H₂ takes place as consecutive reactions: *n*-heptane → monobranched products → multi-branched products [25]. More dibranched and tribranched *C*₇ isomers were therefore obtained at higher conversion. Similar results were reported by Xu et al. [15].

The results for cumene cracking (Fig. 6) revealed that the Pt/WAZ-C catalyst had significantly more B acid sites in H₂ than Pt/WAZ-V did. This was responsible for the much higher catalytic activity in *n*-heptane hydroisomerization observed over the former catalyst than over the latter one. However, Barton et al. [26] pointed out that carbocations are stabilized by the re-

duced WO_x domains. More surface WO_x species were reduced on Pt/WAZ-C than on Pt/WAZ-V (Fig. 4 and Table 1), suggesting that more carbocation intermediates existed on the surface of the former catalyst. This is another reason for the catalytic activity in *n*-heptane hydroisomerization over Pt/WAZ-C being higher than that over Pt/WAZ-V.

4. Conclusions

Alumina-doped Pt/WO₃/ZrO₂ catalysts were prepared using either a constant pH or variable pH method. The preparative method had a significant influence on the catalytic activity in *n*-heptane hydroisomerization. The catalyst prepared using the constant pH method had higher Pt dispersion and its support had more L acid sites, leading to generation of more B acid sites on this catalyst in H₂. The catalysts possessed equivalent numbers of inherent B acid sites, so the significantly higher activity in *n*-heptane hydroisomerization observed with the Pt/WO₃/Al₂O₃-ZrO₂ catalyst prepared using the constant pH method compared with that of the catalyst prepared using the variable pH method was a consequence of generation of more B acid sites on the former catalyst in H₂.

References

- [1] Kaufmann T G, Kaldor A, Stuntz G F, Kerby M C, Ansell L L. *Catal Today*, 2000, 62: 77
- [2] Weyda H, Köhler E. *Catal Today*, 2003, 81: 51
- [3] Parlitz B, Schreier E, Zubowa H L, Eckelt R, Lieske E, Lischke G, Fricke R. *J Catal*, 1995, 155: 1
- [4] Liu P, Zhang X G, Yao Y, Wang J. *Appl Catal A*, 2009, 371: 142
- [5] Miyaji A, Ohnishi R, Okuhara T. *Appl Catal A*, 2004, 262: 143
- [6] Föttinger K, Zorn K, Vinek H. *Appl Catal A*, 2005, 284: 69
- [7] Iglesia E, Barton D G, Soled S L, Miseo S, Baumgartner J E, Gates W E, Fuentes G A, Meitzner G D. *Stud Surf Sci Catal*, 1996, 101: 533
- [8] Jermy B R, Khurshid M, Al-Daous M A, Hattori H, Al-Khattaf S S. *Catal Today*, 2011, 164: 148
- [9] Kaucký D, Wichterlová B, Dedeczek J, Sobalik Z, Jakubec I. *Appl Catal A*, 2011, 397: 82
- [10] Akhmedov V M, Al-Khowaiter S H. *Catal Rev-Sci Eng*, 2007, 49: 33
- [11] Arribas M A, Márquez F, Martínez A. *J Catal*, 2000, 190: 309
- [12] Wang Y J, Zhang H J, Sun B, Tian X G. *Petrochem Technol* (汪颖军,

Graphical Abstract

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Influence of preparative method on Al₂O₃-doped Pt/WO₃-ZrO₂ catalyst for *n*-heptane isomerization

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An Al₂O₃-doped Pt/WO₃/ZrO₂ catalyst prepared using a constant pH method exhibited significantly higher activity in *n*-heptane hydroisomerization than did the corresponding catalyst prepared using a variable pH method. This was because more Brönsted acid sites were generated on the former catalyst in the presence of H₂.

- 张海菊, 孙博, 田性刚. 石油化工, 2008, 37: 960
- [13] Iglesia E, Soled S L, Kramer G M. *J Catal*, 1993, 144: 238
- [14] Hua W M, Sommer J. *Appl Catal A*, 2002, 232: 129
- [15] Xu J S, Ying J Y. *Angew Chem, Int Ed*, 2006, 45: 6700
- [16] Liu Y, Guan Y J, Li C, Lian J, Gan G J, Lim E C, Kooli F. *J Catal*, 2006, 244: 17
- [17] Tu X J, Yue Y H, Wang J, Zhai D W, Hua W M, Gao Z. *Chin J Catal* (涂兴珺, 乐英红, 王捷, 翟德伟, 华伟明, 高滋. 催化学报), 2009, 30: 378
- [18] Nie Y Y, Shang S N, Xu X, Hua W M, Yue Y H, Gao Z. *Appl Catal A*, 2012, 433-434: 69
- [19] Barton D, Shtein M, Wilson R, Soled S, Iglesia E. *J Phys Chem B*, 1999, 103: 630
- [20] Wong S T, Li T, Cheng S, Lee J F, Mou C Y. *J Catal*, 2003, 215: 45
- [21] Xia Q H, Hidajat K, Kawi S. *J Catal*, 2002, 205: 318
- [22] Shishido T, Hattori H. *J Catal*, 1996, 161: 194
- [23] Triwahyono S, Jalil A A, Hattori H. *J Nat Gas Chem*, 2007, 16: 252
- [24] Ebitani K, Tsuji J, Hattori H, Kita K. *J Catal*, 1992, 135: 609
- [25] García-Gutiérrez J L, Cano J L, Alemán-Vázquez L O, Jiménez-Cruz F. *Fuels*, 2012, 94: 532
- [26] Barton D G, Soled S L, Meitzner G D, Fuentes G A, Iglesia E. *J Catal*, 1999, 181: 5

制备方法对 Al_2O_3 掺杂 $\text{Pt}/\text{WO}_3\text{-ZrO}_2$ 催化剂上正庚烷异构化反应的影响

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摘要: 采用恒pH法和非恒pH法制备了 Al_2O_3 掺杂的 $\text{Pt}/\text{WO}_3/\text{ZrO}_2$ 催化剂, 并用 N_2 吸附-脱附、X射线衍射、紫外-可见漫反射、CO化学吸附、X射线光电子能谱、 ^{27}Al 魔角旋转核磁共振和吡啶吸附红外等技术对催化剂进行了表征. 结果表明, 相比于非恒pH法制备的催化剂, 恒pH法制备的催化剂具有较高的比表面积和Pt分散度, 在 H_2 气氛中产生更多的B酸位, 从而表现出更高的催化正庚烷临氢异构化反应活性; 在200 °C和质量空速 0.9 h^{-1} 的反应条件下, 正庚烷转化率70.0%, 明显高于非恒pH法制备的催化剂(43.5%).

关键词: 铂; 氧化钨; 氧化锆; 氧化铝掺杂; 制备方法; 正庚烷临氢异构化; 质子酸位

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1. 前言

为了提高汽油品质, 人们迫切希望找到能够生产出高辛烷值、同时又不含芳烃的清洁燃料化学工艺^[1,2]. $n\text{-C}_{7+}$ (碳数为7和7以上的正构烷烃)临氢异构化是一种具有较大潜力的解决方案, 原油中的 $n\text{-C}_{7+}$ 馏分在催化剂的作用下异构化成支链烷烃, 加到汽油中可提高汽油的辛烷值. 与 $n\text{-C}_4\sim\text{C}_6$ 异构化不同, $n\text{-C}_{7+}$ 异构化反应过程中容易发生裂解, 异构化产物选择性较低, 尤其在高转化率时.

多种催化剂可用于正庚烷异构化反应, 如载Pt或Pd的SAPO分子筛^[3]、沸石^[4]、杂多酸^[5]、 $\text{SO}_4^{2-}/\text{ZrO}_2$ ^[6]和 WO_3/ZrO_2 ^[7-9], 其中 $\text{Pt}/\text{WO}_3/\text{ZrO}_2$ 型催化剂具有良好的反应性能, 比传统的Pt/沸石分子筛催化剂的酸性更强, 所以低温的活性较高^[10-12], 且具有比 $\text{Pt}/\text{SO}_4^{2-}/\text{ZrO}_2$ 催化剂更高的异构化选择性和稳定性^[7,10,13], 因而近年来广受关注. Hua等^[14]发现, 将少量 Al_2O_3 掺入到 $\text{Pt}/\text{WO}_3/\text{ZrO}_2$ 体系中能提高正庚烷异构化活性, 之后Xu等^[15]证实了 Al_2O_3 的促进作用. Liu等^[16]报道, 在 $\text{Pt}/\text{WO}_3/\text{ZrO}_2$ 催化剂

中加入少量ZnO能提高正庚烷异构化选择性, 从而增加异构化产物得率. 我们也发现^[17,18], 将少量 Ga_2O_3 或 In_2O_3 掺入到 $\text{Pt}/\text{WO}_3/\text{ZrO}_2$ 中提高了正庚烷异构化反应活性和选择性. 但是有关制备方法对 $\text{Pt}/\text{WO}_3/\text{ZrO}_2$ 型催化剂上正庚烷异构化反应性能的影响尚未见报道.

本文用恒pH法和非恒pH法制备掺杂少量 Al_2O_3 的 $\text{Pt}/\text{WO}_3/\text{ZrO}_2$ 催化剂, 用于正庚烷异构化反应, 结合表征结果探讨制备方法影响催化剂活性的原因.

2. 实验部分

2.1. 催化剂的制备

将35 g $\text{ZrO}(\text{NO}_3)_2 \cdot 7\text{H}_2\text{O}$ 和计算量的 $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ 溶于400 ml水中, 搅拌下将其与6 mol/L氨水同时逐滴加入200 ml氨水中, 控制整个滴加过程的pH恒定在9, 室温下静置陈化24 h. 所得 $\text{Al}(\text{OH})_3\text{-Zr}(\text{OH})_4$ 沉淀经过滤、洗涤、干燥过夜后, 用偏钨酸铵溶液浸渍, 烘干后于800 °C静态空气中焙烧3 h, 即制得 $\text{WO}_3/\text{Al}_2\text{O}_3\text{-ZrO}_2$, 标记为WAZ-C. 非恒pH法制备 $\text{WO}_3/\text{Al}_2\text{O}_3\text{-ZrO}_2$ (标记为WAZ-V)的过程差别在于, 搅拌下将6 mol/L氨水逐滴加

入 $\text{ZrO}(\text{NO}_3)_2 \cdot 7\text{H}_2\text{O}$ 和 $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ 的混合溶液中,直至最终溶液的pH为9,其它制备过程同上.两个样品中 WO_3 含量均为18%, Al/Zr 摩尔比均为0.02.用 $[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$ 溶液浸渍WAZ-C或WAZ-V,烘干后于450 °C流动空气中焙烧3 h,即制得Pt/WAZ-C和Pt/WAZ-V催化剂,Pt负载量均为1%.

2.2. 催化剂的表征

X射线衍射(XRD)表征在Bruker D8型X射线衍射仪上进行. $\text{Cu K}\alpha$ 射线,管电压40 kV,管电流40 mA,扫描范围 $2\theta = 20^\circ \sim 70^\circ$,扫描速率 $4^\circ/\text{min}$.催化剂的比表面积测试在Micromeritics ASAP 2010型物理吸附仪上进行.测试前样品在300 °C脱气3 h,在液氮温度吸附 N_2 ,用BET公式计算比表面积.紫外-可见漫反射光谱(UV-Vis)表征在配有积分球附件的Shimadzu UV-2450型紫外-可见分光光度计上进行,以 BaSO_4 为参比.

在Micromeritics AutoChem II型仪器上进行CO脉冲化学吸附以测定Pt的分散度.称取0.3 g样品置于U形石英样品管中,在450 °C用空气活化2 h,然后于250 °C用 H_2 还原2 h,用He吹扫1 h后降至室温,待基线平稳后,用5% CO -95% He 为标准吸附气,He气为载气,采用脉冲进样吸附,至峰面积相同,根据气体的累积吸附量来计算Pt的分散度.

甲苯加氢反应在微型反应器中进行,反应温度160 °C,催化剂用量50 mg,甲苯脉冲进样量1 μl , H_2 为载气(40 ml/min).反应前催化剂先在450 °C用空气活化2 h,然后于250 °C用 H_2 还原2 h.

^{27}Al 魔角旋转核磁共振(^{27}Al MAS NMR)表征在Bruker DSX-300型核磁共振仪上进行.X射线光电子能谱(XPS)在Perkin-Elmer PHI 5000C型仪器上测定. $\text{Mg K}\alpha$ 射线源,电子结合能用C 1s (284.6 eV)谱校正,测定前催化剂先在450 °C用空气活化2 h,然后于250 °C用 H_2 还原2 h.

吡啶吸附红外(FT-IR)表征在配有石英样品池的Nicolet Nexus 470型红外光谱仪上进行.样品在300 °C脱气4 h,然后降至100 °C吸附吡啶,于150 °C脱附吡啶后记录FT-IR谱.

异丙苯裂解反应在微型反应器中进行,反应温度250 °C,催化剂用量50 mg,异丙苯脉冲进样量1 μl ,载气流量40 ml/min. H_2 为载气时,反应前催化剂先在450 °C用空气活化2 h,然后于250 °C用 H_2 还原2 h;当以He为载气时,反应前催化剂先在450 °C用空气活化2 h.

2.3. 催化剂的评价

正庚烷临氢异构化反应在常压流动微型反应器中进行,催化剂用量0.3 g,反应温度200 °C.正庚烷由 H_2 (30 ml/min)经过15 °C的饱和器带入反应装置,其中 H_2 与正庚烷的摩尔比为27:1,正庚烷的质量空速为 0.9 h^{-1} .反应前催化剂先在450 °C用空气活化2 h,然后于250 °C用 H_2 还原2 h.产物采用气相色谱仪在线分析,FID检测器,HP-PONA毛细管色谱柱(50 m $\times$ 0.2 mm $\times$ 0.5 μm),柱温70 °C.

3. 结果与讨论

3.1. 催化剂的晶相结构与比表面积

图1是Pt/WAZ-C和Pt/WAZ-V催化剂的XRD谱.由图可见,催化剂中的 ZrO_2 主要是四方晶相,同时存在少量的单斜晶相,其中Pt/WAZ-C催化剂中四方相 ZrO_2 的衍射峰更强,而单斜相 ZrO_2 的衍射峰更弱,表明用恒pH法制备催化剂更有助于催化剂中四方相 ZrO_2 的稳定,抑制高温焙烧后亚稳态的四方晶相向单斜晶相转变.这与恒pH法制备过程中较多的 Al^{3+} 进入 ZrO_2 晶格有关.各催化剂均出现了晶相 WO_3 的特征衍射峰,但Pt/WAZ-C催化剂中的强度更弱,表明其中 WO_3 分散得更好,这与它具有较高的比表面积有关. Pt/WAZ-C和Pt/WAZ-V催化剂的比表面积分别为45和30 m^2/g (见表1).

3.2. UV-Vis光谱与Pt分散度

用UV-Vis光谱测定了WAZ-C和WAZ-V样品的吸收边界能,结果见图2和表1.可以看出,WAZ-C样品的吸收边界能为3.32 eV,略大于WAZ-V样品(3.19 eV),表明前者的 WO_3 颗粒尺寸更小^[9],即 WO_3 分散得更好,与XRD结果一致.

用CO化学吸附测定了Pt/WAZ-C和Pt/WAZ-V催化剂中Pt的分散度,结果列于表1.可以看出,Pt/WAZ-C催化剂的Pt分散度为23%,高于Pt/WAZ-V催化剂的18%.这可能是由于前者具有较高的比表面积.进一步用甲苯加氢脉冲反应考察了催化剂中Pt的金属性.如表1所示,Pt/WAZ-C催化剂上甲苯加氢反应的转化率为41.8%,高于Pt/WAZ-V催化剂的34.7%,表明前者的Pt表现出更好的金属性,这与它具有较高的Pt分散度一致.

3.3. ^{27}Al MAS NMR与XPS结果

为了研究催化剂中Al的配位状态,对Pt/WAZ-C和Pt/WAZ-V催化剂进行了 ^{27}Al MAS NMR表征,结果示于图3.可以看出,催化剂均在 $\delta = 0.4$ 处出现了强核磁共振峰,归属为六配位Al,其中Pt/WAZ-C催化剂的核磁共振峰更窄,说明恒pH法制备的催化剂中六配位Al的化学环

境更加均一。催化剂还在 $\delta = 25$ 左右出现了弱核磁共振峰, 归属为无序状态的Al物种, 这可能与进入 ZrO_2 晶格的Al有关^[20]。经分峰处理, 该Al物种与六配位Al的比值在Pt/WAZ-C和Pt/WAZ-V催化剂中分别为0.51和0.40, 表明恒pH法制备的Pt/WAZ-C催化剂中较多的 Al^{3+} 进入了 ZrO_2 晶格。这是可以理解的, 非恒pH法制备过程中pH不断变化, Al^{3+} 和 Zr^{4+} 在不同pH值时沉淀, Al^{3+} 的分散相对较差; 而恒pH法制备过程中 Al^{3+} 和 Zr^{4+} 同时沉淀, Al^{3+} 的分散较好, 从而焙烧后得到的催化剂中较多的 Al^{3+} 取代 Zr^{4+} , 进入 ZrO_2 晶格。

图4是于250 °C用 H_2 还原的催化剂中W 4f的XPS谱, 通过分峰拟合后的XPS数据列于表1。W 4f_{7/2}结合能位于35.5和34.5 eV附近的峰分别归属为 W^{6+} 和 W^{5+} 物种^[11]。由表可见, Pt/WAZ-C催化剂表面 W^{5+} 与 W^{6+} 量的比值为0.77, 高于Pt/WAZ-V催化剂的0.52, 表明Pt/WAZ-C催化剂表面较多的 W^{6+} 物种还原为 W^{5+} 物种。

3.4. 催化剂的表面酸性

用吡啶吸附FT-IR谱表征了WAZ-C和WAZ-V载体样品的酸性。校正样品质量后, 用1540和1450 cm^{-1} 处吸收峰的面积分别表示样品的相对B酸量和L酸量^[21], 结果见图5。可以看出, WAZ-C样品的B酸量与WAZ-V样品基本相当, 但其L酸量更高。结合图3可认为, 这可能与WAZ-C样品中较多的 Al^{3+} 进入 ZrO_2 晶格有关。

异丙苯裂解是一个典型的B酸催化的反应^[22], 图6给出了不同方法制备的Pt/WAZ-C和Pt/WAZ-V催化剂分别在He和 H_2 气氛中的异丙苯裂解活性。由图可见, 在He气氛中, 异丙苯转化率随着脉冲数逐渐下降, 表明催化剂存在失活现象, 两个催化剂的异丙苯裂解初始活性基本相当, 约为20%, 说明两者的本征B酸量相当。在 H_2 气氛中, 异丙苯转化率随着脉冲数基本保持不变, Pt/WAZ-C催化剂的异丙苯裂解活性(~76%)明显高于Pt/WAZ-V催化剂(~47%), 表明在临氢条件下前者的B酸量明显高于后者。由此可见, Pt/WAZ-C催化剂在 H_2 气氛中产生了更多新的B酸位。Triwahyono等^[23]提出, $\text{Pt}/\text{WO}_3/\text{ZrO}_2$ 催化剂在 H_2 气氛中通过下列途径产生B酸位: H_2 分子在金属Pt上解离吸附成H原子, 后者从Pt溢流到 WO_3/ZrO_2 载体表面, 从而释放一个电子给Lewis酸位

形成B酸中心 H^+ , 同时得到电子的Lewis酸位把电子返还给另一个H原子形成氢负离子 H^- 。Ebitani等^[24]用吡啶吸附FT-IR谱直接证实了 $\text{Pt}/\text{SO}_4^{2-}/\text{ZrO}_2$ 催化剂在 H_2 处理过程中能够形成B酸位。因此, 在 H_2 气氛中Pt/WAZ-C催化剂产生更多的B酸位可归因于较高的Pt分散度和WAZ-C载体上更多的L酸位。

3.5. 催化剂的活性

于200 °C考察了催化剂的正庚烷临氢异构化反应性能, 反应3 h内催化剂的活性基本保持恒定, 3 h后的反应数据列于表2。可以看出, Pt/WAZ-C催化剂上正庚烷转化率为70.0%, 明显高于Pt/WAZ-V催化剂的43.5%, 说明制备方法对催化剂的正庚烷异构化活性有很大影响。Pt/WAZ-C催化剂上异构化选择性(97.5%)略低于Pt/WAZ-V催化剂(98.9%)。从异构化产物分布来看, Pt/WAZ-C催化剂比Pt/WAZ-V生成较多的双支链和三支链产物(27.8%对17.2%)。正庚烷临氢异构化是通过正庚烷→单支链产物→多支链产物的连串反应机理进行的^[25], 因此转化率较高时得到较多的双支链和三支链产物, 与Xu等^[15]报道的结果类似。

异丙苯裂解反应结果(见图6)显示, 在 H_2 气氛中Pt/WAZ-C催化剂的B酸位明显多于Pt/WAZ-V, 这是它具有高得多的催化正庚烷异构化反应活性的主要原因。另一方面, Barton等^[26]指出, 碳正离子被还原的氧化钨物种所稳定, Pt/WAZ-C催化剂比Pt/WAZ-V有更多的氧化钨物种被还原(见图4和表1), 预示了在前者表面可能存在较多的碳正离子中间体, 这也是其活性更高的原因之一。

4. 结论

采用恒pH法和非恒pH法制备了掺杂 Al_2O_3 的 $\text{Pt}/\text{WO}_3/\text{ZrO}_2$ 催化剂, 并用于正庚烷临氢异构化反应中。恒pH法制备的催化剂在 H_2 气氛中产生更多的B酸位, 原因是其具有较高的Pt分散度和相应的载体具有较多的L酸位。考虑到两种方法制备的催化剂的本征B酸量基本相当, 但恒pH法制备的催化剂在 H_2 气氛中产生了更多的B酸位, 这是其催化正庚烷临氢异构化活性明显更高的原因。