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Original article

Effect of WO_x promoter on Pt/ZrO₂-HMS catalysts for *n*-heptane isomerization: Catalytic performance and kinetics study

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ABSTRACT

Platinated W/Zr mixed oxides supported on mesoporous silica with various amounts of Si/Zr, namely Pt-WO₃/ZrO₂(*x*)-HMS, were prepared and studied for *n*-heptane isomerization reaction at 200–350 °C. The various methods such as XRD, XRF, FT-IR, UV-vis DRS, NH₃-TPD, H₂ chemisorption, nitrogen adsorption-desorption, Py-IR, SEM and TGA techniques were used for characterization of these materials. Kinetics of *n*-heptane isomerization was also investigated under various hydrogen. *n*-Heptane pressures and the influence of reaction conditions on catalytic performance were studied. The ideal catalytic performance was observed on HMS with 0.6%Pt/12%WO₃/ZrO₂ and Si/Zr = 10.

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1. Introduction

Current environmental friendly motor gasoline has forced severe controls for reducing the aromatic hydrocarbons. These compounds are harmful to the environment and human health [1]. To avoid reducing of the gasoline octane number with a decrease in aromatic hydrocarbons, *n*-alkanes isomerization was introduced as a desired reaction. An effective bifunctional catalyst is needed for ideal performance of the isomerization reaction. The hydrogenating ability of these bifunctional catalysts encourages the hydrogenation of unsaturated hydrocarbons and their acid properties provide the selective isomerization of *n*-alkanes presented in feedstock into high-octane isomers [2]. Different catalysts were used for this reaction. According to literatures, solid acids [3–6] have shown favorable advantages for isomerization reaction, such as high catalytic activity at low temperature, no corrosion in the reactor and no environmental problems in disposing of the used catalysts [7,8]. Among these super acids, WO₃/ZrO₂ supported catalysts have more stable conversion and the absence of leaching of any catalyst component into the products; however, these catalysts are less active compared to SO₄²⁻/ZrO₂ supported materials [8,9]. Therefore, in the present study we focused on

this support (WO₃/ZrO₂) but with some changes. To increase the surface area of the metal oxide catalysts these oxides can be introduced into mesoporous supports that have a high surface area [10]. Considering that WO₃/ZrO₂ has a good acidity and on the other hand, HMS has a suitable surface area, we predicted that WO₃/ZrO₂-HMS, especially when promoted with Pt and in the presence of hydrogen stream in the feed, would be of interest to explore the catalytic isomerization performance. In the current work, *n*-heptane isomerization on a series of Pt-WO₃/ZrO₂-HMS catalysts was studied and compared with that on Pt/ZrO₂-HMS. The effects of WO₃ addition and Si/Zr molar ratio on the catalytic isomerization reaction were examined. The reasons for the improvement on activity, selectivity, stability, coke deposition, octane-number and kinetics of these catalysts in *n*-heptane isomerization reaction were discussed at the temperature range of 200–350 °C.

2. Results and discussion

2.1. Structure

In our previous work [10], Pt/Zr(*x*)-HMS catalysts were evaluated. These catalysts are the reference catalysts for the prepared catalysts in present work (Pt-W/Zr(*x*)-HMS).

To identify HMS, zirconia and tungsten oxide phases, X-ray diffraction was used. Fig. 1 presents the wide-angle range XRD patterns of the calcined Pt-W/Zr(*x*)-HMS samples with a different

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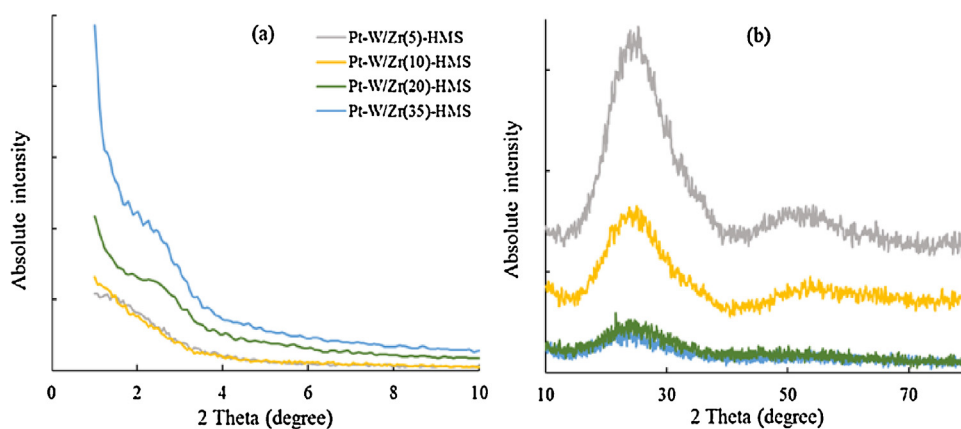


Fig. 1. X-ray diffraction patterns of Pt-W/Zr(x)-HMS catalysts in (a) low angle (1–10°) and (b) high angle (10–80°) regions.

loading of ZrO₂. In all patterns, a strong {100} X-ray reflection at low angle ($2\theta \sim 2.3^\circ$), arising from the hexagonal array of silica tubes, and a broad diffraction line ($2\theta = 20^\circ\text{--}30^\circ$) for the shapeless part of HMS [10] are observed. Meanwhile, XRD patterns show no signals of Pt, ZrO₂ and WO₃ particles, suggesting that these metallic phases were highly dispersed in prepared solids, in well agreement with the H₂ chemisorption and UV–vis DRS results. After incorporating ZrO₂ and WO₃ into the HMS framework, the d_{100} peak shifts to lower angles and broadened, suggesting a lattice expansion during the incorporation and a decrease in the dimensions of the scattering domain.

Table 1 shows the d-spacing (d_{100}), unit cell parameter (a_0) and wall thickness (wt) values that have been calculated from XRD data. These values increase with increasing ZrO₂ content.

Fig. 2 explains the FT-IR spectra at the room temperature for the HMS doped Pt-W/Zr catalysts in the range of 4000–400 cm⁻¹. As expected, these spectra are same together, so we show one of them (Pt-W/Zr(10)-HMS catalyst).

In comparison to the reported IR spectra for Zr(x)-HMS catalysts [10], Pt-W/Zr(x)-HMS catalysts show some added bands. All

bands underwent a red shift towards lower wave numbers and intensified with entering tungsten and increasing zirconium amounts. According to literatures [11,12], these red shifts (especially for Si–O–Si band) are related to the decaying silica framework of HMS after insertion of Zr and W atoms. It can be observed that two new bands with same intensities are emerged at 2900 and 1532 cm⁻¹ in Pt-W/Zr(x)-HMS catalysts. These bands can be related to the vibrations of (W^{x+})_nOH disturbed by the support or a bridged W–OH–Zr species and W=O, respectively [11,12].

To decide the chemical nature and coordination states of tungsten and zirconium, UV–vis DRS of catalysts have been obtained and shown in Fig. 3. To comparison, the UV–vis analysis of the Zr(x)-HMS catalysts is also included as reference. All UV–vis DRS spectra of Zr-HMS samples show the absorption band with maxima about 200 nm. This band is attributable to the charge-transfer transition from the valence band of an oxygen ion (2p character) to the conduction band of isolated Zr(IV) ion (4d character) in tetrahedral arrangement [13,14]. An absorption band with low intensity is also seen at 240 nm, which is normally assigned to Zr(IV) species in monoclinic ZrO₂ phase [13,14]. A band

Table 1
Composition and physico-chemical properties of tungstated zirconia-HMS samples.

Catalysts	Pt-W/Zr(5)-HMS	Pt-W/Zr(10)-HMS	Pt-W/Zr(20)-HMS	Pt-W/Zr(35)-HMS
Surface properties				
S_{BET} (m ² /g)	620	626	640	667
V_p^a (cm ³ /g)	0.21	0.22	0.25	0.31
S_μ (m ² /g)	28	49	67	87
V_μ (cm ³ /g)	0.04	0.08	0.10	0.13
d_p (nm)	2.69	2.85	3.23	4.00
NS_{BET}^b	0.76	0.77	0.78	0.82
M_d^c	68	58	63	64
d_{100}^d (nm)	4.29	4.17	4.03	3.76
a_0^d (nm)	4.95	4.81	4.65	4.34
wt ^d (nm)	2.26	1.96	1.42	0.34
W ^e (wt%)	11.4	11.9	11.7	11.7
Si/Zr ^e	4.1	9.8	19.3	34.4
Acidic properties				
Weak (mmol NH ₃ /g)	0.05	0.09	0.08	0.07
Medium (mmol NH ₃ /g)	0.59	0.59	0.58	0.58
Total acidity (mmol NH ₃ /g)	0.64	0.68	0.66	0.65
B (mmol Py/g)	0.16	0.21	0.18	0.10
B/L	0.12	0.70	0.28	0.13

^a Using BJH method.

^b NS_{BET} is normalized S_{BET} and calculated by the equation of $NS_{\text{BET}} = S_{\text{BET}}$ of catalyst / [(1 - y) × S_{BET} of support], y is the weight fraction of the guest phases [18,19].

^c Using H₂-chemisorption method.

^d d_{100} is calculated from the XRD patterns; a_0 is calculated by equation $a_0 = d_{100} \times 2/\sqrt{3}$ and wt was evaluated by subtracting pore diameter (d_p) from the unit cell parameter [18].

^e Using XRF method.

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