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Article

Experimental and kinetic study of *n*-heptane isomerization on nanoporous Pt-(Re,Sn)/HZSM5-HMS catalysts

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ABSTRACT

Pt-(Sn,Re)/HZSM5-HMS catalysts were evaluated for *n*-heptane isomerization at 200–350 °C. To characterize the catalyst, X-ray diffraction, X-ray fluorescence, Fourier transform infrared spectroscopy, ultraviolet-visible diffuse reflectance spectroscopy, temperature-programmed reduction of H₂, temperature-programmed desorption of NH₃, infrared spectroscopy of adsorbed pyridine, H₂ chemisorption, nitrogen adsorption-desorption, scanning electron microscopy and thermogravimetric analysis were performed. Kinetics of *n*-C₇ isomerization were investigated under various hydrogen and *n*-C₇ pressures, and the effects of reaction conditions on catalytic performance were studied. The results showed that bi- and trimetallic catalysts exhibit better performance than monometallic catalysts for this reaction. For example, a maximum *i*-C₇ selectivity (> 74%) and multibranched isomer selectivity (40%) were observed for Pt-Sn/HZSM5-HMS at 200 °C.

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1. Introduction

One of the most important topics in the petrochemical industry is the production of reformulated gasoline with low aromatic and olefin contents [1]. For this reason, skeletal isomerization of naphtha's C₄–C₇ cuts is an important process in the petroleum refining industry, with the goal of maintaining gasoline octane without adding lead compounds and also having a low concentration of aromatics and olefins. *n*-Heptane (*n*-C₇) isomerization is of notable importance, given that its skeletal isomers increase the octane number from 0 to 42–112 [2]. According to environmental regulations, the resulting branched molecules are useful as clean high-octane fuels [3–6].

An isomerization reaction is performed on bifunctional solid catalysts containing dehydrogenating functionalities (metallic sites) and isomerization/cyclization functionalities (acidic

sites) [7]. These are required for isomerization, ring expansion and dehydrocyclization reactions [8]. Modifying the properties of metallic functionalities (noble metals, especially Pt) by the addition of another metallic part, such as Re, Sn, Ge or Ir, has been further extended for isomerization reactions in recent years, because these metals can closely interact with Pt, partly by chemical affinity, and can modify the activity, selectivity and stability of catalysts [9]. Re and Ir in bimetallic platinated catalysts, even presulfided, create undesirable hydrogenolysis activity of hydrocarbons. Sulfidation pretreatment is a costly operation that must be performed after catalyst regeneration. It must be incorporated in the industrial process to prevent the dangerous exothermic runaway produced by massive C–C bond cleavage of the feedstock in the early stages of reaction. To replace the metallic Pt–Re phase sulfidation, Sn is added to bimetallic catalysts as an inactive modifier [10,11]. It is accepted

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that the catalytic properties of bi- and trimetallic catalysts are based on electronic or geometric considerations [12]. These catalysts modify Pt electronic properties by an interaction between Pt and promoter oxide species or a direct alloy formation and so create significant changes in adsorption energies of chemisorbed hydrocarbons and promote catalytic activity and selectivity [12].

Despite catalyst development for isomerization reactions, the literature does not report any studies on the *n*-C₇ isomerization reaction and its kinetic measurements over bi- and trimetallic Pt-(Re,Sn)/HZSM5-HMS catalysts. In this work, we investigate the effect of Re and Sn on the catalytic properties of Pt/HZSM5-HMS with 30 wt% HZSM-5, which exhibited the best catalytic performance in our previous work [13]. We also study the octane number of products, the reaction kinetics, the effects of reaction temperature and residence time on the activity, selectivity towards the various products (notably isomer products), and the catalytic stability of the *n*-C₇ isomerization reaction in a fixed-bed reactor.

2. Experimental

2.1. Catalyst preparation

Our synthesis method for the HZSM5-HMS composite support has been described in our previous work [13]. Briefly, this support was synthesized by adding 30 wt% of commercial HZSM-5 (Zeolyst international, Si/Al = 14) and appropriate amounts of ethanol, tetraethyl orthosilicate, dodecyl amine, HCl (1 mol/L) and distilled water. After calcining the prepared material at a heating rate of 1 °C/min to 600 °C for 6 h, Re and Sn (were co-impregnated on this support. Bimetallic (Pt(0.3 wt%)-Re(0.3 wt%) and Pt(0.3 wt%)-Sn(0.3 wt%)) and trimetallic (Pt(0.3 wt%)-Re(0.2 wt%)-Sn(0.1 wt%) and Pt(0.3 wt%)-Sn(0.2 wt%)-Re(0.1 wt%)) catalysts were synthesized using the proper amounts of hexachloroplatinic acid, ammonium perrhenate and tin(II) chloride. Then, these prepared catalysts were dried overnight in static air at 110 °C and calcined at 300 °C for 4 h.

All of the chemicals used were purchased from Merck and Aldrich Co. and used without further purification.

2.2. Catalyst characterization

X-ray fluorescence was performed for each metal element (Pt, Sn, Re and Al) contained in the prepared materials with an XRF-8410 Rh apparatus and a voltage of 60 kV.

X-ray diffraction (XRD) patterns of calcined Pt-Re, Pt-Sn, Pt-Re-Sn and Pt-Sn-Re supported on HZSM5-HMS were obtained with an X-PERT diffractometer using Ni-filtered Cu *K*_α radiation at 45 kV and 50 mA with a 0.06° 2θ-step and 1 s per step.

H₂ pulse chemisorption was used for measuring the Pt dispersion. The amounts of chemisorbed hydrogen were determined by a TPD/TPR analyzer (2900 Micromeritics) equipped with a TCD detector. The equation of $Pt_d = N_0/Pt_0 \times 100\%$ (Pt_d : Pt dispersion; N_0 : active site over per weight of catalyst (g); Pt_0 :

total platinum over per weight of catalyst (g)) was used to calculate the metal dispersion, using the assumption H:Pt = 1. For this analysis, the catalysts (0.2 g) were evacuated in argon at 500 °C for 1 h followed by reduction with pure hydrogen (14 mL/min) at 450 °C for 1 h and evacuation at room temperature for 1 h before hydrogen adsorption. The catalysts were saturated by a hydrogen pulse at 25, 300, and 500 °C. The pulse size was 0.5 mL of 5 vol% H₂/Ar gas mixture, and the time between pulses was 3 min. Each measurement ended when constant peak areas revealed no further gas uptake by each catalyst. The total amount of hydrogen uptake (volume at room temperature) equals the sum of hydrogen uptake at different temperatures for each catalyst.

The composite materials were analyzed by Fourier transform infrared (FT-IR) spectroscopy on a BOMEM FT-IR spectrophotometer model Arid-Zone TM, MB series in a wave number range of 400–4000 cm⁻¹. For this analysis, the transparent tablets were prepared with appropriate amounts of the catalysts and KBr.

The ultraviolet-visible diffuse reflectance spectra (UV-vis DRS) of various samples in a 200–800 nm range at room temperature were recorded by a Shimadzu UV-2100 spectrophotometer equipped with a diffuse reflectance attachment, using BaSO₄ as a reference.

The temperature-programmed reduction (TPR) experiments of calcined catalysts were carried out with a TPD/TPR 290 apparatus. At the beginning of each TPR test the catalyst was heated in air at 500 °C for 1 h. Then, 5 vol% H₂/Ar gas mixture was used to reduce the 50 mg samples at a temperature range of 25–750 °C and a ramp of 10 °C/min.

To obtain the N₂ physisorption isotherms, the outgassed samples at -196 °C were analyzed by an ASAP-2010 micromeritics (USA) instrument. The specific surface area (*S*_{BET}), the average pore diameter (*d*_p) and the cumulative pore volume (*V*_p) were calculated by the Brunauer-Emmett-Teller (BET) equation, applying the Barret-Joyner-Halenda method to the adsorption branches of the N₂ isotherms and from the isotherms at *p/p*₀ = 0.99, respectively.

To evaluate the acidity of catalysts, the samples were analyzed by a TPD/TPR analyzer (2900 Micromeritics) equipped with a TCD detector. For this analysis, 0.2 g of each catalyst was pretreated in a pure helium flow (40 mL/min) from room temperature to 600 °C at a heating rate of 10 °C/min for 1 h prior to adsorption of ammonia. Then the samples were cooled to room temperature and saturated with ammonia. Afterwards, desorption profiles of the physically adsorbed ammonia were recorded from 25 to 800 °C at a heating rate of 10 °C/min.

Pyridine adsorption (Py-IR) measurements on prepared catalysts to determine the type of acidic sites were performed on a Fourier-transform infrared spectrometer (Nicolet 170 SX). For this analysis, self-supported wafers of the catalysts with a weight/surface ratio of about 12 mg/cm² were placed into a glass Pyrex cell with greaseless stopcocks and CaF₂ windows. These catalysts were evacuated at 250 °C and 0.01 Pa overnight, exposed to pyridine vapors at 25 °C for 30 min and then outgassed at 200 °C.

To study the catalyst morphology, field emission scanning

electron microscope (FESEM) analysis was conducted on a HITACHI S-4160 instrument operating at an accelerating voltage of 30 kV. These composite catalysts were coated with gold metal prior to analysis.

The coke laid down on the catalyst surface and the thermal stability of the prepared catalysts were measured by thermogravimetric (TG)/differential thermal analysis (DTA) using an STA503M instrument under air atmosphere with a 5 vol% O₂/N₂ gas mixture (60 mL/min) over a range of 25–800 °C with a heating rate of 10 °C/min.

2.3. Reactor test and calculation method

A fixed-bed reactor packed with 1 g of powder catalyst was used for the *n*-C₇ isomerization reaction. Before each test, the catalysts were pretreated in H₂ flow (40 mL/min) at 400 °C for 2 h. For each run, liquid *n*-C₇ feed was pumped into a feed system vaporizer via a syringe pump and mixed with the H₂ stream at various temperatures. The catalytic reaction was conducted under the same conditions as a reactant gas H₂/HC = 7 molar ratio, 1 atm pressure, a temperature range of 200–350 °C and liquid hourly space velocity (LHSV) of 1.0 h⁻¹.

The reaction products were analyzed by online gas chromatography (Agilent Technologies 7890A) equipped with a flame ionization detector (FID).

The catalyst activity (Conv.) and selectivity (Select.) were defined as the following equations:

$$\text{Conv. (\%)} = \text{Percentage of } n\text{-C}_7 \text{ transformed into products} \quad (1)$$

$$\text{Select. (\%)} = \frac{\text{Percentage of } n\text{-C}_7 \text{ transformed into a certain product}}{\text{Total amount of } n\text{-C}_7 \text{ converted}} \quad (2)$$

For the kinetics study, the experiments were carried out at various temperatures (200–350 °C), an inlet *n*-C₇ flow rate in the range of 0.02–0.07 mL/min, and a hydrogen flow rate in the range of 20–45 mL/min. The reaction rate was defined as follows:

$$r \text{ (mol g}^{-1} \text{ s}^{-1}) = \frac{n\text{-C}_7 \text{ flow rate (mL/s)} \cdot n\text{-C}_7 \text{ density (g/mL)} \cdot \text{Conv. (\%)}}{n\text{-C}_7 \text{ molar weight (g/mol)} \cdot \text{weight of catalyst (g)} \cdot \text{impregnated metal (wt\%)}} \quad (3)$$

The *n*-C₇ and hydrogen orders at a constant temperature were measured in the *n*-C₇ pressure range at constant hydrogen pressure and in the hydrogen pressure range at a constant *n*-C₇ pressure, respectively. In this condition, the logarithmic representations of reaction rate against hydrogen or *n*-C₇ pressure were mostly linear and their slopes expressed the order of reaction for the component with varying pressure.

An Arrhenius plot was used for measuring an apparent activation energy ($E_{\text{app}}^{\text{act}}$) of the isomerization reaction. The temperature dependence of the isomerization rate constant (*k*) was evaluated according to the logarithmic form of the Arrhenius equation:

$$\ln k = \ln A - \frac{E_{\text{app}}^{\text{act}}}{RT} \quad (4)$$

The activation energy of various catalysts in the isomerization reaction was determined at similar conditions for conversion levels below 10% where the best linear correlation between the logarithmic isomerization rate constant (ln*k*) and the inverse temperature (1/*T*) was observed.

3. Results and discussion

3.1. Catalyst characterization

Before the catalytic performance test, the prepared catalysts were characterized by several techniques.

The XRF analysis revealed that the metal contents were in close agreement with the expected theoretical levels for all catalysts.

The crystal structures of the bi- and trimetallic catalysts were analyzed by XRD (Fig. 1). In all XRD patterns, a basal peak at $2\theta = 2.3^\circ$, sharp peaks at 6° – 11° and 22° – 25° and a broad diffraction line between 20° and 30° were observed, which show the formation of HMS [14], the ZSM-5 phases [15] and the amorphous part of the substrate, respectively. Corresponding to Fig. 1, the intensity of the HMS peak after impregnation with various metals, especially for Pt-Sn, decreases considerably. This is likely due to an increasing partial lattice disorder upon metal incorporation. Metals or metal alloys in these XRD patterns do not show any peaks. This is due to good metal dispersion on the catalyst surfaces (as confirmed by H₂ chemisorption) or very low metal content in the prepared catalysts (Table 1).

FT-IR spectra of mono-, bi- and trimetallic catalysts, at 400–4000 cm⁻¹, were studied (Fig. 2). In all spectra, the sharp band at 545 cm⁻¹ could be assigned to the structurally sensitive double five-member ring tetrahedral vibrations of HZSM-5. The IR bands at 794 and 1024 cm⁻¹ can be assigned to the symmetric and asymmetric stretching vibrations of the Si–O–Si linkages of the zeolite framework, respectively. A slender and distinct vibration peak for the H–OH bending vibrations of the adsorbed water molecules was observed near 1630 cm⁻¹, and some peaks were observed at 1230, 1090 and 452 cm⁻¹. These peaks were assigned to the asymmetric stretching and bending modes of ≡Si–O–Si≡ of HMS. The IR band near 3500 cm⁻¹ is characteristic of water adsorbed in HZSM-5 [16,17].

UV-vis diffuse reflection spectra of pure, mono-, bi- and trimetallic ZH catalysts are shown in Fig. 3. The UV absorption results for calcined catalysts show three bands. The band near 260 nm is difficult to characterize. Pt⁴⁺ is a low spin *d*⁶ species that has *d*–*d* transfer and ligand to metal charge transfer

Fig. 1. The XRD patterns for prepared catalysts after calcination.

Table 1

Physicochemical properties of the prepared composite catalysts.

Catalyst	S_{BET} (m^2/g)	V_{p} (cm^3/g)	S_{micro} (m^2/g)	$V_{\text{micro-p}}$ (cm^3/g)	d_{p} (nm)	Weak acid ^a	Strong acid ^a	L+B ^b	B/L	Pt ^c (%)	Si/Al ^d
Pt/ZH	1084	1.86	165	0.47	5.13	0.27	0.43	0.70	1.59	93	48.09
Pt-Re/ZH	863	1.15	121	0.31	3.65	0.26	0.38	0.64	1.46	48	56.92
Pt-Re-Sn/ZH	899	1.60	141	0.42	4.94	0.25	0.35	0.60	1.40	52	57.01
Pt-Sn-Re/ZH	910	1.69	145	0.44	5.03	0.26	0.34	0.60	1.31	51	57.33
Pt-Sn/ZH	1002	1.47	132	0.40	4.73	0.25	0.31	0.56	1.24	57	57.90

^a Weak acid and strong acid (vs. mmol NH_3/g) are in the range of 170–250 °C and 340–470 °C, respectively.^b Using the infrared spectrum of pyridine (vs. mmol Py/g).^c Using H_2 -chemisorption.^d Using XRF.

(LMCT) bands. We tentatively presume that this is a charge transfer (CT) band (oxygen to metal) [18–20]. This band can be seen in all spectra. The bands at near 350 and 400 nm must be due to a $d-d$ transition band of Pt [21]. These results allow us to assume that the Pt species interact strongly with the support. A

surface complex $[\text{PtO}_x\text{Cl}_y]$ may be formed, such that this result is in agreement with TPR data (Fig. 4) [18–21]. The chemical environment of metals in other catalysts is greatly different, and therefore the formation of such a complex is possible. Given this, we used TPR tests to obtain further information on this possibility.

We used TPR analysis to characterize catalyst compositions and the interaction of Sn and Re with the active phase. In this experiment, hydrogen consumption was investigated by reoxidized catalysts as a function of temperature. The reduction temperature depends on the oxidation state of metals, the interaction of oxides among themselves and with the support, and on the possible catalytic action of Pt or other metals that are present or generated during reduction [22]. The TPR traces of the catalysts are shown in Fig. 4. These profiles vary notably depending on the catalyst compositions. The monometallic (platinated) catalyst presents a reduction band at 200 °C and a less important reduction band between 300 and 450 °C. This reduction pattern has also been previously reported by other [23]. The first peak is generally presumed to be caused by the reduction of Pt oxide species weakly interacting with ZH, and the second band is from the reduction of Pt oxychlorinated species in strong interaction with the support [23]. Pt-Re samples display two individual reduction peaks. The first peak, at 120–270 °C, corresponds to Pt(II) oxide particle reduction. The

Fig. 2. FT-IR spectra for different powder catalysts. **Fig. 3.** UV-vis DRS of pure, mono-, bi- and trimetallic ZH-30 catalysts. **Fig. 4.** H_2 -TPR profiles for mono-, bi- and trimetallic ZH-30 catalysts.

second peak, at 300–450 °C, accords with the reduction of Re oxide particles neighboring Pt^0 crystals [22] and the less reducible platinum(II) species in the inner region of the framework (as either small PtO particles or Pt^{2+} ions neutralizing the cationic exchange sites, as oxychloride species (PtO_xCl_y)) [24]. The TPR plot of Pt-Sn exhibits three peaks: one peak corresponding to Pt oxide reduction; a larger peak starting at 250 °C, that encompasses the reduction of the less reducible platinum(II) species and a part of the Sn oxides [24]; a third peak at 730 °C that we believe is caused by the reduction of separated Sn oxides or metal ions neutralizing acid sites of the support, similar to that reported for mesoporous catalysts containing other metals [24]. The plot of the Pt-Re-Sn catalyst has an intense peak at 150–250 °C because of the reduced Pt oxide and certain Sn and Re oxides. An intermediate region at 250–350 °C can be attributed to the reduced Re and Sn oxides catalyzed by Pt particles. A third peak at 350–570 °C is caused by the reduced separated Re and small parts of Sn oxide particles. Some parts of these oxides could be strongly bonded with themselves or with the support and so might not be reduced during the TPR experiments. Another peak is observed at 730 °C that is similar to the Pt-Sn catalysts. Based on reported TPR [23], reduction of metallic phases of bi- and trimetallic Al_2O_3 supported catalysts occurs at higher temperatures than with our catalysts. One reason for this may be that Pt species in our synthesized micro/mesoporous materials have better interactions with other loaded metals. In total, the reduction of Pt oxides occurs at lower temperature than with other metals because it is more easily reduced.

The N_2 adsorption-desorption isotherms of Pt-Re, Pt-Sn and Pt-Sn-Re/ZH composite materials similar to Pt/ZH catalyst [13] are type IV with inflection points at about $p/p_0 = 0.25$ –0.4. This confirms mesoporous structures for our synthesized catalysts. In low pressure ranges ($p/p_0 < 0.25$), a similar behavior is observed for bi- and trimetallic catalysts. The monolayer adsorbed N_2 is formed in some microporous channels in HZSM5, and therefore the adsorption rises slowly with the relative pressure, as shown in Fig. 5 and Table 1. This reveals that the second and third metal deposition on micro/mesoporous supports will not create significant changes in the surface proper-

Fig. 6. NH_3 -TPD profiles for prepared catalysts.

ties of the catalyst, except with Re. This may be the cause of non-uniformity in the metal phase loading (Re) or collapse of some micro/mesopores that forms larger pores from the inter-nanoparticle boundaries with diminished pore volume and surface area. Thus, the Pt-Re/ZH catalyst caused higher disorder than other catalysts and shows the largest decrement in S_{BET} and pore volume (V_p). Fig. 5(a) shows one of the t -plots for these catalysts. The t -plot method is used to determine the microporosities. The micropore volume was taken from the positive intercept of the straight line through the t -plot data with the y -axis. Table 1 reveals that metal loading decreases the micropore volume. Pt-Re and Pt-Sn-Re catalysts show the largest and smallest decrement, respectively, which is in agreement with the effect of metal loading on the total pore volume.

Fig. 6 shows NH_3 -TPD profiles of mono-, bi- and trimetallic samples. There are three peaks in the range of 110–800 °C. The low temperature peak at 170–250 °C is characterized as the desorption of ammonia weakly held on the acid sites. The second peak, at 340–470 °C, is assigned to the desorption of ammonia strongly adsorbed on the acid sites. The third peak, accounting for the final temperature of calcination and the treatment temperature, appears to not be desorption of NH_3 , but rather H_2O desorption, which is accompanied by the partial

Fig. 5. (a) BJH desorption $dV/d\log(D)$ pore volume, (b) N_2 adsorption-desorption isotherms, and (c) t -plot curves of composite catalysts at -196 °C.

collapse or phase change of HMS. Fig. 6 presents the maxima of TPD diagrams for bi- and trimetallic catalysts shifts to low temperatures. This means that the strength of acid sites decreases in these catalysts compared with monometallic catalysts. The quantitative mole number of acid sites (NH_3 -TPD results) confirms this (Table 1).

Typical SEM photographs for bi- and trimetallic catalysts were prepared (not shown here). SEM images show that the catalysts lose their morphology after loading their second and third metals and do not show the observed structure for monometallic catalysts [13].

3.2. The *n*-C₇ isomerization reaction

Table 2 shows the activity of our prepared catalysts. The highest conversion of *n*-C₇ at all temperatures, after Pt/ZH, appeared for the Pt-Re/ZH catalyst. Raising the reaction temperature to 350 °C almost linearly increased the *n*-C₇ conversion. This is caused by Re increasing the hydrogenolysis activity and this reaction being favorable at high temperatures, leading to increased conversion. The Pt-Sn/ZH catalyst shows the lowest activity because of Sn modifying both the metal and acid sites. The metal sites are affected through either geometric or electronic effects of Sn. The geometric effect involves the blocking of Pt sites by Sn, preventing the adsorption of the reactants. The electronic effect modifies the electronic structure of Pt by Sn deposits in its vicinity [25]. The selectivity toward cracking, aromatization, hydrogenolysis and other products are also summarized in this table. The aromatization reaction mainly occurs through a bifunctional mechanism in which the acidic function is the rate-determining step [26,27]. Bi- and trimetallic catalysts form very few aromatization products. According to the Haag-Dessau mechanism, the cracking reaction proceeds through a monomolecular reaction mechanism at

high temperatures and low pressures of alkanes over acidic sites [10]. In the monomolecular mechanism, the alkane protonation by Brönsted acid sites is a rate-determining step. As mesoporosity eases hydrogen transfer reactions between olefinic and cyclic intermediates, aromatization and cracking are major reactions for all mesoporous samples (at 350 °C). Therefore, these will be competing reactions. The Pt-Re/ZH catalyst has lower selectivity to aromatization and higher selectivity to cracking than the Pt-Sn/ZH catalyst (however, the differences are negligible), because the addition of Sn decreases the acidity of the support and the fraction of strong acid sites [10]. Thus, the reduction of cracking occurs on the strong acid sites. This is in agreement with our TPR results about the segregated Sn oxide particles or metal ions neutralizing acid sites of the support.

The isomerization products are categorized into two groups as monobranched (MOB) and multibranched (MUB) isomers. In Table 2, we have listed MOB, MUB and total *i*-C₇ selectivity. Because of the thermodynamic limitation for isomerization reactions (although with negligible reaction heat), and also because of increased cracking, the selectivity of *n*-C₇ into *i*-C₇ decreases with increasing temperature. MUB isomers have higher octane numbers, rendering these products more important in the oil industry. The formation, desorption and diffusion of MUB isomers inside the small pores in most of the catalysts are difficult and result in more cracking products. Our prepared catalysts, however, because of a better fit to the pore size and other factors such as catalytic acidity, have better MUB isomer selectivity than monometallic catalysts. According to these data, selectivity to isomerization products for the Pt-Sn/ZH catalyst is higher than the Pt-Re/ZH catalysts. This is likely because destroying the intermediate iso-olefins by hydrogenolysis on the metallic function for the Pt-Re/ZH catalyst [28] and the higher selectivity of the Pt-Sn/ZH catalyst can be

Table 2

Catalytic activity, selectivity, coke amount and RON at various reaction temperatures over different prepared catalysts.

Catalyst	<i>T</i> /°C	Conversion (%)	Selectivity ^a (%)							Coke amount ^b	RON
			MOB	MUB	<i>i</i> -C ₇	Cracked	Aromatic	Hydrogenolysis	Others		
Pt/ZH	200	57.3	25.3	10.5	35.8	13.7	3.6	3.9	43.0	—	18.0
	250	75.8	16.3	6.0	22.3	27.0	4.3	4.3	42.1	—	19.2
	300	95.0	11.3	3.7	15.0	36.6	5.6	4.6	38.2	41.0	56.9
	350	100	7.3	0.8	8.1	44.8	8.3	4.7	34.1	—	53.8
Pt-Re/ZH	200	52.5	29.6	12.6	42.2	21.8	2.7	4.6	28.7	—	53.3
	250	71.6	14.1	8.8	22.9	39.7	3.5	4.9	29.0	—	66.6
	300	92.0	12.4	5.4	17.8	43.7	4.3	5.0	29.2	26.4	68.4
	350	100	5.4	4.0	9.4	48.0	7.5	5.1	30.0	—	83.2
Pt-Re-Sn/ZH	200	50.5	24.8	23.4	48.2	17.0	3.1	4.4	27.3	—	59.1
	250	60.2	11.7	12.6	24.3	38.7	3.9	4.8	28.3	—	82.4
	300	64.2	7.8	8.4	16.2	42.9	4.9	4.9	31.1	24.7	90.9
	350	91.3	5.1	4.0	9.1	46.9	8.0	4.9	31.1	—	100
Pt-Sn-Re/ZH	200	50.2	40.3	14.9	55.2	12.0	3.4	4.2	25.2	—	68.0
	250	58.8	25.5	9.5	35.0	28.7	4.1	4.6	27.6	—	76.3
	300	61.4	16.6	6.8	23.4	35.5	5.1	4.7	31.3	25.9	79.6
	350	70.8	7.7	5.4	13.1	41.7	8.2	4.8	32.2	—	98.0
Pt-Sn/ZH	200	49.2	35.2	39.8	75.0	16.8	3.0	2.3	2.9	—	65.0
	250	54.0	17.2	28.5	45.7	28.3	3.7	2.5	19.8	—	66.2
	300	60.1	12.9	9.2	22.1	41.9	4.5	3.4	28.1	39.6	85.3
	350	66.1	6.5	6.2	12.7	45.6	7.8	3.7	30.2	—	89.2

^a MOB: monobranched isomers; MUB: multibranched isomers; *i*-C₇: MOB + MUB.

^b TOS = 72 h.

attributed to Sn ions in the inner region of the micro/mesoporous framework (see TPR plots). This involves the acidic properties of the support by neutralizing its acid sites (probably strong acid sites that are responsible for cracking) [24]. To raise the octane number, in accordance with environmental limitations, isomer production must increase while production of aromatics, especially benzene, decreases. Our results indicate that our micro/mesoporous catalysts have good selectivity for desirable products.

To investigate the stability of these catalysts and coke formation on the catalyst during this process, the experiments were continued for 72 h under a continuous stream at 300 °C (an optimum temperature). Fig. 7 presents the conversion and the various product selectivities compared with time on stream (TOS) at 300 °C. Changes in the Pt-Sn/ZH catalyst selectivity to the different products are almost the same as the monometallic catalyst, while for Pt-Re/ZH a reduction in the selectivity of cracking products can be seen in the first 2 h. This is caused by the presence of Re, which comparatively increases the catalyst acidity [16], and the interaction between Pt and Re that enhances the resistance of the metallic phase against coke deposition [29]. Therefore, during the initial reaction period, the acid sites are suitable for coke deposition. Thus, the selectivity of cracking products decreases. We also analyzed carbon deposits over the spent catalysts after the stability test (72 h TOS) by TG/DT analysis. The coke contents on the spent catalysts were calculated and summarized in Table 2. These results show that the coke deposition on trimetallic catalysts is lower than on

mono- and bimetallic composite catalysts, which can be confirmed by the lower deactivation observed after 72 h of reaction. Trimetallic catalysts therefore have more stable activity and selectivity. According to the results, Pt-Re-Sn/ZH and Pt-Sn/ZH have the lowest and the highest coke contents, respectively.

To evaluate the catalytic performance of our catalysts, we also examined the temperature and metallic function effects on RON (Table 2). To calculate RON, we used both the reported amounts of RON for earned products [30] and the method described in our reported work [13]. Pt-Re-Sn/ZH at 350 °C provides higher RON compared with other catalysts because of molecules with higher RON_i and as expected from the isomerization and aromatic products.

3.3. Kinetic study

A key goal is determining whether the catalytic conversion is determined solely by the catalyst activity (kinetic regime) or is limited by transport phenomena (diffusion regime). We therefore investigated the reaction kinetics and the mass transfer limitation effects during the reaction. To study the mass transfer limitations, the Koros-Nowak [31] and Madon-Boudart [32,33] tests were used. According to these tests, in the absence of all transport limitations, the reaction rate is proportional to the number of active sites, which in turn is proportional to the catalyst weight. Therefore, we prepared a mixture of each catalyst with an inert powder and measured

Fig. 7. *n*-C₇ conversion and selectivity to various products vs. TOS at 300 °C for different catalysts. (1) Pt-Re/ZH; (2) Pt-Re-Sn/ZH; (3) Pt-Sn-Re/ZH; (4) Pt-Sn/ZH.

their reaction rates. The plot of rate versus catalyst weight is linear and the rate increases proportionally with the weight of catalyst (Fig. 8). This result shows an absence of any mass transfer limitations during the reaction [34]. Therefore, *n*-C₇ conversion rates under these conditions are controlled by the intrinsic reaction kinetics and are free from transport limitations.

Another form of reaction rate r (mol g⁻¹ s⁻¹), according to a power law, is:

$$r = kP_{\text{H}_2}^n P_{\text{C}_7}^m \quad (5)$$

where k is determined by Eq. (4).

To determine the orders of hydrogen and *n*-C₇ in the isomerization reaction, linear fits from double-log plots of the kinetic data measured by varying the partial pressures of hydrogen (2.6–5.9 Pa) and *n*-C₇ (0.002–0.009 Pa) were drawn at different temperatures, and these data are summarized in Table 3. It shows that the orders of H₂ and *n*-C₇ increase with increasing reaction temperature. The order of H₂ at a constant temperature is often negative and at high temperature reaches zero and positive values.

According to the literature [35,36], a number of catalytic reactions involving hydrogen and hydrocarbons, such as isomerization and hydrogenolysis, exhibit a negative dependence on the partial pressure of hydrogen. Studies show that the inhibition effect of H₂ is dependent on experimental conditions such as pressure and temperature.

For our catalysts, when the reaction temperature decreases at low hydrogen pressures, the inhibition effect of hydrogen increases. This effect decreases with increasing temperature until a given temperature (300 and 350 °C for Pt-Sn-Re/ZH catalyst, 350 °C for Pt-Re-Sn/ZH and 250, 300 and 350 °C for Pt-Re/ZH catalyst), after which the inhibiting effect converts to a promoting effect.

To kinetically model this reaction, a simplified mechanism of bifunctional catalytic isomerization was considered (Fig. 9). This mechanism offers a good interpretation aligning with our results. In this mechanism, the olefinic intermediates are generated and hydrogenated by the metal, and the isomerization products are catalyzed by the neighboring acidic function. In this mechanism, we assume that olefin transport from the metallic sites to the acidic sites (step 4) is slow and the rate-determining step [6]. Neglecting the reverse reaction for the low conversion in step (4), the following rate equation r is given:

$$r = k_4 \theta_{n-07,M} \theta_{0,a} \quad (6)$$

$$K_1 = \frac{\theta_{n-07,p}}{P_{n-07} \theta_{0,p}}; K_2 = \frac{\theta_{n-07,M} \theta_{0,p}}{\theta_{n-07,p} \theta_{0,M}}; K_3 = \frac{\theta_{n-07,M} P_{\text{H}_2}}{\theta_{n-07,M}} \quad (7)$$

where r is the reaction rate (mol g⁻¹ s⁻¹), k_4 is the rate constant

Fig. 8. Effect of catalyst weight on *n*-C₇ isomerization reaction rate at 350 °C.

of step 4, K_i is the adsorption equilibrium constant for step i ($K_i = \frac{k_i}{k_{-i}}$), P_{n-07} is the partial pressure of *n*-C₇ (Pa), P_{H_2} is the partial pressure of H₂ (Pa), $\theta_{n-07,M}$ is the coverage of metallic sites by *n*-olefin, $\theta_{n-07,p}$ is the coverage of metallic sites by *n*-C₇, $\theta_{n-07,p}$ is the coverage of support micro/mesopore sites by *n*-C₇, $\theta_{0,a}$ is the empty fraction of acid sites, $\theta_{0,p}$ is the empty fraction of support micro/mesopore sites, and $\theta_{0,M}$ is the empty fraction of metallic sites. The sum of free and covered fractions of different sites is of course one.

Therefore, with these equations, the given assumption and Langmuir adsorption isotherm, the following rate expression can be written:

$$r = k_4 \frac{K_1 K_2 K_3 P_{n-07}}{P_{\text{H}_2} (1 + K_1 P_{n-07})} \quad (8)$$

This equation confirms the inhibiting effect of hydrogen on the isomerization reaction. According to our results, the effect hydrogen pressure has on the reaction rate depends on the reaction temperature. These results show that the acidic function promotes the reaction with increasing temperature. But at some temperatures, the promoting effect was observed for the H₂ pressure, which can be explained by the loss of a catalytic surface saturated in hydrogen. Thus, at these temperatures, the reaction is controlled by both acidic and metallic functions.

To confirm the final equation (Eq. (8)) resulting from the proposed mechanism, the linear transformation of Eq. (8), i.e. plotting $1/r$ as a function of P_{H_2} (P_{n-07} being constant), was evaluated. The plots of our experimental results (not shown here) are close to a straight line starting at the origin. This mechanism supports our reported results for producing isomerized products.

Table 3

Orders of H₂ and *n*-C₇ for *n*-C₇ isomerization.

Catalyst	n_{H_2}				m_{C_7}				$E_{\text{app}}^{\text{act}}$ (kJ/mol)
	200 °C	250 °C	300 °C	350 °C	200 °C	250 °C	300 °C	350 °C	
Pt-Sn/ZH	-1.76	-0.84	-0.50	-0.35	0.30	0.37	0.44	0.88	32.98
Pt-Sn-Re/ZH	-0.21	-0.01	0.01	0.02	0.15	0.17	0.43	0.54	50.97
Pt-Re-Sn/ZH	-0.08	-0.04	-0.03	0.00	0.12	0.24	0.37	0.63	65.00
Pt-Re/ZH	-0.54	0.05	0.08	0.10	0.20	0.35	0.79	1.00	77.16

Fig. 9. Scheme of kinetic modeling for n -C₇ isomerization.

Another possibility from the literature [34] for this observation is the isomerization reaction occurring directly on acid sites assisted by the presence of metal sites and also using active hydride species of hydrogen to reduce the lifetime of the carbenium ions on the catalyst surface. It was also proposed that the promoting effect of hydrogen can be confirmed by the low catalyst deactivation. Our catalyst deactivation results (Table 2) are in concordance with this expression for the promoting effect of hydrogen (Table 3).

The apparent activation energy values for isomerization reactions (E_{app}^{act}) have been determined graphically from an Arrhenius plot (Eq. (4)) in a range of temperatures from 200 to 350 °C and at constant hydrogen and n -C₇ pressures (Table 3). For our prepared catalysts, the E_{app}^{act} values are lower than the reported values (~100–135 kJ/mol) [35,36]. This behavior confirms the better reaction rate for these catalysts. Among our catalysts, Pt-Sn/ZH has the lowest activation energy (32.98 kJ/mol) for the n -C₇ isomerization reaction, so the reaction on this catalyst will be facile, and i -C₇ conversion will be better than with other catalysts.

4. Conclusions

The prepared Pt-(Re,Sn)/HZSM5-HMS catalysts have high conversion (49%–100%), i -C₇ selectivity (9%–75%) and low coke deposition for 72 h TOS (24.7%–39.6%) in the n -heptane isomerization reaction. High activity and selectivity for desirable products show the possibility of achieving high octane gasoline. Among these catalysts, Pt-Sn/ZH is much more selective than the others (75% at 200 °C). The order of activity, selectivity of isomerization products, coke deposition and RON are:

activity Pt-Re/ZH > Pt-Re-Sn/ZH > Pt-Sn-Re/ZH > Pt-Sn/ZH; i -C₇ selectivity Pt-Sn/ZH > Pt-Sn-Re/ZH > Pt-Re-Sn/ZH > Pt-Re/ZH; coke deposition Pt-Sn/ZH > Pt-Re/ZH > Pt-Sn-Re/ZH > Pt-Re-Sn/ZH; RON Pt-Re-Sn/ZH > Pt-Sn-Re/ZH > Pt-Sn/ZH > Pt-Re/ZH. Also, Pt-Sn/ZH produces the least hydrogenolysis products. For aromatic selectivity, according to the results, the differences are negligible. The reaction kinetics measurements show that the n -C₇ conversion rate under experimental conditions is controlled by the intrinsic reaction kinetics and is free from transport limitations, as determined from the Koros-Nowak and Madon-Boudart criteria. The activation energy was 32–78 kJ/mol using bi- and trimetallic catalysts, showing that these catalysts have higher rates in the isomerization reaction than other reported catalysts. Based on this analysis, the major conclusion would appear to be that Pt-Sn/ZH exhibits the best performance in the isomerization reaction, but according to other important products such as cracking, aromatics, hydrogenolysis, coking and the RON results, Pt-Re-Sn/ZH is the better catalyst for industrial aims.

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Graphical Abstract

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Experimental and kinetic study of *n*-heptane isomerization on nanoporous Pt-(Re,Sn)/HZSM5-HMS catalysts

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The characterization of improved catalysts for *n*-C₇ isomerization reaction, the effects of Re and Sn addition and temperature on activity, selectivity, catalytic stability, octane number and kinetics were investigated.

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纳米孔Pt-(Re, Sn)/HZSM5-HMS催化剂上正庚烷异构化反应的实验和动力学研究

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摘要: 在200–350 °C考察了Pt-(Sn,Re)/HZSM5-HMS催化剂上正庚烷异构化反应. 采用X射线衍射、X射线荧光光谱、傅里叶变换红外光谱、紫外-可见光谱、H₂程序升温还原、NH₃程序升温脱附、吸附吡啶红外光谱、H₂化学吸附、N₂吸附-脱附、扫描电镜和热重等技术对催化剂进行了表征. 在不同的H₂和正庚烷分压条件下考察了正庚烷异构化反应动力学,研究了反应条件对催化性能的影响. 结果表明,双金属催化剂和三金属催化剂表现出比单金属催化剂更高的催化性能. 200 °C时Pt-Sn/HZSM5-HMS催化剂表现出最高的异庚烷选择性(>74%)和多支链异构体选择性(40%).

关键词: 双金属催化剂; 三金属催化剂; 正庚烷异构化; 选择性; 多支链异构体

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