



Catalysis, Kinetics and Reaction Engineering

Rare earth metals modified Ni–S₂O₈²⁻/ZrO₂–Al₂O₃ catalysts for *n*-pentane isomerization[☆]

Hua Song^{1,2,*}, Lele Zhao¹, Na Wang¹¹ College of Chemistry & Chemical Engineering, Northeast Petroleum University, Daqing 163318, China² Provincial Key Laboratory of Oil & Gas Chemical Technology, College of Chemistry & Chemical Engineering, Northeast Petroleum University, Daqing 163318, China

ARTICLE INFO

Article history:

Received 1 March 2016

Received in revised form 13 June 2016

Accepted 14 June 2016

Available online 16 June 2016

Keywords:

Rare earths

Solid superacid

Catalyst

Hydroisomerization

ABSTRACT

The effects of adding rare earth (RE) metals, such as Ce, Yb and Pr to Ni–S₂O₈²⁻/ZrO₂–Al₂O₃ (Ni–SZA) on the structure of catalysts as well as their isomerization performance were studied. The prepared catalysts were characterized by XRD, BET, FT-IR, Py-IR, and H₂-TPR. The results showed that the addition of RE metals can increase the strength and amounts of the acid sites, improve the redox properties of catalysts. The Yb–Ni-SZA catalyst showed the best redox properties, which could provide enough metallic sites. In addition, it provided the largest amounts of weak and moderately strong acid sites. Among RE metals modified Ni-SZA catalyst, Yb-Ni-SZA exhibited the highest isopentane yield of 61.7% at 160 °C. The optimum isomerization catalytic performance of the catalysts decreased in the order of Yb-Ni-SZA > Pr-Ni-SZA > Ni-SZA > Ce-Ni-SZA.

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1. Introduction

The increasing interest in improving environmental protection and promoting efficiency of automotive motors encourage the design of environmentally benign catalysts and development of new processes for gasoline production. In view of the branched paraffin has higher octane numbers than linear alkanes, the use of gasoline that contains higher proportions of these compounds is an alternative way in obtaining clean fuel [1]. Usually, the branched paraffins are obtained by isomerization reactions, and C₄–C₆ *n*-paraffin isomerizations are the most common used reactions. The isomerization was usually conducted on liquid and solid acid catalysts. Traditional industrial liquid acid catalysts, such as H₂SO₄, HF and SbF₅/HSO₃F have undesired drawbacks which attributed to their severe corrosivity and difficulty of recover and reuse [2]. The solid acids employed are either chlorided alumina or Pt-mordenite catalysts. For chlorided alumina, constant addition of chloride is necessary and its disposal would cause a serious pollution to the environment. For Pt enhanced zeolites, the disadvantage is the relatively high operating temperature which leads to poor RON results [3]. Sulfate-modified metal oxides, which are a class of strong solid acid catalysts, are found to be active for alkane isomerization at relatively lower temperatures than commercial chloride-platinated-alumina catalyst [4]. Among various sulfated metal oxides, the sulfated zirconia

(SZ) has attracted much attention and has been extensively investigated. However, the isomerization activity over SZ catalyst is still not high enough [5]. To enhance the isomerization activity, monometallic and bimetallic modified SZ catalysts are studied, and the bimetallic modified SZ catalysts exhibit a better isomerization activity.

Rare earth (RE) metals are well known catalyst additives for many reactions [6–9], such as selective catalytic reduction (SCR) of NO_x with ammonia, fluid catalytic cracking (FCC) of hydrocarbons, and fatty acid methyl ester synthesis and *n*-paraffins isomerization. Generally, RE metals are added to disperse and interact with other transition metal oxides to generate increased active sites, enhance the strength and density of the acid sites, and improve the thermal stability of the catalysts.

In the present work, a series of RE metals (Ce, Yb, Pr) were introduced into Ni–S₂O₈²⁻/ZrO₂–Al₂O₃ (Ni–SZA) catalyst. The physicochemical properties of various RE-modified SZA catalysts was comparative studied, and *n*-pentane isomerization as a probe reaction was used to investigate the catalytic performance of prepared catalysts.

2. Experimental

2.1. Catalysts preparation

The ZrO₂–Al₂O₃ binary oxide was prepared by a homogeneous coprecipitation method. For this purpose, an aqueous solution containing the requisite quantities of ZrOCl₂·8H₂O and Al(NO₃)₃·9H₂O were prepared. This solution was hydrolyzed with dilute ammonium hydroxide with vigorous stirring until the pH of the solution reached to 9–10. At this pH, a white precipitate was formed and the precipitate was

[☆] Supported by the Technology Risk Innovation Foundation of China National Petroleum Corporation (07-06D-01-04-03-02).

* Corresponding author.

E-mail address: songhua2004@sina.com (H. Song).

allowed to settle for 24 h. The suspension was then filtered off and washed with deionized water to eliminate the Cl^- ions, and finally dried at 120 °C for 12 h. The powdered $\text{ZrO}_2\text{-Al}_2\text{O}_3$ was immersed in 0.75 mol·L⁻¹ of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution for 6 h to incorporate with $\text{S}_2\text{O}_8^{2-}$ ions. After that, the suspension was centrifuged. The resulted solid sample was dried overnight at 110 °C and then calcined at 650 °C for 3 h, denoted as SZA. The as-prepared SZA were divided into four parts, and each of them was impregnated with $\text{Ce}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$, $\text{Yb}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ and $\text{Pr}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ solution for 6 h, respectively. The resulted precipitations were collected and dried at 120 °C. Subsequently, the dry powders and SZA were impregnated with $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ solution for 6 h, respectively, and then dried overnight at 110 °C. The obtained samples were finally calcinated at 650 °C for 3 h. The prepared catalyst with 1.0 wt% Ni is denoted as Ni-SZA, and the RE metals modified catalysts contained 1.0 wt% RE (Ce, Yb, Pr) and 1.0 wt% Ni are denoted as Ce-Ni-SZA, Yb-Ni-SZA and Pr-Ni-SZA, respectively.

2.2. Catalysts characterization

X-ray powder diffraction (XRD) patterns were recorded on a Rigaku D/max 2200pc diffractometer (40 kV, 20 mA) fitted with Cu K α radiation ($\lambda = 0.15404$ nm). The scan range was from $2\theta = 10^\circ$ to 80° . The crystallite size D_c of the samples was calculated using the Debye-Scherrer's relationship,

$$D_c = 0.9\lambda / (\beta \cos\theta)$$

where D_c is the crystallite size, λ is the incident X-ray wavelength, β is the full width at half-maximum, and θ is the diffraction angle.

The specific surfaces (BET) of the supports and catalysts were obtained from nitrogen adsorption isotherms using Micromeritics adsorption equipment of NOVA2000e. All the samples were outgassed at 200 °C until the vacuum pressure was 800 Pa. The adsorption isotherms for nitrogen were measured at -196 °C.

Fourier transform infrared spectroscopy (FT-IR) of the catalysts was acquired on a Bruker Tensor 27 FT-IR spectrometer. The FT-IR samples were mixed with KBr and compacted into a thin pellet, the contents of the samples in the KBr wafers were maintained 1 wt% in all FT-IR experiments. The spectra were recorded at room temperature.

IR spectra of adsorbed pyridine (Py-IR) were recorded on a Spectrum GX Fourier transform infrared spectrometer at 4 cm⁻¹ resolution. Samples, in the form of self-supported wafers, were pretreated in vacuum for 1 h at 400 °C and exposed to pyridine at 50 °C. After desorption at 150, 300 and 350 °C, the spectra were recorded.

H₂ temperature-programmed reduction (H₂-TPR) experiments were carried out on a Builder PCA-1200 instrument with a H₂/N₂ flow of 40 ml·min⁻¹ from 50 to 700 °C with a ramp of 10 °C·min⁻¹.

2.3. Catalytic activity measurements

The isomerization reaction of *n*-pentane was performed under hydrogen atmosphere in a fixed-bed flow reactor. Prior to the reaction, the catalyst was activated in a hydrogen stream at 300 °C for 3 h, and then cooled to a reaction temperature. A dose of *n*-pentane was passed over the 5 g of activated catalyst under the following reaction conditions: reaction pressure of 2.0 MPa, molar H₂/*n*-pentane ratio of 4:1, and weight hourly space velocity (WHSV) of 1.0 h⁻¹. The products were flash-evaporated into an online FL9790 gas chromatograph equipped with an FID detector.

3. Results and Discussion

3.1. XRD

XRD patterns of various catalysts are illustrated in Fig. 1. All catalysts exhibit the similar XRD patterns. More concretely, all catalysts show the

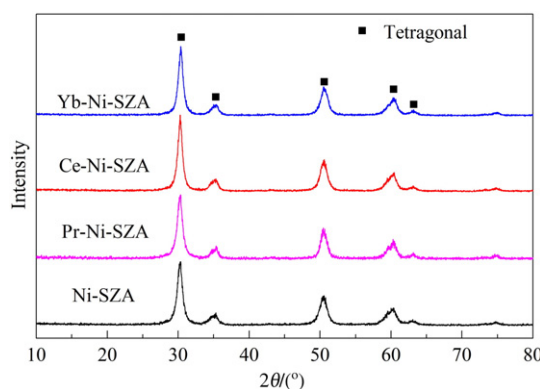


Fig. 1. XRD patterns of Ni-SZA and RE-Ni-SZA catalysts.

diffraction peaks of the tetragonal crystal of ZrO_2 at 2θ of 30.2° , 35.4° , 50.4° , 60.3° and 63.3° . Whilst, no diffraction peaks assigning to Ni, Ce, Yb and Pr are observed, implying that all metal particles have a better dispersion on the SZA supports respectively. In addition, their crystal sizes are not large enough to be detected by XRD [10]. The mean particle diameters (D_c) based on the tetragonal crystal of ZrO_2 calculated from Scherrer's equation for various catalysts are shown in Table 1. Compared with Ni-SZA catalyst, Pr-Ni-SZA catalyst shows similar D_c . However, Ce and Yb modified Ni-SZA catalysts exhibit larger D_c . This indicates that the addition of Ce and Yb could promote the growth of ZrO_2 tetragonal crystal particles.

Table 1

The textural and structural properties of Ni-SZA and RE-Ni-SZA catalysts

Sample	$S_{\text{BET}}^{\text{①}}/\text{m}^2\cdot\text{g}^{-1}$	$d_p^{\text{②}}/\text{nm}$	$V_p^{\text{③}}/\text{cm}^3\cdot\text{g}^{-1}$	$D_c^{\text{④}}/\text{nm}$
Yb-Ni-SZA	93.3	3.36	0.083	10.7
Ce-Ni-SZA	82.1	3.34	0.089	10.8
Pr-Ni-SZA	89.9	3.72	0.084	9.5
Ni-SZA	95.1	3.73	0.089	9.7

① BET surface areas.

② Pore volumes.

③ pore diameter.

④ Calculated from the (Debye-Scherrer's equation) based on the tetragonal ZrO_2 .

3.2. BET

Table 1 lists the data on BET surface areas (S_{BET}), pore volumes (V_p) and pore diameter (d_p) of all catalysts. The S_{BET} , V_p , and d_p of Ni-SZA catalyst is $95.1\text{ m}^2\cdot\text{g}^{-1}$, $0.089\text{ cm}^3\cdot\text{g}^{-1}$, and 3.73 nm , respectively. However, compared with Ni-SZA, all the RE metals modified Ni-SZA catalysts show slightly lower S_{BET} and d_p with similar V_p . In other words, both bimetallic and monometallic modified SZA catalysts show similar pore structures, which indicates that the addition of bimetal could not lead to the serious blockage of pores.

3.3. FT-IR

FT-IR spectra of samples with different RE metals in the region of 4000–450 cm⁻¹ are shown in Fig. 2. The band found at 3414 cm⁻¹ and 1630 cm⁻¹ are the O–H bond vibration. The spectrum of all samples exhibited three bands at 1270 cm⁻¹, 1151 cm⁻¹ and 1072 cm⁻¹, attributed to S=O and S–O vibration modes of surface $\text{S}_2\text{O}_8^{2-}$ species [11]. The characteristic vibration peaks for asymmetric and symmetric stretching frequencies of S=O and S–O bonds can prove that the formation of solid superacid structure [12]. The partially ionic nature of the S=O bond is responsible for the Bronsted acid sites in catalysts [13]. The intensity and splitting extent of the vibration peaks reflect the proportion of acid sites linked to the catalyst. In comparison with Ni-SZA, Yb-Ni-SZA catalyst shows stronger vibration peak for S=O bond, in addition,

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