



Hydrogen spillover behavior of Zn/HZSM-5 showing catalytically active protonic acid sites in the isomerization of *n*-pentane

Sugeng Triwahyono^{a,*}, Aishah Abdul Jalil^b, Rino R. Mukti^c, Malik Musthofa^a, N. Aini M. Razali^b, M. Arif A. Aziz^b

^a Ibnu Sina Institute for Fundamental Science Studies, Faculty of Science, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

^b Department of Chemical Engineering, Faculty of Chemical Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

^c Division of Inorganic and Physical Chemistry, Faculty of Mathematics and Natural Sciences, Institut Teknologi Bandung, Jl. Ganesha 10, Bandung 40132, Indonesia

ARTICLE INFO

Article history:

Received 23 May 2011

Received in revised form 12 August 2011

Accepted 17 August 2011

Available online 24 August 2011

Keywords:

Zn/HZSM-5

Protonic acid sites

Lewis acid sites

Molecular hydrogen

n-Pentane isomerization

ABSTRACT

The impregnation of zinc particles into MFI zeolite (HZSM-5) caused the formation of catalytically active protonic acid sites for isomerizing *n*-pentane in the presence of hydrogen. An infrared (IR) study with preadsorbed pyridine revealed that these protonic acid sites originated from the spillover of molecular hydrogen from the zinc species onto the zeolite surface. The requirements for this spillover effect were further studied by IR spectroscopy of adsorbed ammonia and carbon monoxide. The presence of zinc species in HZSM-5 suggested the exchange of acidic character towards strong Lewis acids rather than Brønsted acid sites. The isomerization of *n*-pentane over the Zn/HZSM-5 catalyst resulted in high activity and stability and the conversion to *iso*-pentane depends on the promotive effect of hydrogen as a carrier gas.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

The isomerization of light paraffins such as *n*-pentane, *n*-hexane and *n*-heptane proceeds via hydrogen dissociation on a metal under a hydrogen atmosphere along with the occurrence of hydrocracking side reactions [1,2]. The promotive effect of hydrogen on the high isomerization activity, such as with Pt/SO₄²⁻-ZrO₂ and Pt/WO₃-ZrO₂ catalysts, has been interpreted by the generation of protonic acid sites via which the hydrogen migrates or spills over from a noble metal site onto the acidic oxide support during the reaction [3–8]. In fact, this hydrogen spillover phenomenon has only been observed for a limited class of catalysts [9,10]. Due to the importance of acid-catalyzed alkane isomerization to achieve the high octane number of high-quality gasoline, further development of these kinds of solid acid catalysts that are stable, regenerable and active at low temperatures is necessary.

Solid acid catalysts such as alumina, zirconia, mesoporous silica and zeolites have been used as supports for promoting metals or noble metals due to their non-corrosive, high surface area and deactivation-free characteristics [11–16]. Bifunctional catalysts that consist of metallic and acidic components effectively promote the isomerization of alkanes [17–21]. However, a major

drawback of using sulfur-based solids is their tendency to form volatile compounds and their intolerance against water poisoning during catalytic reactions, thus preventing the catalyst from being applicable and regenerated. Among those supports, zeolites are especially promising because these crystalline microporous materials are well known for their shape selectivity, good thermal stability, hydrophobicity and strong electron transfer to their enormous acid sites [22–25].

In the case of zeolites, the hydrogen spillover effect has been observed on zeolite-supported metals (bifunctional catalyst) and zeolite physically mixed with metals supported on silica (hybrid catalyst) [2,26–29]. In the presence of platinum as a promoter, the isomerization activity and selectivity of zeolites can be favored over the cracking activity [30]. In addition, the introduction of Zn species into HZSM-5 (medium-pore MFI-type zeolite) can be used to increase the rate and selectivity of other hydrocarbon conversions, such as aromatization reactions, by inhibiting the undesirable β-scission side reaction [31,32]. Nevertheless, the catalytic role of Zn species is controversial. The synergy between acid sites and exchanged cations during alkane activation have been described. In this work, we studied the hydrogen spillover effect of zinc particles impregnated into HZSM-5 (Zn/HZSM-5) and tested them in the isomerization of *n*-pentane. The crystal size has been found to be of paramount importance for advancing the molecular diffusion pathlength in catalysis [30]. Therefore, we used a Zn²⁺/N,N-dimethylformamide solution to impregnate zinc

* Corresponding author. Tel.: +60 7 5536076; fax: +60 7 5536080.

E-mail address: sugeng@utm.my (S. Triwahyono).

particles with sizes ranging from 10 to 15 nm into the commercial zeolite.

Although many studies have used IR spectroscopy to investigate the hydrogen spillover effect [28,29], the requirement of a solid acid catalyst for this effect is not clear. We carefully examined the nature of zeolite acid sites before and after metal impregnation to understand the promotive effect of zinc particles in the presence of hydrogen. The spillover effect was monitored in detail by IR spectroscopy using pyridine as a molecular probe under a hydrogen atmosphere. The role of the zinc particles in zeolite was also studied with IR spectroscopy using carbon monoxide and ammonia adsorption. Based on these complementary IR characterizations, the requirement of the solid acid catalyst for a hydrogen spillover effect has been clarified. The formation of protonic acid sites catalyzes the isomerization of *n*-pentane.

2. Experimental

2.1. Preparation of catalyst

Commercial HZSM-5 (Zeolyst) with an Si/Al atomic ratio of 80 was used as a support for the zinc catalyst. This commercial zeolite contains only Brønsted acid sites after treatment at 773 K for 3 h [5]. The Zn²⁺/N,N-dimethylformamide solution was used as the zinc particle precursor and was prepared following the procedures of Jalil et al. [33]. In brief, a N,N-dimethylformamide solution (Merck) containing naphthalene and tetraethylammonium perchlorate was added to one compartment of a cell equipped with a zinc plate (2 cm × 2 cm) as an anode and a platinum plate (2 cm × 2 cm) as a cathode. The electrodeposition of Zn²⁺ was then executed at 273 K. The Zn/HZSM-5 was prepared by impregnation of HZSM-5 with the Zn²⁺/N,N-dimethylformamide solution at 353 K, followed by drying at 393 K overnight and calcining at 823 K for 3 h in the air. The amount of zinc particles was adjusted to 5 wt% in the catalyst.

2.2. Characterization of catalyst

The crystallinity of HZSM-5 and Zn/HZSM-5 was confirmed by X-ray diffraction (XRD) recorded on a powder diffractometer (40 kV, 40 mA) using a Cu K α radiation source. While, X-ray photoelectron spectroscopy (XPS) of Zn/HZSM-5 was conducted on a Kratos Ultra spectrometer with MgK α radiation source (10 mA, 15 kV) and the XPS peaks are internally referenced to the binding energy of C (1s) peak at 284.5 ± 0.1 eV. The BET specific surface area was calculated from the adsorption data of N₂ adsorption–desorption isotherms at the relative pressure of 0.01–0.2 on a Quantachrome Autosorb-1 instrument. Prior to analysis, the sample was outgassed at 573 K for 3 h. For imaging of the zinc oxide particles, a powder form of the zinc oxide particles was obtained by separating the solid from Zn²⁺/N,N-dimethylformamide solution by centrifugation at 20,000 rpm for 30 min. The solid was then dried at 393 K overnight and calcined at 823 K for 3 h in the air. The morphology and size of the zinc oxide particles in the powder form were observed using a transmission electron microscope (TEM). For the TEM observations of ZnO particle and Zn/HZSM-5 samples, a powder sample dissolved in hexane and dropped onto the copper grid. A field-emission scanning electron microscope equipped with an energy dispersion X-ray spectrometer (SEM-EDX) was used to observe the morphology as well as to obtain the elemental analysis of the sample. Before observation by SEM-EDX, the sample was coated by Pt using a sputtering instrument.

2.3. IR spectroscopy

IR spectroscopy of adsorbed pyridine was used to evaluate several types of acid sites such as Brønsted, Lewis or protonic sites as

a result of the hydrogen spillover effect. In addition, ammonia and carbon monoxide were adsorbed to observe the acid strength. The IR spectra were recorded on a transmission spectrometer. The sample was prepared as a self-supporting wafer and activated under vacuum at 623 K for 3 h in accordance to Ref. [34]. The adsorption of pyridine (2 Torr) was conducted at 423 K for 30 min, followed by outgassing at 598 K for 30 min. For ammonia (5 Torr), the adsorption was conducted at 373 K for 30 min, followed by outgassing at 373 and 473 K for 30 min, respectively. The adsorption of carbon monoxide (2 Torr) was conducted at room temperature for 10 and 30 min. All spectra were recorded at room temperature. To compare the surface coverage of the adsorbed species between different wafer thicknesses, all spectra were normalized using the overtone and combination vibrations of the MFI between 2105 and 1740 cm⁻¹ after activation [35–37].

To study the generation and elimination of protonic acid sites formed after introducing hydrogen molecules on the catalyst, the pyridine-adsorbed catalyst was exposed to 50 Torr of hydrogen at room temperature. The catalyst was then heated stepwise from room temperature to 398 K with heating increments of 25 K. To remove the hydrogen, the catalyst was outgassed by stepwise heating from 323 to 573 K with heating increments of 50 K.

2.4. Isomerization of *n*-pentane

Isomerization of *n*-pentane was performed on a microcatalytic pulse reactor at 523 K. Initially, the catalyst was treated in an oxygen stream ($F_{\text{Oxygen}} = 100$ ml/min) for 1 h followed by hydrogen stream ($F_{\text{Hydrogen}} = 100$ ml/min) for 3 h at 673 K and then cooled down to reaction temperature of 523 K. A dose of *n*-pentane (43 μ mol) then was passed over 0.3 g of activated catalyst, and the products were trapped at 77 K before flash-evaporation into an online 6090N Agilent gas chromatograph equipped with a VZ-7 packed column and FID detector. The intervals between each dose were kept constant at 30 min.

The selectivity for a specific product (S_i) was calculated according to Eq. (1)

$$S_i = \frac{C_i}{C_1 + C_2 + C_3 + C_4 + iC_5} \times 100\% \quad (1)$$

where C_i is the molar concentration of a particular compound. Whereas C_1 , C_2 , C_3 , C_4 and iC_5 are the molar concentrations of methane, ethane, propane, butane and *iso*-pentane, respectively.

The specific rate of *n*-pentane conversion ($r_{n\text{-pentane}}$) from the differential conversion data was determined by Eq. (2)

$$r_{n\text{-pentane}} = k \frac{C_1 + C_2 + C_3 + C_4 + iC_5}{C_1 + C_2 + C_3 + C_4 + iC_5 + C_{5(\text{res})}} \quad (2)$$

where the rate constant (k) was determined by the molar concentration of *n*-pentane divided by the surface area of catalyst per unit time. $C_{5(\text{res})}$ represented the molar concentration of residual *n*-pentane in the product mixture. In this experiment, k was 2.89×10^{-7} mol s⁻¹ m⁻²-cat, with the assumption that the retention time for *n*-pentane in the catalyst bed was negligibly small.

3. Results and discussion

3.1. Structural properties of HZSM-5 and Zn/HZSM-5

Fig. 1 shows the XRD pattern of HZSM-5 and Zn/HZSM-5, confirming that the loading of Zn²⁺ does not change the peak position of parent HZSM-5. Physicochemical analysis by N₂ adsorption–desorption isotherms revealed that the BET specific surface areas of HZSM-5 and Zn/HZSM-5 were slightly different (511 and 495 m²/g, respectively). The small decrease in the BET specific surface area of HZSM-5 was due to the 5 wt% loading of

Download English Version:

<https://daneshyari.com/en/article/41296>

Download Persian Version:

<https://daneshyari.com/article/41296>

[Daneshyari.com](https://daneshyari.com)