SYNTHESIS OF HIGH SILICA ZSM-5 AND ITS PERFOMANCE IN n-HEXANE CONVERSION.

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TÓM TẮT

Zeolite ZSM-5 với hàm lượng Silic cao được tổng hợp bằng phương pháp gây mầm, có sử dụng chất tạo cấu trúc. Nguồn silic và nguồn nhôm là sol silic hoạt động và boehmite nhôm tự điều chế. Mẫu tổng hợp được đặc trưng cấu trúc bằng các phương pháp phổ nhiễu xạ Rơn ghen và phổ hấp thu hồng ngoại. Dạng axit của zeolite ZSM-5 được điều chế bằng phương pháp trao đổi ion ba lần với dung dịch $(NH_4)_2SO_4$. Platin được tẩm lên ZSM-5 với các hàm lượng khác nhau, từ 0,6% đến 1,2% khối lượng.

Các mẫu Pt/HZSM-5 đã điều chế được thử nghiệm hoạt tính đối với phản ứng hydro-isomer hóa n-hexane. Nguyên liệu và sản phẩm được phân tích bằng máy sắc ký khí, đầu dò FID. Trong các điều kiện của thí nghiệm, các sản phẩm isomer chủ yếu là 2-methyl pentane và 3-methyl pentane, cùng với các sản phẩm cracking. Hiệu suất phản ứng và tỉ lệ các sản phẩm cracking tăng theo nhiệt độ phản ứng. Hàm lượng sản phẩm isomer thu được lớn nhất ở nhiệt độ phản ứng 280^0C. Ảnh hưởng của hàm lượng Platin trên xúc tác cũng được khảo sát, mẫu 1%Pt/HZSM-5 cho độ chuyển hóa cao nhất.

ABSTRACT

High silica ZSM-5 was synthesized by templating and seeding method. The silica and alumina sources were home-made silica sol and boehmite. These synthesized zeolites were characterized by XRD and IR methods. Common wet ion exchange method with $(NH_4)_2SO_4$ solution was used to obtain HZSM-5 from NaZSM-5. Platinum was impregnated on HZSM-5 resulting in 0,6% to 1,2%w/w platinum.

Catalytic performance of these prepared Pt/HZSM-5 samples was investigated in hydro-isomerization process of n-hexane. The feed and products were analyzed by GC, detector FID. Under experimental conditions, the main products obtained as isomers are 2-methyl-pentane and 3-methyl-pentane, accompanied with the cracking products. The conversion rate and the yield of cracking products increased with the reaction temperature. The isomers products were reaching to maximum value at 280^0C. Also, the influence of impregnated platinum onto conversion rate was investigated, showing the highest rate with 1%Pt/HZSM-5.

Keywords: ZSM-5, isomer, sysnthesis,zeolite, n-hexane.

I. INTRODUCTION:

Isomerization of light alkanes is a way to increase octan number, especially for the n-alkanes [5]. This process could be used in improving octan number of the light naphtha fraction or condensate in order to receive branched and dibranched alkanes. With the isomerazation process, the RON of light naphtha could increase from ~64 to ~80 [4].

The commercial catalysts used for isomerization are platinum/H-mordenite or platinum/clorinated alumina. Pt/H-Mor had the advantages of sulfur and water resistance while Pt/clorinated alumina required lower reaction temperature. In this

paper, we have studied another zeolitic catalytic system based on ZSM-5 zeolite. In our former papers [1,2], we recognized that the Si/Al ratio of the zeolite took effect directly on the acidity so that its performance in n-hexan conversion. High silica ZSM-5, which its preparation procedure was shown in this paper, has low acidity so that it could suit for making catalysts for isomerization process.

II. EXPERIMENTAL:

Synthesis of high Silica ZSM-5:

High silica ZSM-5 was prepared by the hydrothermal method. The chemicals used to synthesize ZSM-5 were silica sol and boehmite, tetra propyl ammonium bromide (TPA-Br) as the templating agent, NaOH, ZSM-5 seed and distilled water. The silica sol was made from water glass and contained 16,15% SiO_2. At first, boehmite was added to a stirring NaOH solution at 70^oC until the solution became clear. Other chemicals were added to the aluminate solution when it had been cooled down. After added ZSM-5 seed and stirred vigorously for 2h, the gel was obtained had the molar composition 0.1TPABr 4.5Na_2O 0.4 Al_2O_3 40SiO_2. 1300H_2O was riped for one day at room temperature and was processed 32h at 170^oC in an autoclave. The synthesized sample was washed with deionized water, dried at 110^oC for 2h and calcined at 500^oC for 3h in an oxygen stream.

Preparation of these catalysts:

HZSM-5 was prepared from NaZSM-5 by triple exchanges with $(NH_4)_2SO_4$ solution. After that, the sample was washed, dried and calcined as the procedure above. The amount of exchanged sodium was determined by AAS method. A solution of H_2PtCl_6 was used to do the impregnation as the procedure shown in [3]. This solution was added dropwise to a stirred HZSM-5 slurry at 60^oC for 10h. The Pt/HZSM-5 samples were evaporated until dryness and treated in a nitrogen flux at 500^oC for 3h. The Platinum loading sample was 0.6, 0.8, 1.0 and 1.2wt%. These samples were grounded and crushed in to small pellet with the diameter between 0.3 – 0.6 mm.

Catalyst Characterization:

XRD data for synthesized ZSM-5 was obtained on a Phillips Roengent Instrument. Nitrogen adsorption-desorption isotherms were obtained at 77^oK by a Chembet 3000 apparatus. IR method was used to get some further information about the crystallinity of the zeolite. The synthesized sample was mixed with KBr with the ratio ZSM-5/KBr = 1/200 w/w and grounded into pearce. IR data was obtained on a Brucker Tensor 37 instrument. TPD – Ammonia was used to determine the acidity of these samples. The catalyst was activated in a nitrogen flux for 5 hour at 500^oC with the flow rate of 2 l/h. After that, the sample was cooled down to room temperature and adsopted NH_3 for 10min. Physical desorption of the adsopted samples was carried out at 100^oC for 2 hour in a nitrogen flux with the flow rate of 2 l/h. Temperature program desoption was set linear from 100 – 550^oC with the temperature increasing rate of 3^oC/min. The desorpted Ammonia was determined by UV-Vis analysis (phenat method). The acid concentration of these samples were evaluated by the total desorption amount of Ammonia.

Catalyst Performance:

Catalyst performance of these prepared Pt/HZSM-5 were carried out in an hydro-isomerization apparatus. Catalyst was placed in a 4mm diameter fixed-bed reactor constructed of Pyrex glass. The catalyst was located between two layers of sand. A layer of quartz wool was placed at the bottom of the reactor to serve as the heating zone. A thermo-couple was placed outside of the reactor, in the middle of the catalyst bed. A nitrogen flux (99,99%) was used as vector gas with the flow rate of 1l/h passed through a saturator containing n-hexane (China). The saturator was placed in an ice bed to cool n-hexane down to 0^oC. The vapor pressure of n-hexane is 45mmHg at 0^oC. A hydrogen flux was

used as a diluted stream. Both nitrogen and hydrogen flux were passed through two columns containing zeolite 4A to remove moisture. Reaction temperature was chosen between 250 – 400^{o}C.

Before activities testing, all the prepared catalysts were activated 4 hour in a hydrogen flux at 450^{o}C to reduce platinum oxide to platinum metal. The measurements performed with constant hydrogen and nitrogen flow at 1l/h, constant amount of catalyst (300mg).

The products in gas phase were analyzed by a Gas Chromatography (Varian Series 2800), flame ionization detector. The products were separated by a packed column containing 15% n-Decyl Phtalate on Chromosoft. The conversion rate, isomer selectivity and cracking selectivity were calculate directly on Chromato integration report.

Total Conversion (%) = [(original reactant(%)) – (remaining reactant(%))]*100% /[original reactant(%)].

Cracking selectivity (%) = [cracking product (%)/total conversion (%)]*100%.

Isomerization selectivity (%) = [isomer product(%)/total conversion(%)]*100%.

III. RESULTS:

Synthesis of ZSM-5:

XRD Data and IR were shown in figure 1 and 2. The specific peaks of MFI zeolite type appeared on the XRD spectrum confirmed the existence of crystalline ZSM-5 phase in the synthesized ZSM-5 sample [6]. These peaks occurred distinctly even after calcination.

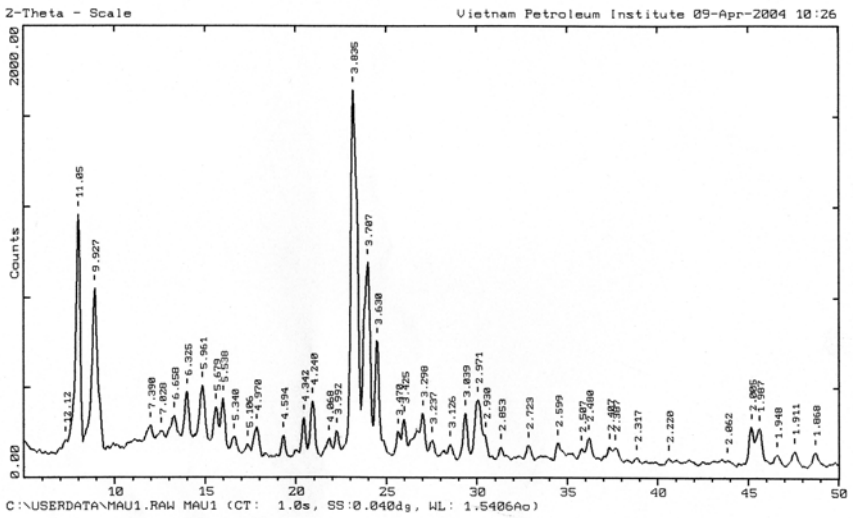

Figure 1: XRD Data of the synthesized ZSM-5

The peak 547,55 cm^{-1} and 1221,78 cm^{-1} on the IR spectrum confirmed once again the existence and purity of the ZSM-5 sample. Other phases detected on the IR spectrum were mordenite (peak 620 cm^{-1}) and α-quartz (peak 700 cm^{-1}), but their amounts were not significant.

The BET surface area of the zeolite was 207,15m^2/g, suggesting a well-order structure. AAS analysis of the sodium content on the NaZSM-5 sample and the exchaged sample shows the exchanging rate of 98.56%.

ICP analysis was used to obtain silica concentration of the sample, the aluminum concentration was identified by AAS method, resulting in the modulus of the synthesized zeolite of 59.3.

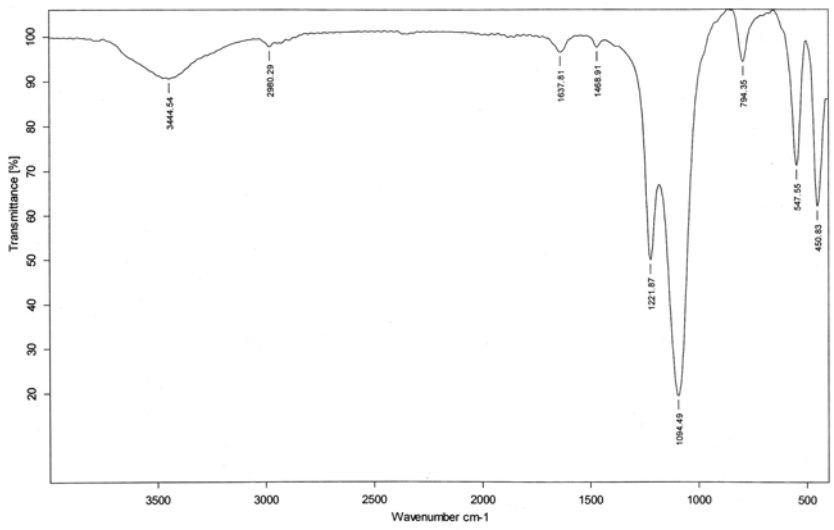

Figure 2: IR Data of the synthesized ZSM-5.

All the TPD Ammonia spectrum of these prepared samples had two peaks, one at low temperature and the other at higher temperature. The low temperature peaks occurred at 200 – 220^{0}C and the high ones at 330 – 334^{0}C. The total acidity of the samples were decreased as the increasing of the platinum loaded amount on the the zeolite.

Sample name	Low temperature peak ^{0}C	High temperature peak ^{0}C	Total acidity (mmol NH_3/gr)
0.6%Pt/HZM-5	223	332	0.493
0.8%Pt/HZM-5	220	334	0.452
1.0%Pt/HZM-5	212	330	0.418
1.2%Pt/HZM-5	203	331	0.391

Table 1: TPD-NH_3 Data of these Pt/HZSM-5 catalysts.

Reaction of n-hexan over Pt/HZSM-5 catalysts:

Conversion rate and selectivities were achieved from the reaction of n-hexan over Pt/HZSM-5 with various platinum concentration. The conversion increased as the increasing of reaction temperature (figure 3). The conversion rate increased slowly from 280 – 340^{o}C while the selectivity of isomers decreased more rapidly (figure 4). The isomer selectivity was highest at 250^{o}C and still very high at 280 – 310^{o}C. So we could recognized that, the isomerate can be obtained highest at the reaction temperature of 280^{o}C on the samples containing 0.8 – 1.0%Pt.

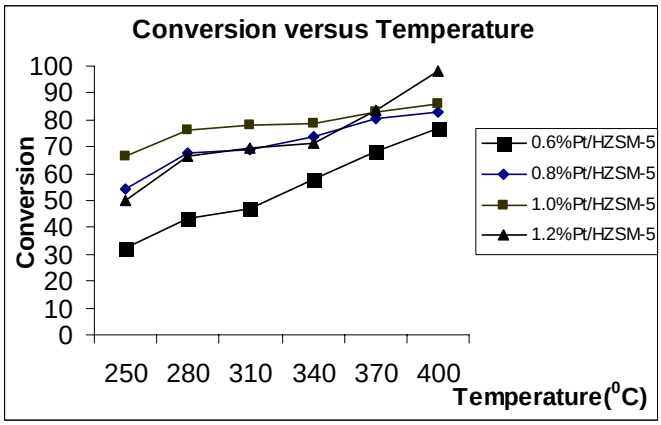

Figure 3: Conversion rate versus reaction temperature.

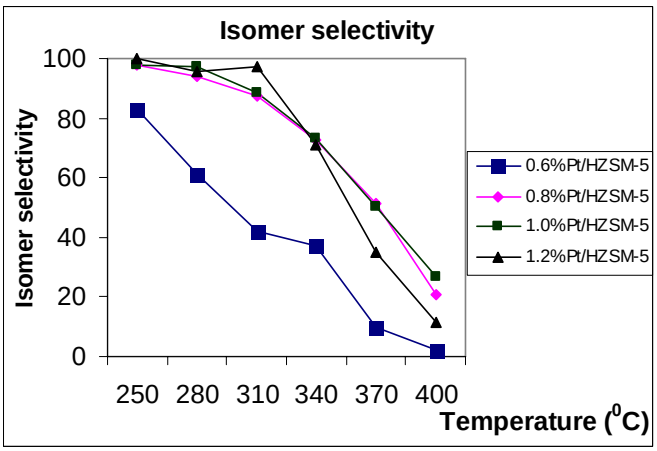

Figure 4: Isomerization selectivity versus reaction temperature.

The platinum concentration took effect directly on the conversion rate and isomer selectivity. The 0.6%Pt/HZSM-5 sample performed low conversion and isomer selectivity while others took the contrary results. The conversion yields reach to about 98% while the yield of cracking products was nearly 75% with the 1.2%Pt/HZSM-5 sample (figure 5). After four hour working, the catalyst color still remained unchanged, so that no coke was formed, qualitatively.

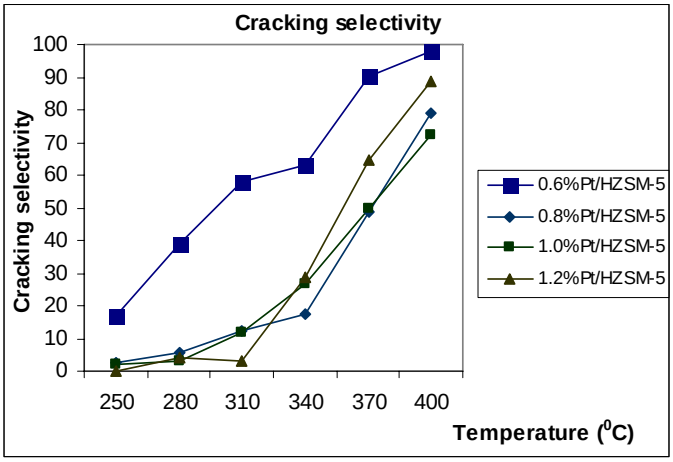

Figure 5: Cracking selectivity versus reaction temperature.

IV. CONCLUSIONS:

Catalytic performance of these Platinum loaded HSZM-5 were studied. These catalysts were active and selective bifunctional catalysts for isomerization of n-hexane. The reaction of n-hexane on Pt/HZSM-5 had two ways: isomerization and cracking. The cracking selectivity increased with the increasing of reaction temperature as well as the conversion rate while the isomerization selectivity varied to the opposite way. So if we want to achieve more isomerate products, the reaction temperature should be around 280^{o}C and the platinum amount should be between 0.8 – 1.0 wt%.

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