

Research on butene oligomerization reaction over the hemicellulose modified HZSM-5

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Abstract: The HZSM-5 was synthesized with modifying by different contents of hemicellulose. The morphology, texture and acidity were characterized with XRD, SEM, N₂ adsorption-desorption, NH₃-TPD and Py-IR. Butene oligomerization over the modified HZSM-5 was tested. The results indicated that the HZSM-5 with 1.6% hemicellulose exhibited the best activity and stability on the butene oligomerization reaction. The conversion can maintain about 80% after 140 h on stream with the highest selectivities of the trimer, tetramer and diesel component in the products, which may be related with its high BET surface and mesoporous volume, and the strongest acidity.

Key words: hemicellulose; modified; HZSM-5; butene oligomerization

With the growth demand of oil and the less oil storage in China, the oil production is difficult to self-sufficiency and the shortage of oil has become an inevitable fact^[1]. There is rich of coal with less oil and gas energy structure in China. Hence, reinforcing the clean and high utilization of coal, developing non-oil route to produce clean fuel has important strategic significance for producing environmental friendly liquid fuels as well as adjusting energy structure. On the other hand, with the progress of catalytic cracking and Fischer-Tropsch synthesis technology^[2,3], olefin resources are increasingly abundant. Furthermore, with the MTO process achieving milestone progress in China, developing coal chemical industry combined with the MTO/MTP process, and using the light olefin to produce high quality liquid fuels can be an important comprehensive route in the utilization of olefin downstream products^[4,5].

Oligomerization, refers to the process of a certain number of monomer olefin polymerized to the compound with one or more tectonic units connected to repeat^[5]. The oligomerization of light olefins (ethene, propene and butene) is an important way to produce environmental friendly liquid fuels without sulfur and aromatics. As the difference of catalysts and reaction conditions, the polymerization degree, levels of branched chain and the proportion of gasoline and diesel components in products will also be different^[6,7]. As early as

1935, oligomerization was already applied to chemical industry. Initially, the American UOP company used diatomite phosphate catalytic C₄ or C₃₋₄ fraction to have non-selective oligomerization with the main products of gasoline^[8,9]. Until the 1980s, the MOGD technology developed by Mobile, using HZSM-5 zeolite as catalyst and C₄ as raw material, made the oligomerization technology of producing diesel and/or gasoline products another great progress^[10,11]. However, the oligomerization technology in China was dated from 1950s-60s and there was a big gap in operating equipment and preparing catalysts to reach international level^[12]. With the rapid development of science and technology in recent years, the oligomerization process in China has also made new breakthroughs^[5,13-15]. Though the olefins oligomerization technology has already been industrialized, developing and optimizing of catalysts are still the key to technological progress. The light olefin oligomerization is usually conducted on solid acid catalysts, such as solid phosphoric acid catalysts^[16], zeolite catalysts^[17] and Ni supported zeolite catalysts^[18]. The solid phosphate catalyst is not very appreciated recently because of its easy clay, high degree branched chain of products, corrosion to equipment and not easy to regeneration^[16]. At the same time, the zeolite catalysts are widely studied for their advantages of environmental friendly, easy to regeneration and the ability to

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regulate oil-gas ratio^[19,20], especially for the HZSM-5 zeolite with MFI three-dimensional channel structure and good acidity. As a result of the mesoporous and shape selective properties, it exhibits high coking resistance with products not easy to be branched. The ZSM-5 zeolite is regarded as the most promising catalyst for conversion of C₃ and C₄ alkenes to high quality liquid fuels^[21,22]. In order to improve the catalytic ability of HZSM-5 to oligomerization, researches on modifying its structure with hierarchical channel and enhancing acidity have been widely reported^[23,24]. Hemicellulose as the second most abundant renewable biomass is widespread in nature. The large number of hydroxyl and carboxylic groups on it provide a powerful basis structure for it as additive to modify the channel structure and acidity of HZSM-5^[25].

In this work, based on the traditional hydro-thermal synthesis, hemicellulose was added to modify the properties of HZSM-5, to explore the influence of different contents of hemicellulose on HZSM-5. Butene oligomerization was as probe reaction to investigate the catalytic ability of modified HZSM-5 by different contents of hemicellulose. XRD, SEM, N₂ adsorption/desorption, NH₃-TPD and Py-IR are used to characterize the structure and acidity of modified HZSM-5. Moreover, the different structure and acidity of catalysts influenced on the products distribution of the butene oligomerization to high-quality liquid fuels reaction were also analyzed.

1 Experimental

1.1 Catalysts preparation

The preparation of HZSM-5 zeolite: 1.53 g sodium hydroxide (NaOH) was dissolved in 150 mL deionized water. Then, a certain amount of sodium aluminate (NaAlO₂), 55.32 g tetrapropylammonium hydroxide (TPAOH) and 71.93 g tetraethyl orthosilicate (TEOS) were added into the NaOH solution under magnetic stirring. The obtained solution was hydrolyzed at room temperature for 45 h, and transferred into teflon-lined stainless-steel autoclave to crystallize at 150 °C for 72 h. Later, the product could be obtained by centrifugation, washed by deionized water until neutral, dried at 110 °C overnight and calcinated at 550 °C for 5 h to get the Na-ZSM-5. The HZSM-5 were obtained through ion-exchange with aqueous NH₄NO₃ solution (1 mol/L) at 60 °C for 2 h by 3 times, followed by washed with deionized water, dried at 110 °C overnight and calcinated at 550 °C for 5 h.

The preparation of hemicellulose modified HZSM-5: a certain quality of hemicellulose (obtained from a viscose fiber factory of Tangshan Sanyou Chemi-cal Industry Co.) was dissolved to the system at the beginning and the mass fraction

contents of hemicellulose were controlled at 0.4%, 0.8%, 1.6% and 2.4% in the solution. Other steps were consistent with the method in preparation of HZSM-5, and the final products were denoted as HZSM-5-Hc-1, HZSM-5-Hc-2, HZSM-5-Hc-3, and HZSM-5-Hc-4.

1.2 Catalysts characterization

X-ray diffractograms (XRD) were obtained employing Bruker D8 Advance X-ray diffractometer with Cu K α radiation (30 kV, 30 mA) in the range of 2θ of 5°–50° at a scanning rate of 2°/min. Scanning electron microscopy (SEM) was carried out in Hitachi S-4800 microscope operated at an accelerating voltage of 10.0 kV. Nitrogen adsorption/desorption isotherms were measured at –196 °C on a Micromeritics ASAP 2020 adsorption apparatus. Before measurement, the samples were degassed at 320 °C for 4 h, and then performed the N₂ adsorption/desorption experiment at –196 °C. Temperature-programmed desorption of ammonia (NH₃-TPD) was performed in an Auto-Chem II 2920 chemisorption analyzer, and the thermal conductivity detector (TCD) was used to record desorption curve synchronously. Fourier transform infrared (FT-IR) spectra were measured on a Nicolet 6700 FT-IR spectrometer. Before testing, the sample cell was evacuated to 10⁻² Pa at 450 °C. After that, pyridine vapor was introduced into the cell at room temperature for equilibration and the spectra were recorded after evacuation at 150 °C for 1 h to get the FT-IR spectra for pyridine adsorption (Py-IR).

1.3 Evaluation on butene oligomerization

The oligomerization of butene was carried out in a continuous flowed fixed-bed at 4.0 MPa and 270 °C. 1.5 g catalyst (40–60 mesh) was mixed with the same volume of silicon carbide (40–60 mesh) to avoid local overheating. Before reaction, the catalysts were pre-treated at 400 °C for 4 h in a nitrogen flow (20 mL/min). When catalysts bed was cooled to the reaction temperature, butene (in the liquid phase) was fed to an evaporator with 180 °C by a Series II digital pump, and then introduced to the reactor by flowing nitrogen to start the reaction.

To avoid the condensed and stranded of heavy oil phase in the system, the products of oligomerization reaction were collected in a hot trap with 200 °C and followed by a cold trap with ice water, to collect heavy oil and light quality liquid products, respectively. The liquid products from both hot and cold trap were analyzed by a GC (Agilent 7820) equipped with DB-1 chromatographic column and FID detector. The gas compositions were performed on an Agilent 7890A fitted with Porapak Q packed column, 5A zeolite packed column and

HP-PLOT Al₂O₃ “S” capillary column. The liquid products of the butene oligomerization reactions are referred to naphtha, diesel and heavy fractions. These fractions were segmented through SIMDIS according to the cut points: naphtha (C₅-173.9 °C), diesel (173.9–391.1 °C) and heavy fraction (391.1–1000 °C)^[22]. In order to close mass balance, the non-condensable vapors were quantified by a wet gas flowmeter. Only experiments with mass balances (MB) of 95% or higher were considered for discussion.

2 Results and discussion

2.1 Catalysts characterization

2.1.1 Structure characterization of the catalyst

Figure 1 shows the XRD patterns of all samples. All zeolites with or without hemicellulose have peaks at 2θ of 7.9°, 8.8°, 23.1°, 23.9° and 24.4°, which exhibit the characteristic peaks of MFI structure. It is noting that there is slight difference for the relative intensities of 2θ at 7.9° and 23.1° with increasing hemicellulose, and HZSM-5-Hc-2 shows the least relative intensities at 7.9° and 23.1°. This may indicate that the addition of hemicellulose can affect the relative crystallinity of each crystal face. Sano et al^[26] considered OH groups in cellulose as favourable sites for zeolite crystallization, and believed the hydroxyl group played an important role in the formation and crystallization of molecular sieve. Valtchev et al^[27] also reported the high activity of cellulose in the zeolite crystallization due to the high abundance of reactive hydroxyl groups. It was inferred that hemicellulose as the polymer of several kinds of monosaccharide had a large number of hydroxyl groups and these hydroxyl groups could act as an intervention or promoter in the nucleation and growth of ZSM-5. So, in the process of forming the molecular sieve, these hydroxyl groups will have selective effect on the growth of different crystal surface and the relative crystallinity of different crystal surface changed.

The morphology SEM images of all samples are given in Figure 2. It can be seen from Figure 2 that the sample without hemicellulose HZSM-5(a) indicates irregular and hexagon particles coexisting, while HZSM-5-Hc-1(b) shows more hexagon particles with increasing hemicellulose content,. When the mass fraction of hemicellulose is 0.8%, HZSM-5-Hc-2(c) shows the most orderly morphology with a maximum of the hexagon crystals. This phenomenon is consistent with the XRD result, illustrating that the different contents of hemicellulose could have various influence on some crystal surfaces and morphology structure of ZSM-5.

The textural structure properties of all samples characterized by N₂ adsorption-desorption are shown in Table 1. The BET surface area of HZSM-5 is 364 m²/g. With increasing content of hemicellulose, the BET surface areas of HZSM-5-Hc-1 and HZSM-5-Hc-2 are 359 and 398 m²/g, respectively. When the mass fraction of hemicellulose is 1.6%, HZSM-5-Hc-3 has the largest BET surface area of 582 m²/g. However, with further increase in the content of hemicellulose the BET surface area of HZSM-5-Hc-4 reduces to 389 m²/g. At the same time, with increasing content of hemicellulose the mesoporous volumes of HZSM-5-Hc-1, HZSM-5-Hc-2 and HZSM-5-Hc-3 are 0.20, 0.32, and 0.44 cm³/g, respectively, which become larger ordinally. However, with further increase in the content of hemicellulose, the mesoporous volume of HZSM-5-Hc-4 was reduced to 0.31 cm³/g. It can be seen that hemicellulose can affect the BET surface area and mesoporous volume of ZSM-5, which may resulted from the macromolecular carbon skeleton structure of hemicellulose. The hemicellulose acts as carbon template in the zeolite synthesis process, leading to larger BET surface area and more mesopore structure produced. When the mass fraction of hemicellulose is 1.6%, it can enlarge the BET surface area and mesopore structure significantly.

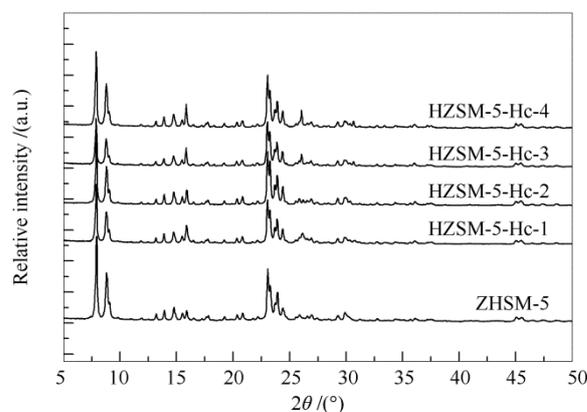


Fig. 1 XRD patterns of different zeolites

Table 1 Textural properties of different zeolites

Catalyst	S_{BET} $A/(m^2 g^{-1})$	Pore volume $v/(cm^3 g^{-1})$	
		v_{micro}	v_{meso}
HZSM-5	364	0.15	0.25
HZSM-5-Hc-1	359	0.13	0.20
HZSM-5-Hc-2	398	0.14	0.32
HZSM-5-Hc-3	582	0.19	0.44
HZSM-5-Hc-4	389	0.14	0.31

note: S_{BET} , BET surface area; v_{micro} , micropore volume determined by t-plot; v_{meso} , mesopore volume determined by $v_{total} - v_{micro}$

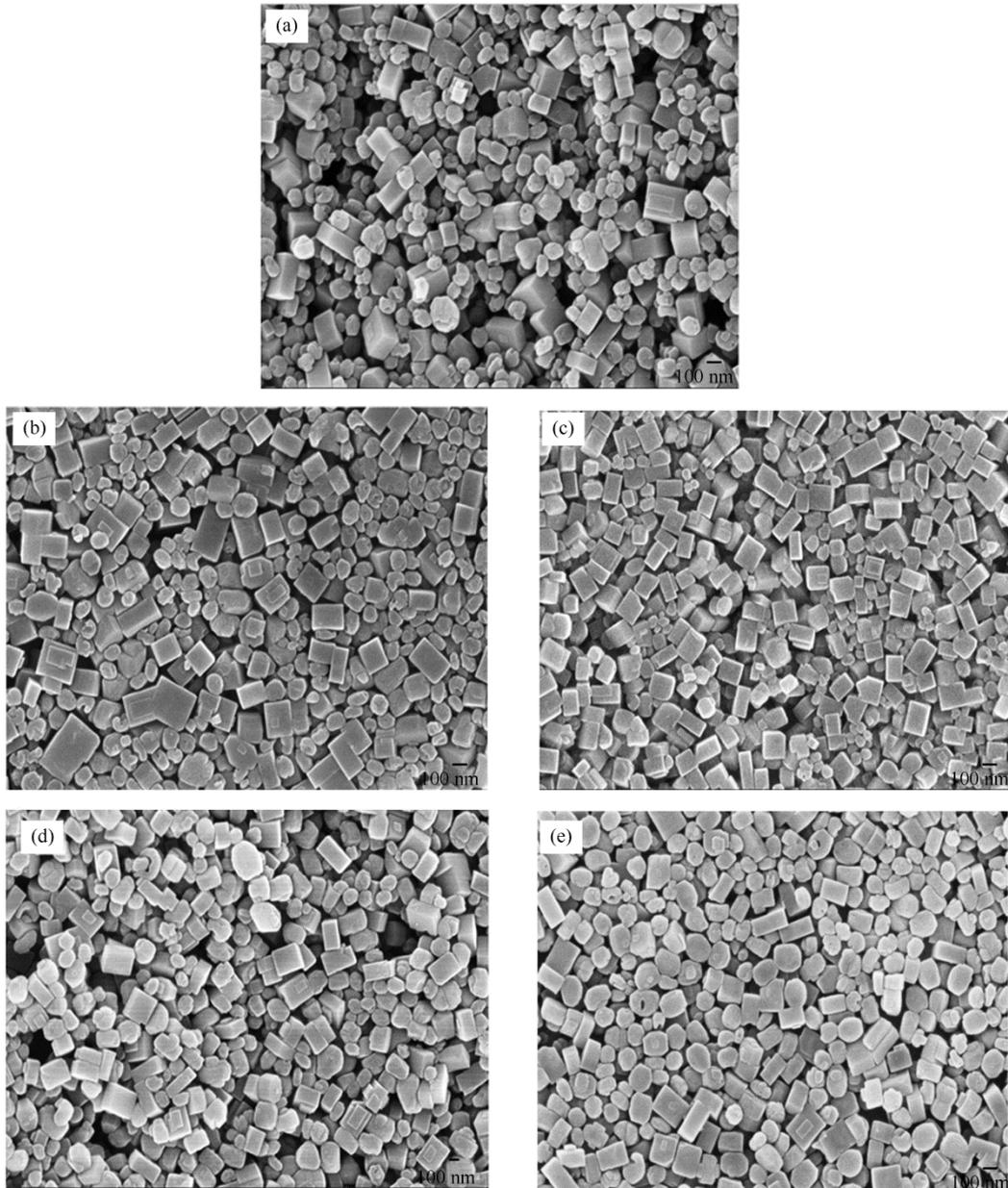


Fig. 2 SEM images of different zeolites

(a): HZSM-5; (b): HZSM-5-Hc-1; (c): HZSM-5-Hc-2; (d): HZSM-5-Hc-3; (e): HZSM-5-Hc-4

Table 2 NH₃-TPD and Py-IR results for different zeolites

Catalysts	Acidity by strength ^a /(mmol g ⁻¹)			Acidity by type ^b /(mmol g ⁻¹)	
	weak	medium	total	Brønsted	Lewis
HZSM-5	0.357	0.225	0.600	0.532	0.045
HZSM-5-Hc-1	0.512	0.467	0.979	0.809	0.049
HZSM-5-Hc-2	0.667	0.536	1.203	0.893	0.058
HZSM-5-Hc-3	0.859	0.621	1.480	1.209	0.075
HZSM-5-Hc-4	0.592	0.356	0.948	0.531	0.039

a: density of the acid sites, assorted according to the acidic strength, determined by NH₃-TPD. Medium, NH₃ desorbed at 300–500 °C; weak, NH₃ desorbed at 100–300 °C;

b: density of the acid sites, assorted according to the acidic type, determined by Py-IR

2.1.2 Acidity characterization of the catalyst

In order to investigate the effect of hemicellulose on the acidity of HZSM-5, NH₃-TPD and Py-IR are carried, as presented in Figure 3, and the quantitative results are listed in Table 2. There is only one distinct desorption peak of HZSM-5 at about 200 °C, indicating it mainly possess weak acidic sites and a small amount of medium acidic sites. With increasing content of hemicellulose the weak and medium strong acidic sites of HZSM-5-Hc-1, HZSM-5-Hc-2 and HZSM-5-Hc-3 gradually were enhance. However, as the content of hemicellulose increases further, the acid quantity of HZSM-5-Hc-4 was reduced. It is demonstrated that the addition of hemicellulose can improve the acidity of HZSM-5 in a certain level, and with increasing hemicellulose content, the acidity of catalyst has a tendency to increase first and decrease then. HZSM-5-Hc-3 has the strongest acidity.

Figure 4 shows the Py-IR spectra of all samples. The peaks at 1450 and 1520 cm⁻¹ are corresponding to Lewis and Brønsted acid sites, respectively. The sharply peak at 1490 cm⁻¹ is attributed to the vibration of the pyridine ring on Lewis and Brønsted acid sites. The result of Table 2 shows that the amount of the Brønsted and Lewis acid sites of HZSM-5 are 0.532 and 0.045 mmol/g, respectively. With increasing hemicellulose content, the Brønsted and Lewis acid sites of HZSM-5-Hc-1, HZSM-5-Hc-2 and HZSM-5-Hc-3 gradually enhance, while those of HZSM-5-Hc-4 decrease. Among all samples, HZSM-5-Hc-3 possesses the most quantity of Brønsted and Lewis sites, being 1.209 and 0.075 mmol/g, respectively, illustrating that the addition of hemicellulose can improve the acidity of HZSM-5 to some extent, especially for Brønsted acid sites. With increasing content of hemicellulose, the acidity has a tendency to increase first and decrease then. HZSM-5-Hc-3 possesses the strongest acidity. This rule is fully consistent with the NH₃-TPD results.

2.2 Catalytic evaluation on butene oligomerization

The catalytic results of butene oligomerization over all samples are shown in Figure 5 and the products collected after 24 h of time-on-stream at 270 °C and 4 MPa are analysed in Table 3.

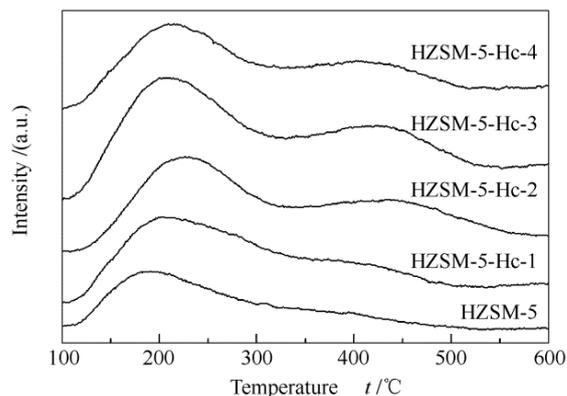


Fig. 3 NH₃-TPD profiles of different zeolites

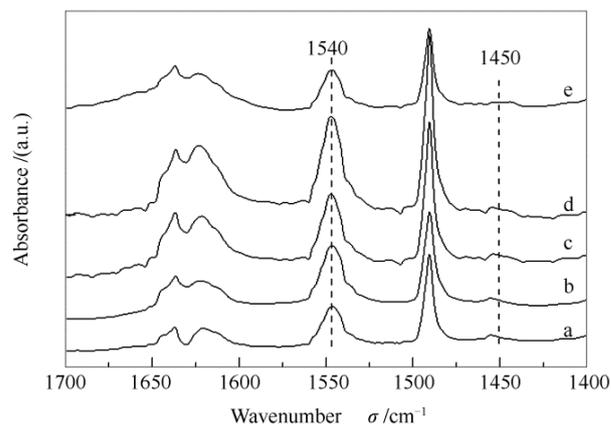


Fig. 4 Py-IR spectra of different zeolites

(a): HZSM-5; (b): HZSM-5-Hc-1; (c): HZSM-5-Hc-2; (d): HZSM-5-Hc-3; (e): HZSM-5-Hc-4

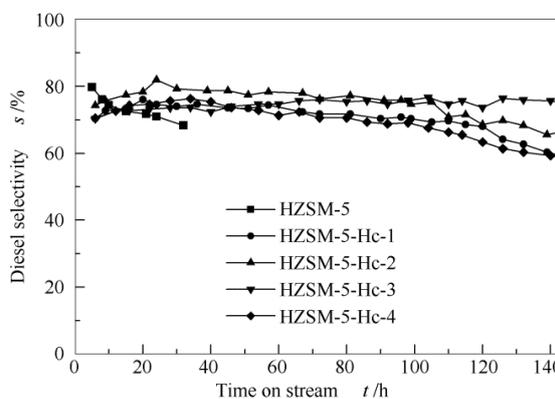
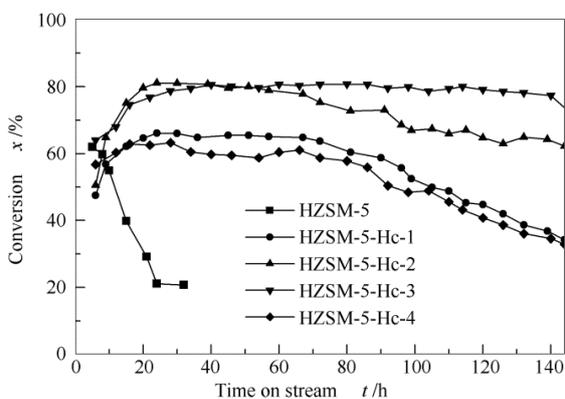


Fig. 5 Results of butene oligomerization with time on stream (TOS) over different catalyst

Table 3 Catalytic results at 24 h for the butene oligomerization over different catalysts

Catalyst	Conversion <i>x</i> /%	Selectivity <i>s</i> /%		Carbon atom distribution <i>w</i> /%			
		naphtha	diesel	C ₈	C ₁₂	C ₁₆	C ₂₀₊
HZSM-5	21	29	71	58	36	5	1
HZSM-5-Hc-1	66	25	75	49	41	7	2
HZSM-5-Hc-2	80	18	82	37	49	11	3
HZSM-5-Hc-3	79	26	74	29	38	19	14
HZSM-5-Hc-4	63	24	76	42	40	12	6

The weight hourly space velocity (WHSV) is kept at 4.8 g/(g h). As Figure 5 shown, the butene conversion on HZSM-5 without hemicellulose is 21% after 24 h of time-on-stream with the lowest conversion and poor activity. With increasing content of hemicellulose, the butene conversion on HZSM-5-Hc-1, HZSM-5-Hc-2, and HZSM-5-Hc-3 gradually improved. The conversion on HZSM-5-Hc-1 is 66% at 24 h, which was higher than HZSM-5 obviously. HZSM-5-Hc-2 is further improved on the basis of HZSM-5-Hc-1. The conversion is up to 80% at 24 h although the overall activity is better than HZSM-5-Hc-1, while the stability needs to be further improved. The conversion on HZSM-5-Hc-3 is 79% at 24 h, but it increases steadily to 80% until 36 h and remained after 140 h, which also has obvious advantages on overall catalytic capacity compared with HZSM-5-Hc-2. However, as the content of hemicellulose increases further, the catalytic ability declines and the conversion on HZSM-5-Hc-4 decreases to 63% even lower than HZSM-5-Hc-2. This phenomenon is good enough to verify the acidity results of different contents of hemicellulose modified HZSM-5. HZSM-5-Hc-3 shows the best acidity and stability on butene oligomerization with the strongest acidity, which consistent with the literatures.

The liquid products of reaction over all samples are investigated by GC analysis. As for the HZSM-5 catalyst without hemicellulose, the product distribution is mainly composed of dimer (58%) and trimer (36%). When the hemicellulose is introduced, the selectivity of dimer reduces gradually and then increases with increasing concentration of hemicellulose. The liquid product of reaction over HZSM-5-Hc-3 has the most proportion of three and more polymerized products, as well as the most abundant of diesel components. This may related to its largest mesoporous volume and the strongest acidity.

3 Conclusions

In summary, the hemicellulose modified HZSM-5 catalyst was successfully prepared and the catalytic activity of prepared HZSM-5 was evaluated on butene oligomerization reaction. All the results showed that the content of hemicellulose had great effect on the structure, acidity,

catalytic activity and stability of HZSM-5. When the mass fraction of hemicellulose was 0.8%, HZSM-5-Hc-2 showed the most orderly morphology with a maximum of the hexagon crystals. When the hemicellulose was 1.6%, HZSM-5-Hc-3 had high BET surface and mesoporous volume, the strongest acidity, and the best activity and stability on butene oligomerization. The butene conversion on HZSM-5-Hc-3 remained at about 80% with the most of trimer and tetramer products, and the selectivity of diesel was also the highest during 140 h time on stream. Thus, the addition of hemicellulose can affect the morphology, textural structure properties and acidity of HZSM-5 to some degree. Proper content of hemicellulose can improve the mesoporous volume, acidity as well as the catalytic ability of HZSM-5 on light of olefin oligomerization significantly.

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