The Effect of SiO₂/Al₂O₃ Ratio on Hydroisomerization Reaction Performance of Pd/SAPO-31 Catalysts

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Abstract. SAPO-31 molecular sieves with various $(SiO_2)/(Al_2O_3)$ ratio were synthesized using di-n-butylamine (DBA) as the template. The samples were well characterized by XRD, N2 sorption-desorption, SEM, NH_3-TPD and Py-IR. The results showed that the sample had good crystallinity (SiO_2/Al_2O_3 ratio of 0.6). Isomerization of deoxidized vegetable oil is carried in a fixed-bed reactor with 100ml catalyst at 2.0MPa, 350°C, WHSV 1.5, hydrogen-oil ratio 500:1. The highest biodiesel yield of 92.2wt% was obtained over the Pd/SAPO-31(0.6) catalyst with solidifying point 0°C, flash point 60°C and cetane number 74. Catalyst had no loss of activity and shows high stability and excellent hydroisomerization performance.

Keywords: SAPO-31, biodiesel, hydroisomerization dewaxing, SiO_2/Al_2O_3 ratio, Pd

1 Introduction

With growing environmental concerns and stringent emission norms, biomass is considered a promising renewable energy resource, which involves the use of triglycerides of carbonic acids to produce bio-derived diesel. This energy source is regarded as an attractive alternative and has been extensively studied due to the nature of its widespread avail ability, abundant reserves and sulfur or nitrogen-free compounds [1].

Biodiesel produced from palm oil and jatropha oil has physichemical and fuel properties that are similar to those of petroleum-based diesel. Biodiesel is a kind of renewable, efficient and safe clean energy, which can reduce carbon emissions by 50%~90% in the whole life cycle. In general, the production of biodiesel can be accomplished via a two-step press, which consists of an initial triglyceride transformation to n-alkanes followed by their hydroisomerization, whereas hydroisomerization as the most critical step is carried out using proprietary catalyst to tailor the cold low properties by converting n-parains to iso-parains. Therefore, the dvelopment of eicient and cheap hydroisomerization catalysts for skeletal branching of long n-alkanes without cracking is a scientiic challenge [2, 3].

The production of clean biodiesel with *iso*-C14~C18 components by the hydrodeoxygenation and hydroisomerization of vegetable oils is regarded as an attractive alternative and has been studied worldwide due to the nature of vegetable oils such as widespread availability, abundant reserves and free of sulfur or nitrogen compounds [4]. Moreover, the products of n-alkane hydroisomerization from vegetable oil, which in the range of diesel oil and jet fuel, can be directly used as fuel.

2 Experiment

2.1 Synthesis of SAPO-31 Molecular Sieves with Various SiO₂/Al₂O₃ Ratio

The SAPO-31 molecular sieves were hydrothermally synthe-sized using the following starting materials. Orthophos-phoric acid (85wt% H_3PO_4, Tianjin Guangfu Technology Company, China), Peudo Behmite (71.34wt% Al_2O_3, Catapal B, Sasol), Ludoxution (26.85wt% SiO_2, Qingdao Yumin Company, China) and di-n-butylamine (DBA, 99wt%, Sinopharm, China) were used as phosphorus, aluminum, silica sources and templates, respectively.

The composition of the initial gel was $xSiO_2$: $1.0Al_2O_3$: $1.0P_2O_5$: 1.4DPA: $40H_2O$ (mol ratio), the samples were referred to as S31-(x), where x is the SiO_2/Al_2O_3 ratio, x=0.4~1.0. In all of the syntheses, the reactive gels were prepared as follows: the pseudo-bhmite, ludox and templatewere added to a mixture of

phosphoric acid and deionized water under vigorous stirring. The homogeneous gel was transferred into a stainless steel autoclave with a teflon liner and exposed to hydrothermal treatment at 180°C for 24h. The reaction product was cooled, separated from the mother liquor by iltration, washed with distilled water, dried at 110°C overnight and calcined in air at 600°C for 6h to remove the template.

Isomerization of n-hexadecane or deoxidized vegetable oil was carried in a fixed-bed, tubular reactor at pressure 2.0MPa, reaction temperature 350°C, WHSV 1.5, hydrogen-oil ratio 500:1, taking 10 and 100ml of catayst. The products of the reaction were analyzed by gas chromatography. Prior to the tests, the catalyst was reduced in situ with hydrogen at 400°C for 4h. Then, the catalyst was cooled to the initial reaction temperature, and the n-hexadecane or deoxidized vegetable oil feedstock was fed into the reactor.

2.2   Characterization

Chemical compositions of the synthesized SAPO-31 molecular sieve samples were determined by X-ray fluorescence (XRF) spectroscopy on a Bruker SRS-3400 instrument. X-ray diffraction (XRD) patterns of the synthesized SAPO-31 molecular sieve samples were recorded on a Bruker D8 Advance diffractometer using CuKα (k=1.5406 Å) irradiation at 40 kV and 40 mA with a Lynx eye detector. The relative crystallinity of SAPO-31 molecular sieve samples is based on the percentage of the diffraction peak areas at 2θ=20-25° to all the diffraction peaks areas. The morphology of the samples was examined by scanning electronic microscopy (SEM) on a FEI Sirion microscope. The size of the metal particles was estimated by transmission electron microscopy (TEM) using a JEOL JEM 2100 microscope operating at 200 kV. N_2 adsorption-desorption characterization was performed using an Autosorb-iQ2 apparatus (Quantachrome Instruments). Prior to the adsorption measurements, each SAPO-31 molecular sieve sample was outgassed under a vacuum of $1.0*10^{-3}$ Pa for 12h at 300°C. The surface area and pore volume were determined according to the Brunauer-Emmett-Teller (BET) method and the t-plot method, respectively. The IR spectroscopy of the adsorbed pyridine (Py-IR) was conducted on a Perkin Elmer Spectrum Fourier transform infrared spectrometer (PE-100). The SAPO-31 molecular sieve samples were dehydrated at 350°C for 2h under a vacuum of $5.0*10^{-3}$ Pa, the adsorption of pure pyridine vapor at 90°C for 30 min. After reaching equilibrium, the pyridine-adsorbed system was evacuated at 150, 250 and 350°C, respectively. Finally, the spectra were recorded.

3   Results and Discussion

3.1   XRD and Chemical Composition

Through XRD characterization, a series of SAPO-31 molecular sieves with various SiO_2/Al_2O_3 ratio were synthesized to investigate the effect of SiO_2/Al_2O_3 ratio on structure of SAPO-31 molecular sieve, the results are shown in Figure 1 and Table 1.

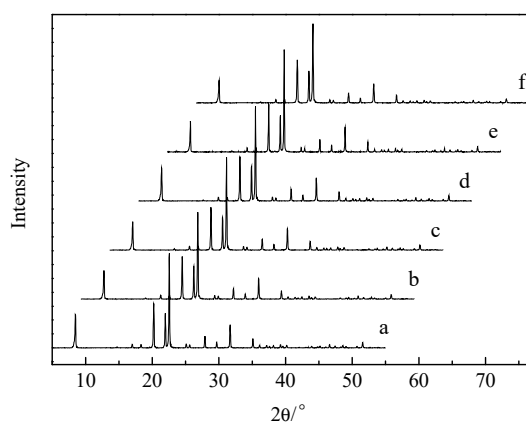**Figure 1.** XRD of SAPO-31 molecular sieves with various SiO_2/Al_2O_3 ratio: (a)S31-0.4, (b)S31-0.5, (c)S31-0.6, (d)S31-0.7, (e)S31-0.8, (f)S31-1.0

Table 1. Relative crystallinity and chemical composition of SAPO-31 molecular sieves

Sample	Composition of the products[a]	SiO$_2$/Al$_2$O$_3$ mol ratio		Relative crystallinity, %
		In reactant gel	In the products[a]	
S31-0.4	Si$_{0.053}$Al$_{0.521}$P$_{0.445}$O$_2$	0.40	0.20	96
S31-0.5	Si$_{0.067}$Al$_{0.513}$P$_{0.439}$O$_2$	0.50	0.26	99
S31-0.6	Si$_{0.077}$Al$_{0.510}$P$_{0.433}$O$_2$	0.60	0.30	100
S31-0.7	Si$_{0.114}$Al$_{0.494}$P$_{0.412}$O$_2$	0.70	0.46	100
S31-0.8	Si$_{0.083}$Al$_{0.503}$P$_{0.432}$O$_2$	0.80	0.33	95
S31-1.0	Si$_{0.144}$Al$_{0.477}$P$_{0.398}$O$_2$	1.00	0.60	90

[a] Determined by the XRF method

Figure 1 shows the powder X-ray difraction patterns of SAPO-31 molecular sieve samples with SiO$_2$/Al$_2$O$_3$ ratio=0.4~1.0 in the initial gel. All of the prepared samples exhibited characteristic diffraction peaks at 2θ of 8.49º, 20.18º and 22.58º which are exclusively indexed to the ATO topology.

It is important to note that no additional peaks were observed in the spectral patterns, indicating that the SAPO-31 molecular sieve samples that were synthesized using the DBA template were largely free from impurities. The crystallinity of SAPO-31 molecular sieves is higher and no crystallization appears, which means that pure phase SAPO-31 molecular sieves are synthesized. Additionally, the high intensity of the XRD peaks indicated that the as-synthesized samples were highly crystalline materials.

As shown in Table 1, the relative crystallinity of SAPO-31 samples is high with SiO$_2$/Al$_2$O$_3$ ratio below 0.8 in the initial gel, but the relative crystallinity of samples has larger decrease with SiO$_2$/Al$_2$O$_3$ ratio more than 1.0, this may be the Si content is higher in the initial gel, then some non-skeleton appears in the process of molecular sieve crystallization with skeleton P replaced by Si or P and Al replaced by two Si. The highest relative crystallinity of SAPO-31 molecular sieve samples was obtained at SiO$_2$/Al$_2$O$_3$ ratio of 0.6-0.7.

3.2 N$_2$ Physical Adsorption

The surface area and pore volume are important indexes of the composite material. The N$_2$ adsorption data for SAPO-31 materials of various SiO$_2$/Al$_2$O$_3$ ratio are shown in Figure 2 and Table 2.
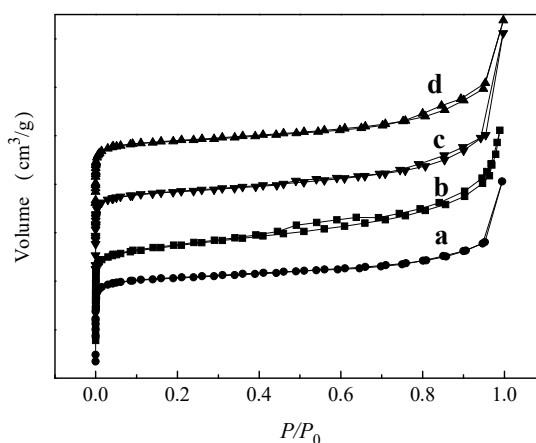

Figure 2. N$_2$ adsorption-desorption isotherms of S31-(x) samples: (a)S31-0.5, (b)S31-0.6, (c)S31-0.7, (d)S31-0.8

Figure 2 shows the N$_2$ adsorption curves for the SAPO-31 molecular sieve samples with various SiO$_2$/Al$_2$O$_3$ ratio. The hysteresis loop at $P/P0 = (0.50$-$0.8)$ on the isotherms indicates the existence of secondary mesoporosity. In addition, the nitrogen adsorption that is observed at higher pressures may due to multilayer adsorption on the surface of the aggregates which means the presence of crystalline intergranular pores in the samples due to crystals.
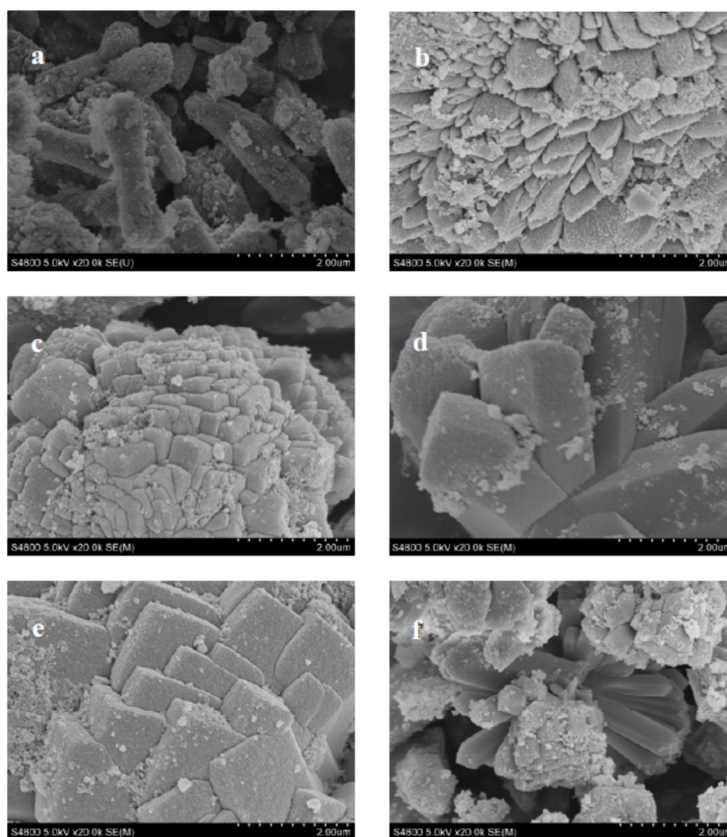
Table 2. Chemical composition and the textural properties of the S31(x) samples

Sample	Surface area, m^2/g			Pore volume, cm^3/g		
	BET	Micropore	External	Total	Micropore	Mesopore
S31-0.5	168	143	25	0.144	0.056	0.088
S31-0.6	171	129	42	0.143	0.051	0.092
S31-0.7	184	150	34	0.159	0.060	0.099
S31-0.8	185	147	38	0.164	0.061	0.103

As shown in Table 2, the BET surface area and total pore volume increase gradually with the increase of SiO_2/Al_2O_3 ratio, especially the increase of micropore surface area and mesoporous pore volume.

3.3   SEM

The SEM images show the morphology of the as-prepared SAPO-31 molecular sieve samples (Figure 3). As shown in Figure 3, the SAPO-31 sample is in aggregate form, the morphology of molecular sieves with various SiO_2/Al_2O_3 ratio is not identical. The samples present the rod structure with a relatively low s SiO_2/Al_2O_3 ratio, then the samples present cubic stack structure with the increase of SiO_2/Al_2O_3 ratio. The single grain length of the sample S31 (0.6) is about 600nm and the grain width is about 400nm.

Figure 3. SEM of S31-(x) samples: (a)S31-0.4, (b)S31-0.5, (c)S31-0.6, (d)S31-0.7, (e)S31-0.8, (f)S31-1.0

3.4   NH₃-TPD

NH₃-TPD characterizations were made in order to study the effect of various SiO_2/Al_2O_3 ratio on the acidity of SAPO-31 molecular sieve, the results are shown in Figure 4 and Table 3.
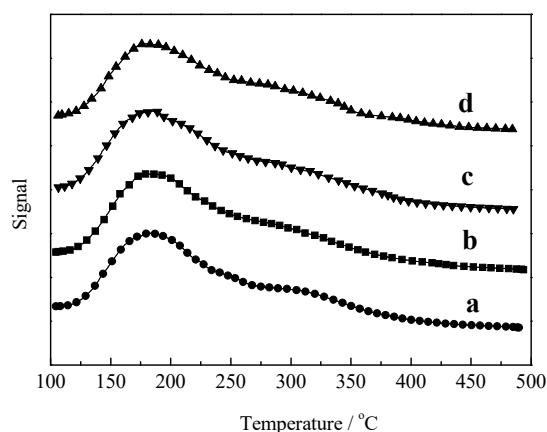
Figure 4. NH3-TPD characterizations of S31-(x) samples: (a)S31-0.5, (b)S31-0.6, (c)S31-0.7, (d)S31-0.8

As shown in the Figure 4, the SAPO-31 molecular sieve samples have two peakes of ammonia stripping, which had respectively corresponded to the weak acid and medium acid sites, ammonia stripping peak area corresponding to medium acid sites increases gradually with the increase of SiO_2/Al_2O_3 ratio.

Table 3. NH₃-TPD data of S31-(x) samples

Sample	Temperature of NH₃ desorption, °C		Acidity, mmol/g		
	I	II	I	II	Total
S31-0.5	179	243	0.203	0.260	0.463
S31-0.6	178	250	0.212	0.273	0.485
S31-0.7	179	254	0.270	0.280	0.550
S31-0.8	180	259	0.285	0.295	0.580

As seen in the Table 3, total Acidity and medium Acidity of SAPO-31 molecular sieve samples in the amount of have increased gradually with the increase of SiO_2/Al_2O_3 ratio, and peak temperature moves to high temperature, which means medium acid sites and acid strength in the samples increase gradually.
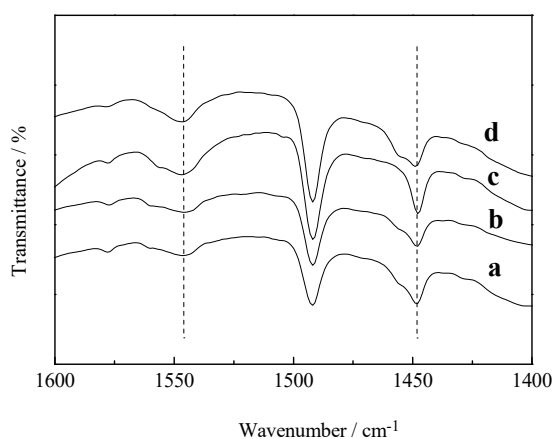
3.5 Py-IR

Figure 5. Py-IR chromatogram of S31-(x) samples: (a)S31-0.5, (b)S31-0.6, (c)S31-0.7, (d)S31-0.8

The amount and strength of the Brønsted acid sites are typically associated with the location of silicon atoms in the crystalline framework of silicoaluminophosphate. The characteristics of these acid sites

inluence the catalytic activity and selectivity to isomerization products in n-alkane hydroisomerization. Therefore, to quantify the Brønsted acid sites of different strength, the Py-IR spectra of SAPO-311 with various SiO_2/Al_2O_3 ratios were recorded using pyridine as a base probe molecule.

As shown in Figure 5, the characteristic adsorption peak are found at $1540cm^{-1}$ and $1450cm^{-1}$ respectively corresponding to B acid site and L acid site.

Table 4 indicates that the total amount of B acid sites increase with the increase of SiO_2/Al_2O_3 ratio in the samples, especially, the B acidicy increases obviously, and B/L ratio also increases.

Table 4. Py-IR data of the S31-(x) samples

Sample	Total acidity, mmol/g	Brönsted acidity, mmol/g	Lewis acidity, mmol/g	B/L ratio
S31-0.5	0.463	0.263	0.200	1.32
S31-0.6	0.485	0.279	0.206	1.36
S31-0.7	0.550	0.330	0.220	1.50
S31-0.8	0.580	0.355	0.225	1.58

3.6 Catalytic Experiment Evaluation on 10ml

The complex-support catalysts were prepared by combine SAPO-31 molecular sieves with various SiO_2/Al_2O_3 ratio with alumina carrier, then loaded with 0.5wt%Pd.

In order to study the relationship between temperature, conversion and selectivity, the hydroisomerization experiments of n-hexadecane were carried in a fixed-bed, tubular reactor at pressure 2.0MPa, reaction temperature 350°C, WHSV 1.5, hydrogen-oil ratio 500:1, taking 10ml of catayst. The products of the reaction were analyzed by gas chromatography. The results were shown in Figure 6.
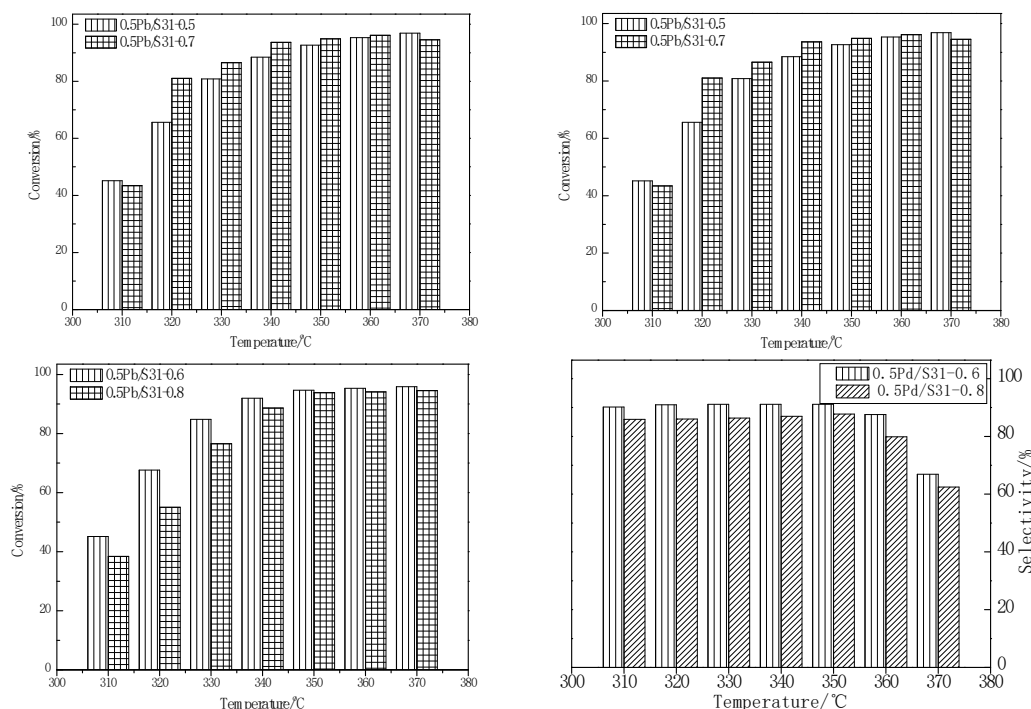

Figure 6. The hydroisomerization reaction performance of 0.5Pd/S31 catalyst with various SiO_2/Al_2O_3 ratio

From Figure 6, it can be seen that the conversion of n-hexadecane increases with the the crease of reaction temperature. The conversion of n-hexadecane will not be further improved with the increases of reaction temperature when the reaction temperature is higher than 340°C. Under the same reaction

temperature, the S31-0.6 molecular sieve catalyst has the highest n-hexadecane conversion and selectivity of i-hexadecane, this is due to the catalyst with suitable amount of acid and acid strength.

Using Ludox and the pseudo-boehmite, SAPO-31 molecular sieves of different chemical compositions and acidity were synthesized by changing the SiO_2/Al_2O_3 ratio in the initial gel. The micropore surface area and mesopore Pore volume of the SAPO-31 molecular sieve samples increase obviously with the increases of SiO_2/Al_2O_3 ratio in the initial, the total acidity, medium acidity and B acidity increase gradually, the relative crystallinity rise first and then fall. The highest i-hexadecane yield is obtained over 0.5Pd/S31-0.6 at the same n-hexadecane conversion.

3.7   Comparison of Catalytic Properties of 0.5Pd/S31 and 0.5Pt/ZSM22 Catalysts

The 0.5Pt/ZSM22 catalysts were prepared by combine the ZSM-22 molecular sieves with alumina carrier, then loaded with 0.5wt%Pt. The 0.5Pd/S31 catalysts were prepared by combine the optimal SAPO-31 molecular sieves (SiO_2/Al_2O_3 ratio=0.6) with alumina carrier, then loaded with 0.5wt%Pd.

The hydroisomerization experiments of deoxidized vegetable oil was carried in a fixed-bed, down-flow, taking 100ml of catayst. The reaction conditions and results are shown in Table 5.

Table 5. Reaction condition and results of the 0.5Pd/S31 and 0.5Pt/ZSM22 catalysts

Reaction condition	0.5Pd/S31	0.5Pt/ZSM22
Reaction temperature, °C	350	295
Reaction press, MPa	2.0	3.0
WHSV, h^{-1}	1.5	1.0
Hydrogen-oil ratio (volume ratio)	500	800
Total yield, %	98.5	95.5
Diesel yield over 160°C, %	92.2	89.6
Condensation point, °C	0	0

From TAble 5, it can be seen that the total yield and diesel yield of 0.5Pd/S31 are much higher than 0.5Pt/ZSM22. Because the acid strength of ZSM-22 molecular sieve is higher than SAPO-31 molecular sieves, which means the cracking properties of the 0.5Pt/ZSM22 is higher.

3.8   The Activity and Stability Experiments over 1500h

In order to investigate the activity and stability of the catalyst, the hydroisomerization experiments of deoxidized vegetable oil was carried in a fixed-bed, down-flow, tubular reactor at pressure 2.0MPa, reaction temperature 350°C, WHSV 1.5, hydrogen-oil ratio 500:1, taking 100ml of catayst. Prior to the tests, the catalyst was reduced in situ with hydrogen at 400 for 4h. Then, the catalyst was cooled to the initial reaction temperature, and the deoxidized vegetable oil was fed into the reactor.
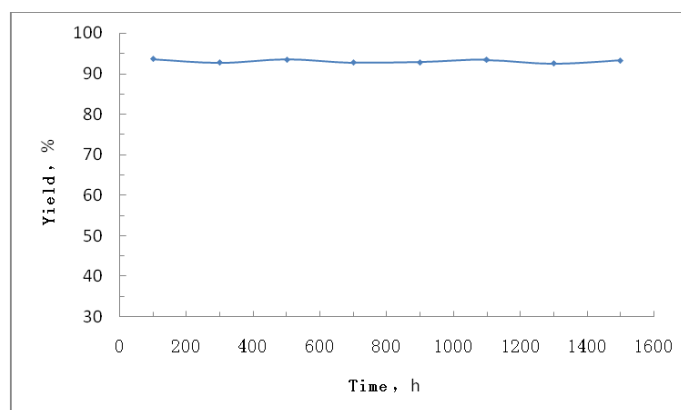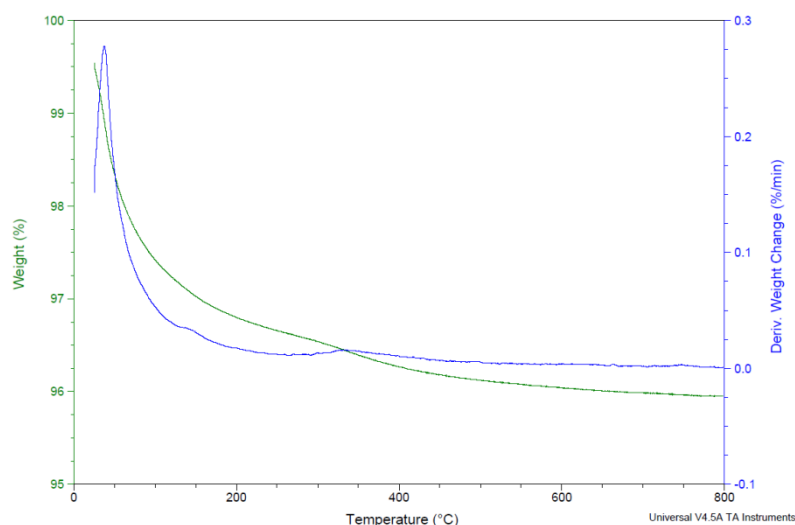

Figure 7. Diesel Yeild over 1500h

Table 6. Results of the 0.5Pd/S31 catalyst

Properties of products	Result
Reaction time, h	1500
Dieselyield over 160°C, %	92.2
Flash point, °C	60
Cetane number	74
Condensation point, °C	0

Results of the activity and stability of the 0.5Pd/S31 catalyst are shown in Figure 7 and Table 6. The performance comparison of the catalyst before and after reaction are shown in Table 7 and Figure 8.

Figure 8. TGA curves of the catalyst before and after reaction

Table 7. The performance comparison of the catalyst before and after reaction

Sample	Surface area, m^2/g	Total Pore volume, cm^3/g	Pd metal dispersion, %	Brönsted, $\mu mol/g$	TGA of the catalyst before and after reaction, %
Before reaction	219	0.244	26.5	25.6	--
After reaction	188	0.247	21.9	19.1	40.003*

* weight loss of the catalyst after reaction occurs at 80°C.

As shown in Figure 7 and Table 6, the diesel yield is stable in the reaction experiments over 1500h, the surface area of the catalyst after reaction over 1500h decrease slightly, but the total pore volume did not change basically. Pd metal dispersion decrease slightly, possibly due to a slight increase in the size of the metal cluster after reaction and a certain degree of reunion.

As shown in Figure 8 and Table 7, B acidity decreases slightly, and that may be due to the metal clusters to cover part of acid sites. The catalyst after reaction are heated from room temperature to 800°C in air, weight loss 4.003% is physical adsorption water, which occurs mainly in below 100°C. A small weight loss over 300-350°C range shows that no carbon deposition appears and the activity of catalyst is stable.

4   Conclusion

(1) Using Ludoxution and the pseudo boehmite, SAPO-31 molecular sieves of different chemical compositions and acidity were synthesized by changing the SiO_2/Al_2O_3 ratio in the initial gel. The

micropore surface area and mesopore Pore volume of the SAPO-31 molecular sieve samples increase obviously with the increases of SiO_2/Al_2O_3 ratio in the initial, the total acidity, medium acidity and B acidity increase gradually, the relative crystallinity rise first and then fall.

(2) Feed as deoxidized n-hexadecane, isomerization is carried in a fixed-bed reactor, taking 10ml of catalyst, the highest i-hexadecane yield is obtained over 0.5Pd/S31-0.6 at the same n-hexadecane conversion.

(3) Feed as deoxidized vegetable oil, isomerization is carried in a fixed-bed reactor, at pressure 2.0MPa, reaction temperature 350°C, WHSV 1.5, hydrogen-oil ratio 500:1, taking 100ml of catalyst, The highest biodiesel yield of 92.2% is obtained over the 0.5Pd/SAPO-31 catalyst, with solidifying point 0°C, flash point 60°C, cetane number 74. catalyst does not lose activity, and has high stability and excellent hydroisomerization dewaxing performance.

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