HYDROISOMERIZATION OF N-TETRADECANE OVER P MODIFIED Pt/SAPO-11 CATALYST

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Introduction

As is well known, the hydroisomerization process uses a metal/acid zeolite catalyst that has been described as bifunctional[1]. Noble metal such as Pt, Pd, and bimetal supported on ZSM-12, mordenite, USY, L-zeolite and β-zeolite have been employed as the bifunctional catalysts for hydrocarbon hydroisomerization process[2]. With these classical catalysts, high isomerization selectivity has been obtained only at relatively low conversion levels, but the selectivity decreases drastically at higher conversion levels and thus the formation of cracking products predominates.

Recently, great improvements have been achieved by using SAPO-11 supported Pd or Pt catalysts[3,4,5,6,7]. Generally SAPO-11 has a lower acidity than zeolites[8], and has been proved to more suitable for constituting catalysts that manifest better performance for long-chain hydrocarbon isomerization. The aim of this work is to investigate the effect of the phosphor modification of SAPO-11 on the catalytic activity, product selectivities and time-on-stream stability. The effects of reaction conditions on the catalytic performance were tested by varying reaction parameters such as temperature, pressure and WHSV, as well as the H_2/CH (H_2 to hydrocarbon) ratio. The obtained data were compared with our previous findings and used to interpret the formation of feed isomers as well as their distributions.

Experimental

Catalyst. The calcined SAPO-11 sample was mixed with a certain amount of alumina, and extruded into cylindrical shape. After drying at 120℃, the extrudate was crushed and sieved to obtain particles with a diameter of about 0.5mm. For P modification, the particle was impregnated with a dilute orthophosphoric acid, followed by drying and calcination at 120℃ and 500℃, respectively. The amount of P in the sample was designed to be 1% by weight.

SAPO-11 supported Pt catalysts were prepared by incipient wetness method. The obtained samples containing 0.4% platinum are denoted as 0.4Pt/SAPO-11 for non-modified and 0.4Pt/SAPO-11(P) for P-modified samples, respectively. The acidity of support was measured by NH_3-TPD, and the dispersion of Pt was estimated by H_2 chemisorption measurement at room temperature on a self-equipped apparatus system. Details on these characterizations can be found elsewhere[9].

Catalytic activity measurements. Hydroconversions of *n*-tetradecane were carried out in a 10ml fixed bed reactor system. Previous to activity measurements, the catalyst was pretreated in-situ first with air, then with H_2 up to 400℃ for 2h. Reaction products were analyzed in a GC with a flame-ionization detector. Product identification was achieved by GC-MS and by comparing the retention time of some pure compounds with separate GC injections. The carbon numbers of all the peaks were settled, but only some of the structures could be identified.

Results and Discussion

The hydroconversion of n-tetradecane on the two Pt/SAPO-11 catalysts gave both isomerization and cracking products, but with a higher selectivity to feed isomers at low temperatures. The cracking products consisted of spectra of C_1-C_{13} hydrocarbons with pretty high percentage of C_3-C_7. Minor amount of C_1 and C_2 were obtained, which suggests that the hydrogenolysis on the Pt/SAPO-11 catalysts of 0.4 metal loading is negligible.

As was expected, the conversion of *n*-tetradecane increased with reaction temperature, while the selectivity to tetradecane isomers decreased gradually. At higher temperatures, with conversion level reaching more than 90%, the cracking reactions became pronounced, giving an isomerization selectivity of less than 10%. As shown in **Fig1**, both the activity and isomerization selectivity are improved by P modification, especially at low temperature range. This may be attributed to the increase of weak acidity by P modification as indicated by NH_3-TPD data.

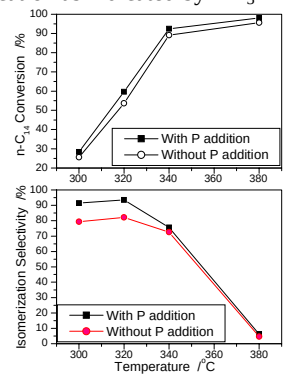

Fig1. Effect of reaction temperature on the hydroconversion of n-C_{14} over 0.4Pt/SAPO-11(P) and 0.4Pt/SAPO-11 catalysts
Condition: P=30atm, WHSV=2.0h^{-1}, H_2/C_{14}=8.7(mol/mol).

Comparing these results with our previous findings[10], which shown more than 80% isomerization selectivity of even at 90% conversion over a SAPO-11 catalyst of the same metal loading, we come to the conclusion that the catalytic behavior is largely influenced by the nature of SAPO-11 molecular sieve.

The effect of total reaction pressure on n-C_{14} hydroconversion was investigated, and the results are presented in **Table1**. As shown in the table, both the conversion of n-C_{14} and the yield of feed isomers decrease with increasing pressure. The results indicate a negative reaction order with respect to hydrogen, which is consistent with the known data[11,12].

Table1. Effect of Pressure on N-C_{14} Hydroconversion over 0.4Pt/SAPO-11(P) Catalyst

P atm	Conv %	Y_{iso} %	S_{iso} %	Monomers /%	Distribution of monomers		
					3	2, 4	5, 6, 7
10	84.8	77.4	91.3	61	0.21	0.28	0.51
20	68.7	61.8	90.0	76	0.21	0.27	0.52
30	59.6	55.8	93.5	78	0.22	0.30	0.49

Reaction conditions: temperature 320℃; Whsv2.0 h^{-1}; H_2/CH 8.7

As shown in **Table2**, the conversion of n-C_{14} and the yield of liquid as well as the yield of isomers increased with decreasing whsv. The retention time of feed on the catalyst increases with the decreasing of whsv, and thus the increase of conversion is expectable.

The influence of H_2/CH ratio on n-C_{14} hydroconversion is shown in **Table3**, the conversion of n-C_{14} decreases with increasing the partial pressure of hydrogen (the H_2/n-C_{14}(mole) from 4.3 to 8.7), while the isomerization selectivity increases. The changes are relatively small with a higher WHSV of 4.1h^{-1}. It should be point out that at pretty low H_2/CH ratio, catalyst deactivation became predominant. All these reflect the importance of H_2 in the

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isomerization process. And the role of H_2 during isomerization might be the same as we have discussed in a previous paper[1 3].

Table2 Effect of WHSV on N-C_{14} Hydroconversion over 0.4Pt/SAPO-11(P) Catalyst

WHSV h^{-1}	Y_l %	Conv %	Y_{iso} %	S_{iso} %	Monomers /%	Dis. of monomers 3	2, 4	5, 6,7
4.1	98.4	34.3	32.7	95.3	87	0.20	0.32	0.48
3.0	99.1	44.6	42.6	95.5	85	0.19	0.29	0.52
2.0	98.8	59.6	55.8	93.5	78	0.22	0.30	0.49
1.0	97.6	83.8	74.8	89.2	64	0.22	0.30	0.48

Temperature320℃ Pressure 30atm; H_2/CH 8.7mol/mol

Table3. Effect of H_2/CH Ratio on the Hydroisomerization of N-C_{14} over 0.4Pt/SAPO-11(P) Catalyst at 30atm

Temp ℃	H_2/CH mol/mol	Whsv h^{-1}	Conv %	Y_{iso} %	S_{iso} %	Monomers %	Dis.of monomers 3	2, 4	5, 6,7
300	4.3	2.0	39.8	33.6	84.6	85	0.21	0.31	0.48
300	8.7	2.0	28.4	25.9	91.5	86	0.23	0.29	0.48
320	4.3	4.1	37.0	33.3	90.2	84	0.21	0.30	0.49
320	8.7	4.1	34.3	32.7	95.3	87	0.20	0.31	0.49

It was found that the catalytic behavior of 0.4Pt/SAPO-11(P) catalyst with time on stream was largely influenced by operating parameters. A larger H_2 partial pressure inhibited the *n*-tetradecane conversion, while a slower deactivation was observed. Noticeable catalyst deactivation was observed at a lower reaction pressure, especially at atmospheric pressure, while at pressures higher than 10atm, the isomerization process was stabilized in 30 minutes (**Fig2**).

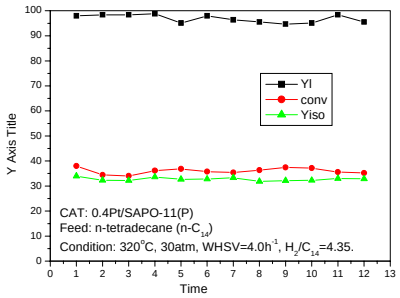

Figure 2 Catalytic performance of 0.4Pt/SAPO-11(P) catalyst in n-C_{14} hydroconversion. (Yl=Yield of Liquid)

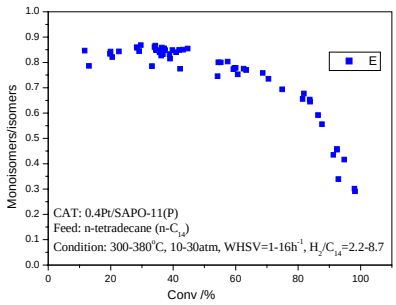

Figure 3. Change of Monoisomers/isomers ratio as a function of the n-tetradecane conversion over 0.4Pt/SAPO-11(P) catalyst

Though the change of reaction variables, such as pressure, whsv and H_2/CH ratio, did affect the distribution of the isomerization products (Table 1-3). It has been found that the distribution can only be correlated with conversion level of n-C_{14} as shown in **Fig.3**. The content of mono-isomers in the isomerization products decreases with increasing conversion level, indicating secondary transformation of mono-branched isomers to multi-branched isomers. However, the distribution of mono-branched isomers was found to be independent of conversion level. In the conversion range up to 90%, the distribution of positional mono–branched isomers changes little (**Fig4**). Of the mono-branched isomers, most are central positional methyl branched isomers, namely, 4-, 5-, 6-, 7-methyltridecane, which is highly desired components for diesel and lube base oil.

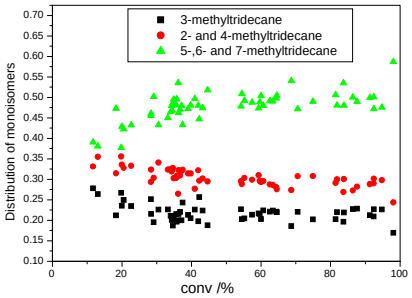

Figure 4. The distribution of mono-branched isomers as a function of n-tetradecane conversion over 0.4Pt/SAPO-11(P) catalyst

Conclusions

An increase of activity was observed with the P modified catalyst, and isomerization selectivity was also improved especially at low temperature with a conversion up to 85%. The content of mono-isomers decreased with increasing conversion levels of n-tetradecane, while the distribution of the mono-isomers changed little. The high Pt dispersion and relatively large amount of weak acidity of P modified Pt/SAPO-11 catalyst account for the improved hydroisomerization performance. Comparing these results with our previous findings, we come to the conclusion that the catalytic behavior is largely influenced by the nature of SAPO-11 molecular sieve.

Acknowledgement. Financial aid from Fushun Petrochemical Company is gratefully acknowledged. The authors thank the State key laboratory of Coal Conversion for basic sample characterizations and collecting the GC-MS data. The authors are indebt to Dr. Zhao Liangfu, Ms. Li Yuan, Ms. Wang Hairong and Mr. Dong Lingyao who participated in this work.

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