

Hydroisomerization of Light Alkanes over Zeolites

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Introduction

The hydroisomerization of light alkanes is an important process in mineral oil refining [1]. In this process, the light normal alkanes (i.e., n-butane, n-pentane and n-hexane) are isomerized to their more branched counterparts in the presence of hydrogen over a bifunctional catalyst containing both acidity (e.g., zeolites) and hydrogenation/dehydrogenation (e.g., Pt or Pd) functions. Examples of such catalysts are Pt on chlorided alumina, Pt on zeolite H-mordenite or Pt on sulfated zirconia. The octane number of light alkanes increases with the degree of branching. For example, the RON (Research Octane Number) of n-hexane is only 31 while the RON's of 2-methylpentane, 3-methylpentane, 2,2-dimethylbutane and 2,3-dimethylbutane are 74, 76, 94 and 105, respectively. The hydroisomerization represents an efficient way to enhance the octane number of gasoline.

The hydroisomerization is a reaction controlled by the thermodynamic equilibrium. At higher reaction temperature the equilibrium shifts towards the lower octane isomers (e.g., from dimethylbutanes via methylpentanes to n-hexane). Therefore, it's desirable to develop a more active catalyst to carry out this reaction at a lower temperature. One task of our research presented in the present paper is to find a zeolite with stronger acidity (therefore, higher activity at lower temperature) without the restrictions posed by the shape selectivities. Because the bulkier isomers with more methyl groups are the targeted high octane products, the hydroisomerization of light alkanes over zeolite catalysts exhibits an example showing that the shape selectivities are undesirable for certain refining applications. On the other hand, for another task of the present studies, we make use of the shape selective properties of zeolites with the hydroisomerization of light alkanes to characterize their structure-property relationship. In this paper, our results from n-hexane hydroisomerization over a series of Pd-loaded zeolite catalysts will be discussed.

Experimental

Calcined zeolites such as SSZ-32, SSZ-25, ZSM-5, TNU-9, SSZ-26, mordenite and Y were ion exchanged with aqueous NH_4NO_3 solution to create their NH_4 -forms. They were then ion exchanged with aqueous $(\text{NH}_3)_4\text{Pd}(\text{NO}_3)_2$ solution to load each zeolite with 0.5 wt% Pd. The resulting catalysts were subsequently calcined. The Pd-loaded zeolites were reduced in hydrogen prior to the catalytic experiments. The reactions were carried out in a flow type fixed bed reactor with pure n-hexane as feed at temperatures between 475-615 K, pressure of 1480 kPa, LHSV of 1 h^{-1} and molar H_2 to hydrocarbon ratio of 6:1. The reaction products were analyzed with an on-line GC. The parent zeolites and the prepared Pd-zeolite catalysts were characterized via XRD, SEM, N_2 adsorption and elemental analyses. The Pd-zeolite catalysts were also analyzed with H_2 chemisorption to determine the Pd dispersion.

Results and Discussion

Results from XRD and N_2 adsorption reveal that the Pd-loaded catalysts retained the structural features of the parent zeolites. Results from elemental analyses indicate that Pd-loading was ~0.5 wt.% for all the catalysts studied here, implying that basically all the Pd was exchanged from the solution into the zeolites. The Pd dispersion was >50%.

As demonstrated by Weitkamp, the rates of hydroisomerization and hydrocracking of alkanes as two competitive reactions strongly depend on the carbon numbers in the feed molecules [2]. Light alkanes such as n-hexane can be cracked only slowly via the secondary carbenium ions as transition states, leading to a high selectivity to isomerization. Table 1 shows the results from hydroisomerization and hydrocracking of n-hexane over a series of Pd-loaded zeolites at the maximum isomer yields. With a low temperature of 533 K for the maximum isomer yields, zeolites ZSM-5 (10-ring), TNU-9 (10-ring) and SSZ-26 (12x10-ring) exhibit promising high activities although their dimethylbutane yields are still low relative to those of mordenite (12x8-ring) and Y (12-ring). Especially with SSZ-26, its relatively small 12-rings (6.4x7.0 Å and 5.9x7.0 Å) appear to become critical to the formation of 2,2-dimethylbutane (kinetic diameter 6.2 Å). More 2,2-dimethylbutane is produced in zeolites mordenite (6.5x7.0 Å) and Y (7.4 Å) which have slightly larger 12-rings. As presented in Table 1, due to the shape selectivities associated with pore sizes, the yield and selectivity of n-hexane to 2,2-Dimethylbutane and 2,3-dimethylbutane appear to be a useful tool for distinguishing between 10-ring zeolites (SSZ-32, SSZ-25, ZSM-5 and TNU-9) and 12-ring zeolites (mordenite and Y).

Table 1. Hydroisomerization and hydrocracking of n-hexane on various Pd/zeolites at maximum isomer yields

Zeolite	Temp. at Max. Isomer Yield, K	Max. Isomer Yield, mol%	Distribution, mol%			
			2,2-DM-C4	2,3-DM-C4	2-M-C5	3-M-C5
SSZ-32	578	68.5	0.1	2.1	59.0	38.9
SSZ-25	544	74.5	0.5	5.1	57.3	37.1
ZSM-5	533	74.4	0.2	3.0	59.6	37.2
TNU-9	533	77.4	2.6	13.1	51.8	32.5
SSZ-26	533	78.8	9.9	12.8	47.0	30.3
Mordenite	567	78.6	21.5	10.8	40.7	27.0
Y	578	79.5	21.9	10.0	41.2	27.0

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