Catalysis Letters 7 (1990) 383–388

SECONDARY SHAPE SELECTIVITY IN ZEOLITE CATALYSIS

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Received 10 August 1990; accepted 9 October 1990

Shape selectivity, zeolites, cracking, hydrocracking.

Over zeolite SSZ-16, n-hexane inhibits the cracking of n-hexadecane under hydrocracking conditions due to shape selectivity. We call this specific phenomenon "secondary" shape selectivity. The reason for this term is that the cracking selectivity of the zeolite is affected by one of the reactants. Whenever feed mixtures are reacted over zeolite catalysts, this type of shape selectivity can affect reaction selectivity.

1. Introduction

Shape selectivity in zeolites has been divided into three categories: reactant, transition state, and product. The phenomena associated with those catagories have been discussed previously in the literature [1]. In most cases, the observed shape selective effects are caused by steric constraints imposed on a molecule or transition state by a restrictive pore system. For example, in reactant shape selectivity, the pores of the zeolite are small enough to exclude one reactant molecule but not a smaller reactant molecule. An example of this is the use of erionite to crack certain hydrocarbons [2]. Erionite has pore openings with kinetic diameters of 4.3 Å, large enough to admit linear alkanes such as n-hexane, but too small to admit methyl-branched alkanes such as 3-methylpentane. Therefore, if a mixture of n-hexane and 3-methylpentane is exposed to erionite, only the n-hexane will enter the zeolite pores and react. Interactions between n-hexane and 3-methylpentane do not affect this type of shape selectivity. In such cases, when the shape selectivity is a result of direct interactions between a molecule and a pore system, we prefer to use the term "primary" shape selectivity.

In zeolite catalysis, "secondary" shape selectivity occurs when one type of molecule effects the behavior of another type in a way which does not occur in a less hindered environment.

Molecules can interfere with each other in unrestricted environments. Two examples of this are: 1) a molecule with a higher boiling point will preferentially adsorb onto a catalyst surface, and 2) a highly polar molecule will adsorb on a polar catalytic surface instead of a non-polar molecule [3]. In both of these cases, the preferentially adsorbed molecule will have a greater chance to undergo catalysis and it will impede the reaction of the less strongly adsorbed molecule. One of these effects could be combined with the primary shape selective phenomena discussed above, but the result would not be secondary shape selectivity.

Secondary shape selectivity occurs when one molecule interferes with the reactivity of another one strictly because of steric constraints imposed by the pores. As opposed to the boiling point and electrostatic effects discussed in the preceding paragraph, secondary shape selectivity is a phenomenon which does not happen in an unhindered environment. The phenomenon of shape selectivity is a steric one, and if we are going to attach any modifiers to it such as 'secondary', we want to make sure that we are describing steric effects due to restrictive pores, not indirect steric effects due to boiling point or electrostatic interactions.

An example of secondary shape selectivity is given in a paper by Namba et al. [4]. In that paper, they showed that 2,2-dimethylbutane retards the cracking of n-octane in ZSM-5. They attributed this to the difficulty 2,2-dimethylbutane has in diffusing through the pores of ZSM-5. In effect, 2,2-dimethylbutane hindered the diffusion of the sterically smaller n-octane. Because 2,2-dimethylbutane is lower boiling and no more polar than n-octane, 2,2-dimethylbutane would not block n-octane from reacting in an unhindered environment. Therefore, this phenomenon would not occur in the absence of a restrictive pore system and it fits our definition of secondary shape selectivity.

In this paper, we show how a reactant which is *smaller* (and lower boiling) than another reactant can completely inhibit the cracking of a larger molecule even though the two reactants have similar polarities. Although this is a size effect opposite to what Namba et al. observed with ZSM-5, both phenomena are examples of secondary shape selectivity.

It is important to understand these phenomena because the reactants and products in industrial zeolite catalysis are usually complex mixtures of molecules. Our goal is to control the way they react, and understanding the fundamental interactions which occur will help us do that.

2. Experimental and results

CATALYSTS

SSZ-16 and ZSM-5 were prepared as described in the patent and open literature [5,6]. The materials were 100% crystalline according to X-ray diffraction data. The SiO_2/Al_2O_3 ratio of SSZ-16 was 12 and that of ZSM-5 was 35. The cation used to balance the zeolite exchange sites was $H+$.

CATALYTIC REACTIONS

The hydrocarbon reactions were carried out in 6.4 mm diameter × 914 mm long stainless steel reactor tubes with 0.5 g of the zeolite powder loaded into the center of the tube. Alundum was added above the catalyst for preheating the feed. Glass wool plugs separated the catalyst from the alundum. The hydrocarbon feed and hydrogen gas flowed downward over the catalyst at the run conditions described below.

Each zeolite, SSZ-16 or ZSM-5, was run with three feeds, n-hexane (nC6), n-hexadecane (nC16), and a 50/50 (by volume) mixture of the two hydrocarbons. The nC6 and nC16 were both 99 + % pure from Aldrich Chemical Co. The run conditions were as follows: total pressure was 1200 psig, hydrogen flow rate was 147 ml/min at STP, feed rate for nC6 was 1 ml/hr, feed rate for nC16 was 1 ml/hr, and the feed rate for 50/50 (by volume) nC6 plus nC16 was 2 ml/hr. (Thus, the molar ratio of hydrogen to nC6 was 51 and the ratio of hydrogen to nC16 was 115. Also, the hydrogen partial pressure for all of the runs was between 1170 and 1190 psia.) The nC6 cracking conversion is defined as 100 (wt% C6's in the feed − wt% C6's in product)/(wt% C6's in the feed) and for nC16, 100(wt% C16's in feed − wt% C16's in product)/(wt% C16's in feed). For the run using ZSM-5 as the catalyst and the nC6 plus nC16 feed, defining the nC6 conversion is complicated by the fact that nC16 reacts and produces some nC6. So the nC6 conversion for this run is defined as 100 (wt% nC6 in feed − wt% nC6 in product + wt% nC6 produced from nC16)/(wt% nC6 in feed). The nC6 produced from nC16 is estimated from the run using pure nC16 feed. The estimate is valid because the C7 + product distribution does not change for the ZSM-5 runs with nC16 and with nC16 + nC6 feeds. The correction is small: nC6 from nC16 equals 2 wt%.

The products from the runs were analyzed by on-line gas chromatography with a flame ionization detector. The peak areas (wt%) of the products are uncorrected for response factors. Several analyses of the product stream for each run showed

Table 1
Results for cracking alkanes over SSZ-16 and ZSM-5 [a]

Catalyst	Feed	Temp (°C)	nC6 conv. (wt%)	nC16 conv. (wt%)
SSZ-16	nC6	332	50	–
SSZ-16	nC16	332	–	74
SSZ-16	nC6+nC16	332	62	<1
25M-5	nC6	271	56	–
Z5M-5	nC16	271	–	53
ZSM-5	nC6+nC16	271	4	53

[a] See text for run conditions and definition of terms.

that less than 2% change in conversion occurred over 20 hours. The results are in table 1.

3. Discussion

Using ZSM-5, a medium-pore zeolite, as the catalyst, nC6 and nC16 convert to similar extents when run separately (table 1). But when the two feeds are reacted simultaneously, nC6 has little or no effect on nC16 conversion, but nC16 greatly retards nC6 conversion. This is probably not related to the diffusion phenomenon described by Namba et al. in which sterically larger (but lower boiling) 2,2-dimethylbutane inhibits the cracking of n-octane [4]. Here, because nC16 is much higher boiling than nC6, selective adsorption of nC16 in the zeolite pores is the likely cause for the inhibition of nC6 cracking, and this is not a shape selectivity effect. Steijns et al. observed this phenomenon when hydrocracking n-heptane and n-decane over Y-zeolite [3].

SSZ-16, a small-pore zeolite which adsorbs only linear alkanes [7], gives different results. In this case, when nC6 and nC16 are run separately, considerable conversion of each occurs just as for ZSM-5. However, when the two feeds are reacted together, nC16 causes a slight increase in the nC6 conversion, but nC6 completely eliminates nC16 conversion. Because the two molecules have similar polarities and nC6 is both smaller and lower boiling than nC16, this phenomenon has no parallel to any effect in catalysis not involving restricted pores. Unquestionably, this is a steric effect in which the nC6 together with the SSZ-16 pores keep nC16 from reacting. Because nC16 reacts over SSZ-16 when fed alone, the selective cracking of nC6 from a 50/50 mixture of nC6 and nC16 is due to both the restrictive pores of SSZ-16 and the presence of nC6. The nC6 does not inhibit the cracking of nC16 in less restricted environments such as the ZSM-5 pores. Therefore, this is a well-defined example of secondary shape selectivity.

We do not know what are the specific interactions between the reactants and the zeolite pores which cause this phenomenon to happen. However, we had hints that lighter molecules could hinder the adsorption of heavier ones in SSZ-16. In pore probe experiments [7], we observed that a few percent of gaseous products from nC6 cracking reduces the nC6 concentration in SSZ-16 pores by a factor of greater than ten. This great depletion does not occur during nC6 cracking over other zeolites such as ZSM-5. Perhaps nC6 causes the nC16 concentration in the SSZ-16 pores to decrease in a similar way when these two molecules are both present in the feed. If so, this would be an example of reactant secondary shape selectivity caused by a reactant molecule.

The example given in this paper is different from those given by Namba et al. [4]. In this case, a smaller molecule hinders the conversion of a larger one, while in the paper by Namba et al., examples are given of larger molecules hindering the conversion of smaller ones. In a different experiment, Chen [3c] demonstrated that benzene inhibits n-hexane isomerization in mordenite, but not in Y-zeolite. That may be a case of secondary shape selectivity, but because benzene is much more polar than hexane, it is not clear whether the cause of the different behaviors of these two zeolites is the difference in pore structure or the difference in acidity.

No doubt several types of secondary shape selectivity exist, e.g. reactant, product, and transition state, and these types of secondary shape selectivity could be caused by both reactants and products.

Acknowledgements

The authors wish to thank J. Eddings, L. Yuen, R.A. van Nordstrand, J.A. Duisman and other members of the Process Research Division for their help and Chevron Research and Technology Co. for its support.

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