

Shape-Selective Platinum/ZSM-5 Catalysts

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Shape-selective hydrogenation catalysts containing platinum dispersed inside the channels of ZSM-5 crystals have been prepared. A competitive olefin hydrogenation test was developed to assess the location of active metal sites in ZSM-5-supported catalysts.

INTRODUCTION

The small uniform pores and large intracrystalline volumes characteristic of zeolites make them ideally suited as shape-selective catalysts or catalyst supports (1). Since the first demonstration of molecular shape-selective zeolite catalysis by Weisz and Frillette in 1960 (2), numerous articles and patents have appeared in the literature. The vast majority of these involved the use of small-pore zeolites in which the pore openings consisted of 8-membered oxygen rings, such as zeolite A and erionite. The molecular sieving action of these zeolites was due to the fact that the intracrystalline space of these zeolites was inaccessible to molecules having a critical diameter larger than about 5 Å, thereby permitting the selective reaction of linear compounds in the presence of their branched isomers. Significantly less use has been made of the large-pore zeolites with pore openings consisting of 12-membered oxygen rings, typical of faujasites, since these zeolites were incapable of discriminating effectively between molecules having critical diameters less than 8 Å.

With the discovery of ZSM-5, a zeolite of novel structure (3) possessing pore openings composed of 10-membered oxygen rings and intermediate in size between the small-pore and large-pore zeolites, it became feasible to perform shape-selective separations hitherto unobtainable.

ZSM-5 at room temperature totally excludes such highly branched molecules as 1,3,5-trimethylbenzene, 2,2,4-trimethylpentane, and 3,3-diethylpentane, while, unlike the small-pore zeolites, permitting entry of many simple aromatic and branched hydrocarbons (4). The use of ZSM-5 for the shape-selective acid-catalyzed cracking of linear and singly branched paraffins, as well as the selective alkylation of aromatics, has been reported (5, 6). Separation of *p*-xylene from its isomers (7), as well as the selective alkylation of toluene to produce *p*-xylene (8), has also been accomplished by means of ZSM-5, due to differences in diffusional rates of the xylene isomers in the zeolite.

Whereas the use of H-ZSM-5 as a shape-selective acid catalyst has been extensively demonstrated, the possibility of using ZSM-5 as a shape-selective support for metal-catalyzed reactions has received relatively little attention. The ability of zeolites to function as shape-selective supports for platinum-catalyzed hydrogenations has been reported for a platinum co-crystallized A zeolite (9) and for an externally poisoned, sodium back-exchanged, platinum mordenite (10).

We now wish to report on the preparation of stable shape-selective hydrogenation catalysts containing platinum dispersed inside the channels of ZSM-5, and to describe the competitive hydrogenation test developed to assess the location of the

active metal sites in these catalysts (see Ref. (11), which contains a preliminary report).

EXPERIMENTAL

The ZSM-5 zeolites used as starting materials had been synthesized by standard procedures (12), calcined, and then ammonium ion-exchanged. All had silica/alumina ratios of about 70.

Platinum was incorporated in ZSM-5 by direct exchange of the ammonium, sodium, or cesium forms of ZSM-5 with dilute aqueous solutions of $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$.

Elemental platinum analyses were obtained from Galbraith Laboratories or by titration of the ammonia evolved during thermal decomposition of small samples on a TGA balance under flowing hydrogen.

For catalytic evaluation, the platinum tetramine-exchanged samples were reduced directly in the reactor in a stream of hydrogen and olefins, typically hexene-1 and 4,4-dimethylhexene-1. Shape-selective catalysts were also obtained by heating the platinum-exchanged zeolites in flowing oxygen to 350°C at 0.5°C/min, followed by hydrogen treatment at 500°C for ½ h.

Acidity suppression prior to testing was accomplished by either injecting ammonia into the reactor containing the catalyst at a temperature below 300°C, or by neutralizing the reduced catalyst with dilute aqueous cesium hydroxide.

Competitive reactions were performed in a down-flow fixed-bed glass reactor connected to an on-line gas chromatograph containing a 12-foot *n*-octane-Durapak column. An equimolar mixture of olefins was admitted into the reactor by means of a Sage syringe pump and diluted with a five-fold excess of hydrogen.

Platinum dispersion was measured for an oxygen-treated shape-selective Pt/ZSM-5 catalyst containing 3% platinum. The platinum dispersion was 20% as determined by the pulsed hydrogen chemisorption technique.

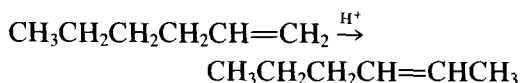
RESULTS AND DISCUSSION

In order to demonstrate the intra-zeolitic nature of the active platinum sites in Pt/ZSM-5 catalysts, it was necessary to develop a catalytic test to distinguish between internal and external platinum.

Diffusion-Controlled Shape-Selective Reactions in H-ZSM-5

During the past few years there has been considerable interest in the accurate measurement of diffusion rates of various hydrocarbons in zeolites as a means of characterizing and defining the shape-selective properties of these zeolites (13). Numerous reports have shown that diffusivity measurements can provide important information directly related to the catalytic properties of zeolitic materials in such diffusion-controlled processes as *para*-selective aromatic conversions (14). To supplement such physical approaches, we set out to establish a rapid, simple, and highly sensitive chemical test capable of measuring the relative competitive diffusivities of various organic molecules within zeolites under reaction conditions. This chemical test would permit the measurement of relative diffusivities of molecules which diffuse too rapidly to be measured directly and, in addition, would not be limited to temperatures far below those used in the actual catalytic processes.

The test reaction chosen for this purpose was the acid-catalyzed isomerization of terminal olefins to their internal isomers:



At temperatures below 200°C, the H-ZSM-5 acid-catalyzed isomerization of hexene-1 to hexene-2 occurred quite rapidly and cleanly, i.e., with no significant cracking observable. Unlike the cracking reaction of hexane, the isomerization of hexene-1 was found to be largely diffusion-controlled over H-ZSM-5, despite the relatively small steric size of the linear

TABLE 1
Hexene-1 Isomerization Over H-ZSM-5

ZSM-5	meq (H ⁺ /g)	T (°C)	WHSV ^a	% Isomerization
H-ZSM-5 (L)	0.35	100	0.25	15.5
	0.35	125	0.25	34.7
	0.35	150	0.25	74.5
H-ZSM-5 (S)	0.44	100	5	95.7
	0.44	100	0.5	97.2
	0.44	125	95	27

Note. L, Large crystal; S, small crystal.

^a Hexene (150 mmHg) in N₂.

hexene molecule (see Table 1). Thus, a small-crystal H-ZSM-5 was at least two orders of magnitude ($k_{\text{small crystal}}/k_{\text{large crystal}} = 150$ per acid site at 125°C) more active than the larger crystals.

Competitive Isomerizations

The relative diffusivities of variously shaped olefins in ZSM-5 were obtained from competitive isomerization reactions conducted over H-ZSM-5 at temperatures in the 100–175°C range (see Table 2). Both single- and double-branched molecules were studied, and in all cases the shape-selectivities were somewhat greater for the larger crystal size catalyst.

The selectivities observed over the large-crystal catalyst, under conditions of exten-

sive diffusion control, can be used to estimate the relative diffusivities of the various olefins in ZSM-5. If one makes the reasonable assumption of comparable intrinsic reaction rates and comparable sorption equilibria for all the terminal olefins, the relative effective diffusivities would be proportional to the square of the observed selectivities (13). On this basis, the relative diffusivities of the four olefins in ZSM-5 at 150–175°C are hexene-1 [1.0], 6-methylheptene-1 [8], 3-ethylpentene-1 [1200], and 4,4-dimethylhexene-1 [14,000].

Effects of Cations on Diffusional Selectivities

The shape-selectivity of diffusion-controlled reactions in zeolites can be accentuated by the presence of large cations exchanged into the acidic zeolite. In particular, the preference for linear olefins was enhanced for both cesium and tetramethylammonium ion partially exchanged small-crystal H-ZSM-5, as shown in Table 3.

Diagnostic Test for Intrazeolitic Platinum in ZSM-5

In view of the large difference in the diffusivities of the linear olefin hexene-1 and the highly branched olefin 4,4-dimethylhexene-1 in ZSM-5, the competitive hydroge-

TABLE 2
Competitive Isomerizations

Catalyst	Linear olefin	Branched olefin	% Conversion		Selectivity ^a
			Linear	Branched	
H-ZSM-5 (S)	Hexene-1	6-Me heptene-1	59	47	1.4
	Hexene-1	3-Et pentene-1	64	10	9.7
	Hexene-1	4,4-diMe hexene-1	47	2.6	25
H-ZSM-5 (L)	Hexene-1	6-Me heptene-1	41	25	2.8
	Hexene-1	3-Et pentene-1	64	2.8	35
	Hexene-1	4,4-diMe hexene-1	54	0.65	120

Note. L, Large crystal, reactions conducted at 150–175°C. S, small crystal, reactions conducted at 100–125°C.

^a Selectivity calculated assuming first-order kinetics.

TABLE 3
Effect of Cation Exchange on Diffusional Selectivity

Catalyst	Temperature (°C)	Selectivity (hexene-1/6-Me heptene-1)
H-ZSM-5	105	1.4
Cs-H-ZSM-5	100	3.0
TMA-H-ZSM-5	100	3.3

nation of an equimolar mixture of these two olefins was used to assess the location of platinum in Pt/ZSM-5 catalysts. Non-shape-selective platinum, such as that in 0.5% Pt on alumina, did not show any preferential hydrogenation of the linear olefin; in fact, slightly greater hydrogenation of the highly branched olefin was noted. Preferential hydrogenation of the linear olefin would therefore indicate the presence of intra-zeolitic platinum.

Preparation of Platinum/ZSM-5 Catalysts

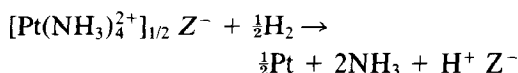
Platinum incorporation. In sharp contrast to the octahedral, hexa-coordinated complexes of cobalt, rhodium and ruthenium, the tetra-coordinated square planar complexes of platinum(II) and palladium(II) can be readily ion-exchanged into ZSM-5. Thus, when a sample of Cs-ZSM-5, prepared from an NH₄-ZSM-5 containing 0.35 meq NH₃/g zeolite, was stirred overnight at 50°C with an aqueous solution of Pt(NH₃)₄Cl₂, quantitative exchange took place, as evidenced by the basic nitrogen content of 0.71 meq/g. Palladium exchange was similarly quantitative.

The facile introduction of square-planar complexes into ZSM-5 is quite consistent with the postulated structure of ZSM-5 with its elliptical, noncircular pore opening. The shorter dimension of these elliptical pores would interfere only with passage of octahedral complexes and not with two-dimensional square complexes.

The platinum content of the zeolites can be controlled by adjustment of the amount of tetramine complex used or by back-exchange with cesium ions. Platinum contents

of the catalysts evaluated ranged from 0.6 to greater than 3 wt%.

Platinum activation. The thermal decomposition of platinum tetramine complexes in zeolites results in the deposition of elemental platinum and the liberation of ammonia with the concomitant formation of the acid form of the zeolite (15). The thermogravimetric reduction of Pt(NH₃)₄²⁺ in ZSM-5 in flowing hydrogen, together with the simultaneous titration of evolved ammonia, is depicted in Fig. 1.



Since acid sites are generated stoichiometrically during platinum reduction, it is advisable to inject ammonia over the reduced Pt/ZSM-5 catalysts prior to testing so as to minimize acid-catalyzed reactions.

Considerable attention has been focused on the problem of preparing well-dispersed platinum metal inside Y-type zeolites (16). In a hydrogen atmosphere, even at 350°C,

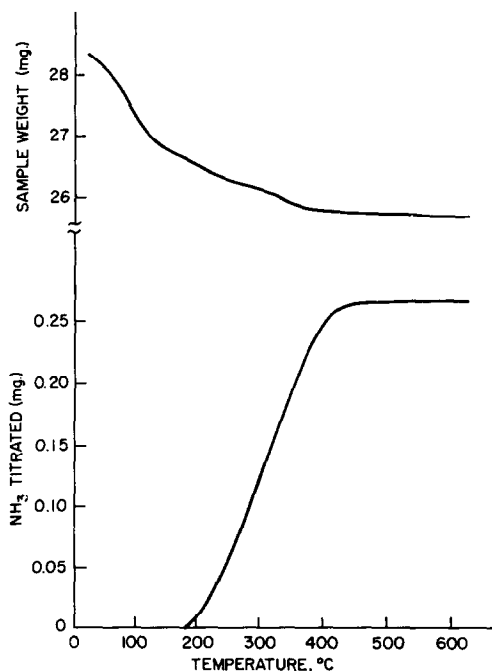


FIG. 1. Thermal decomposition of Pt(NH₃)₄²⁺ ZSM-5 in hydrogen.

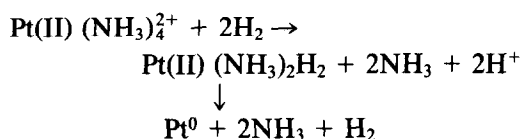
TABLE 4
Effect of Pretreatment on Hydrogenation Selectivity

Catalyst	Temperature (°C)	Pretreatment	WHSV	% Hydrogenation	
				Hexene-1	4,4-Dimethylhexene-1
1% Pt/Cs-ZSM-5	275	300°C, H ₂ only, 1 h	25	29	39
1% Pt/Cs-ZSM-5	275	H ₂ + olefin mixture, 400°C	70	90	1
0.5% Pt/Al ₂ O ₃	275	H ₂	—	27	35

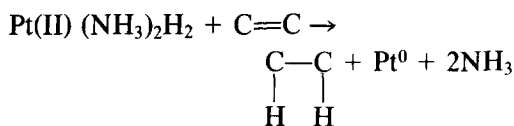
considerable migration and agglomeration of platinum atoms was observed. It was only by heating slowly in oxygen to 350°C, followed by H₂ reduction, that a well-dispersed platinum cluster of less than 10 Å was obtained (17). In a similar sense, we observed that a 1% platinum-containing large-crystal ZSM-5 catalyst, when reduced in flowing hydrogen for 1 h at 300°C, yielded in an active olefin hydrogenation catalyst which, however, failed to exhibit any shape-selective properties.

When, however, this same catalyst was reduced in H₂ in the presence of olefins, a highly selective hydrogenation catalyst was obtained (Table 4). This pretreatment resulted in a catalyst whose hydrogenation activity for the linear olefin was substantially enhanced while that of the branched olefin was greatly reduced.

Platinum migration and agglomeration during hydrogen reduction has been attributed to the formation of an unstable neutral, and hence mobile, platinum hydride (17).



The beneficial role of olefin could conceivably be that of a hydride trap, decomposing the platinum hydride before it can migrate while being itself reduced to the saturated paraffin at the same time.



Platinum tetramine decomposition in flowing oxygen while heating to 300°C at 0.5°C/min, followed by hydrogen treatment at 500°C for 1–2 h, also resulted in highly shape-selective Pt/ZSM-5 catalysts.

Acidity suppression prior to testing was accomplished by either of two methods: (1) injection of ammonia below 300°C, or (2) neutralization with aqueous cesium hydroxide after tetramine decomposition. The results for two such catalysts prepared from a 70:1 silica/alumina ratio large crystal ZSM-5 and containing 3% Pt are

Catalyst neutralization	% Olefin hydrogenation at 300°C	
	Hexene-1	4,4-Dimethylhexene-1
NH ₃ injection	83	1.6
CsOH treatment	75	0.2

Effect of Temperature on Hydrogenation Activity

The effect of temperature was quite distinct for the nonselective catalyst and the shape-selective catalyst. The nonselective catalyst, which was prepared by pretreatment with hydrogen only at 300°C, exhibited decreasing conversions at higher temperatures, as shown in Table 5. In contrast, the activity and selectivity of the shape-se-

TABLE 5
Effect of Temperature on Conversion

Catalyst	Temperature (°C)	% Hydrogenation	
		Hexene	diMe hexene
Nonselective Pt/ZSM-5	200	44.0	59.4
	250	39.5	47.9
	275	29.9	38.9
Selective Pt-ZSM-5	200	11.4	0.2
	250	82.7	0.3
	275	90.0	0.2

lective catalyst increased with increasing temperature.

The reduced activity of the nonselective catalyst at higher temperatures may be attributed to olefin-platinum complex equilibria, with higher temperatures favoring dissociation. A similar effect has been reported for platinum on alumina at temperatures above 200°C (18). The equilibria are apparently shifted for platinum located within the zeolite favoring complex formation even at higher temperatures, and consequently no decrease in activity with temperature was observed. At higher temperatures, therefore, the intrazeolitic platinum appears to be more active than external platinum (18).

Selective Hydrogenation of other Olefins

To confirm the reliability of the competitive hydrogenation test developed, the competitive hydrogenation of other olefinic mixtures was investigated. The results are shown in Table 6.

Styrene was selectively hydrogenated in the presence of 2-methylstyrene, a molecule deemed to diffuse relatively slowly in ZSM-5, as evidenced by the reported selective *para* ethylation of toluene over H-ZSM-5. In contrast, no hydrogenation selectivity was observed with a 0.5% Pt on alumina catalyst.

Small-Crystal ZSM-5

The data presented to this point was all obtained on a catalyst prepared from a large-crystal ZSM-5. To determine whether platinum would also behave in a shape-selective manner in a small-crystal ZSM-5, a cesium back-exchanged Pt(NH₃)₄²⁺-ZSM-5 sample was prepared. Pretreatment of this catalyst in the presence of olefins and hydrogen did indeed result in a shape-selective hydrogenation catalyst, as shown in Table 7. Furthermore, extended thermal treatment in hydrogen at 450°C enhanced the selectivity, indicating that platinum once formed inside the zeolite does not migrate rapidly to the external surface, even in the case of a small-crystal ZSM-5, whereas external platinum undergoes some agglomeration. In a competitive experiment, styrene was completely hydrogenated, while less than 10% of the 2-methylstyrene was converted.

Addition of a bulky phosphine, tri-*p*-tolyl phosphine, equivalent to 17 mol P/mol Pt on the sample, greatly suppressed the hydrogenation of 2-methylstyrene as expected; some decrease in styrene conversion was also noted. The extremely high

TABLE 6
Shape-Selective Competitive Hydrogenations

Linear olefin	Branched olefin	Temperature (°C)	% Hydrogenation	
			Linear	Branched
Pentene-1	4,4-Dimethylpentene-1	300	97	2
Heptene-1	4,4-Dimethylpentene-1	300	91	1.1
Hexene-1	6-Methylheptene-1	300	25	2
Styrene	2-Methylstyrene	425	50	2

TABLE 7
 Selective Hydrogenation over a 1.6% Pt/Cs-ZSM-5 Catalyst

Treatment	Temperature (°C)	WHSV	% Styrene hydrogenation	% 2-Methyl styrene hydrogenation
Olefin + H ₂ to 450°C	350	8	97	18
Additional 16 h in H ₂ at 450°C	350	20	99	9
Addition of tri- <i>p</i> -tolyl phosphine	350	20	79	0.5
Second addition of phosphine	350	8	93	1
	350	8	64	0.5

shape-selectivity remaining clearly supports the presence of intrazeolitic platinum. It is reasonable that such intracrystalline platinum would be less susceptible to poisoning by large hetero-substituted compounds and less effected by deactivation due to coking.

To determine whether cesium ion was required in order to obtain a shape-selective hydrogenation catalyst, an ammonium platinum containing small-crystal ZSM-5 sample was prepared. After pretreatment at 450°C in the presence of olefins and hydrogen, shape-selective hydrogenation was indeed observed. At 375°C, 48% hydrogenation of styrene was obtained, whereas only 2% of the 2-methylstyrene was hydrogenated. However, this catalyst was substantially less active than the cesium-containing catalyst, suggesting that some platinum migration and agglomeration had occurred.

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