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Paraffin Dehydrocyclization: Isotope Effect and Competitive Conversion of Alkane/Naphthene Mixture with a Pt–Mg(Al) Oxide Catalyst

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The kinetic isotope effect and the lack of deuterium–hydrogen exchange in the unconverted reactants show that chemisorption of the reactant is the slow step of the dehydrocyclization mechanism with a Pt–SiO$_2$ catalyst. While the chemisorption was nearly irreversible for a Pt–SiO$_2$ catalyst, this was not the case for a Pt–Sn–SiO$_2$ and Pt–Mg(Al)O catalysts. Data from the competitive conversion of a mixture of n-C$_8$H$_{18}$ and n-C$_8$D$_{18}$ show that there is a kinetic isotope effect for the dehydrocyclization reaction and that the magnitude of the effect for Pt–Mg(Al)O ($\sim$2.0) falls between those of Pt–SiO$_2$ and Pt–Sn–SiO$_2$. The slight reversibility of the chemisorption step indicates that the Mg(Al)O support interacts with Pt but not to the extent that tin does in a silica-supported catalyst with a Pt : Sn = 1 : 1 ratio. The kinetic isotope effect for Pt–Mg(Al)O is about 2 and is comparable to the one obtained with a Pt–Sn–SiO$_2$ catalyst but is considerably lower than the value of 3.5 obtained with a Pt–SiO$_2$ catalyst. © 1997 Academic Press

INTRODUCTION

A number of reactions occur during naphtha reforming and the most important are the aromatization reactions: dehydrogenation of cycloalkanes, dehydroisomerization of alkyl cyclopentanes, and dehydrocyclization of acyclic hydrocarbons (1). The most rapid and thermodynamically favorable reaction is dehydrogenation of six-carbon cyclohexane rings and conventional reforming catalyst accomplish this reaction with almost perfect selectivity (1). Likewise, there are catalysts that are highly selective for the dehydroisomerization of alkylcyclopentanes. However, the selectivity for the dehydrocyclization of alkanes is much poorer, and the situation becomes even worse for the C$_6$–C$_7$-alkanes (2). It was therefore a distinct advance when Chevron Research Company announced the development of a molecular sieve material that had a high selectivity for the dehydrocyclization of these lower carbon number alkanes and which could function in a refinery process (2–4). The Chevron development followed from the observation by Bernard that a Pt/KL zeolite catalyst is a much more active and selective for the aromatization of n-hexane than conventional naphtha reforming catalysts (5, 6).

The announcement of the Chevron Aromax Catalyst caused much attention to be directed toward determining the reason why the Pt/KL zeolite catalyst exhibits superior selectivity. Two prominent views attributed this selectivity to unique properties that Pt possesses when incorporated in the zeolite: one of these proposed a shape selective “molecular die” (7, 8) or an “enzyme-like” complex confined to a specific structure (9, 10) and to electron-deficient or electron-enriched Pt sites (11–15). However, other workers showed that selective aromatization also could occur when Pt was supported on other materials with less stringent spatial requirements; these materials included dealuminated Y-zeolite (16), undeactivated Pt/SiO$_2$ (17), and Pt/Mg(Al)O (18). Iglesia *et al.* (19) consider the Pt to be the same, or nearly so, when it is supported on SiO$_2$ or located within the KL-zeolite cavity. Rather than special electronic or spatial requirements these authors attribute the special selectivity for hexane dehydrocyclization to Pt without carbon and the KL zeolite is very adept at providing this protection to Pt.

Iglesia and Baumgartner (17) reported a small kinetic isotope effect that was similar for Pt–KL zeolite (1.15–1.25) and fresh Pt–SiO$_2$ (1.35–1.45). These authors compared the rates of separately converting heptane and deuterated heptane. These are only slightly higher than the values of 1.0 reported for n-heptane dehydrocyclization (20). Iglesia and Baumgartner reported a much smaller (negative) kinetic isotope effect (0.75–0.8) for the steady-state Pt–SiO$_2$ catalyst. A large kinetic isotope (3.3–4.0) effect was reported for the Te–NaX zeolite catalyst where it was claimed that aromatization occurred by a pathway that includes the consecutive dehydrogenation of n-heptane to a triene followed by a thermal cyclization (19).

Based upon data for the competitive conversion of a mixture of a cyclohexane or alkyl cyclohexane and an n-alkane, the mechanism was considered to require either adsorption of the reactants or desorption of the aromatic products as the rate limiting step (20). Extending these studies, Shi and Davis (21) found that essentially no H/D exchange occurs in the reactants at 482°C compared to that which occurs at

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350°C. The lack of exchange in the reactants and exchange in the products that is consistent with a H/D statistical distribution were considered to demonstrate that a competitive and essentially irreversible adsorption of the reactant was the rate limiting step. It was found that, under similar reaction conditions, more exchange occurred in the alkane reactant with the Pt–Sn–SiO_2 catalyst than was observed with the Pt–SiO_2 catalyst, showing that the Sn altered the Pt so that some H/D exchange occurred (22). Furthermore, unlike some of the earlier studies, a large (about 3.5) kinetic isotope effect was found for the Pt–SiO_2 catalyst (21). In view of the differences that were observed for the Pt–SiO_2 and Pt–Sn–SiO_2, it appeared desirable to undertake studies to determine the kinetic isotope effect for a Pt–Mg(Al)O catalyst, and that is the topic of this paper.

EXPERIMENTAL

The reaction was carried out at 482°C in a conventional flow apparatus. The catalyst occupied a length that was more than three times the diameter of the glass reactor. A thermowell extended into the middle of the catalyst bed. Runs were effected at atmospheric pressure. The liquid hourly space velocity (LHSV) was 1.65 unless stated otherwise. Liquid products were collected at intervals and analyzed using gas chromatographs with a 60-ft capillary DB-5 column. The deuterium content was calculated from relative ion intensities in the parent ion masses, obtained from GC-MS operated at 70 eV after correcting for the natural abundance of ^{13}C ($M+1$ and $M+2$ peaks).

Catalyst. The Mg(Al) oxide was prepared by precipitation from a 1 *M* solution of Mg plus Al that was prepared by adding magnesium and aluminum nitrates to provide a Mg : Al atomic ratio = 5 : 1 (18, 23–26). A solution of potassium carbonate and potassium hydroxide was added with stirring to the Mg(Al) nitrate solution that was heated at 60°C. The amount of potassium carbonate that was added was equal to one-half the moles of Al. The potassium hydroxide solution (0.01 *M*) was added in an amount and at a rate so as to maintain the pH in the range of 8.5 to 9.5. The precipitate was collected by filtration and was washed three times with distilled water (repeated redispersion/filtration cycles). After drying at 80°C overnight, the precipitate was impregnated with an aqueous solution of $Pt(NH_3)_4Cl_4$. The solid was dried at 100°C and then calcined in air at 600°C for 3 h. This material had a BET surface area of 250 m^2/g. The final catalyst contained 0.38 wt% platinum. The sample was treated in a H_2/He flow at 400°C for 6 h and the sample was then evacuated at 400°C before being cooled for the adsorption measurements using either hydrogen or carbon monoxide. Hydrogen was adsorbed at 0°C and CO was adsorbed at 23°C. The fraction of surface platinum was calculated to be 0.098 for hydrogen adsorption and 0.145 for CO.

Prior to the activity measurements, the catalyst was reduced *in situ* in flowing hydrogen at 482°C for about 18 h. For runs where hydrogen was added, the flow was adjusted to the appropriate value before introduction of the reactant using a syringe pump. When hydrogen was not added during the run, the flow was terminated when the flow of the hydrocarbon was started.

Reagents. *n*-Octane-d_{18} was purchased from Cambridge Isotope Laboratories and the unlabeled materials were purchased from Aldrich Chemical Company. All reagents used in this study were 99% or higher purity and were used without further purification.

RESULTS

The conversions, based upon disappearance of each reactant, of a mixture of methylcyclohexane (MCH) and *n*-octane-d_0 (C_8) (MCH/$C_8 = 1.2$) show that MCH is converted more rapidly than C_8 (Table 1, Fig. 1). The data provided for conversion are based on weight of catalyst (left axis) and on surface Pt atom (right axis) based on the hydrogen chemisorption measurements. For a Pt–SiO_2 or Pt–Al_2O_3 catalyst, the conversion ratio of MCH/C_8 is about 1.2 for an equimolar mixture of these two reactants (20). The uncorrected MCH/C_8 conversion ratio with the Pt–Mg(Al)O catalyst was about 4 (Fig. 2); correcting for the slight excess of MCH in the reaction mixture decreases this ratio to 3.4. Thus, the Pt–Mg(Al)O catalyst does not appear to adhere to the essentially equal chemisorption probability for MCH and C_8 that was observed with the Pt–SiO_2 and Pt–Al_2O_3 catalysts (20).

The Pt–Mg(Al)O catalyst is only slightly more active for converting MCH alone than it is when it is present in the MCH/C_8 mixture. If we correct the MCH conversion obtained with the mixture for the molar ratio difference (dividing by 1.17) and for the difference in the space velocities utilized (1.6 for the mixture and 2.6 for MCH alone) we observe that MCH alone is converted only about twice as rapidly as when it was converted in the mixture (Fig. 3).

TABLE 1

Conversion of Methylcyclohexane and Normal Octane in Percentage

Time (h)	Conversion of MCH	Conversion of normal octane
1	49	14
1.5	38	8.8
2	38	8.7
2.5	38	9.6
3	36	11
3.5	34	6
4	31	6.8
4.5	31	9.4
5	27	6.9

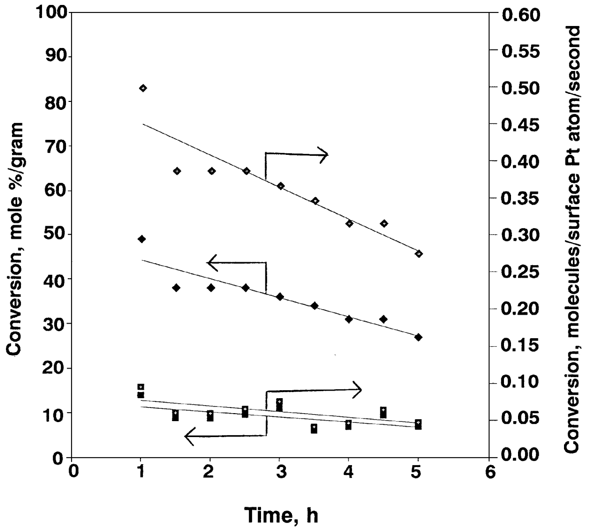

FIG. 1. The conversion of methylcyclohexane (MCH) (◆) and *n*-octane (C_8) (■) at increasing times on stream (482°C; 1 atm, no added H_2; LHSV = 1.65; MCH/C_8 = 1.17; left axis, conversion per gram catalyst; right axis, conversion per surface Pt atom).

Furthermore, the catalyst deactivation rate appeared to be about the same with pure MCH as it was with the MCH/C_8 mixture. In this respect the Pt–Mg(Al)O catalyst differs from that of the Pt–SiO_2 or Pt–Al_2O_3 catalysts where the MCH alone was converted at least 20 times more rapidly than in the mixture and that the decline in activity for the conversion of MCH alone was much slower than the aging rate when converting the mixture (20).

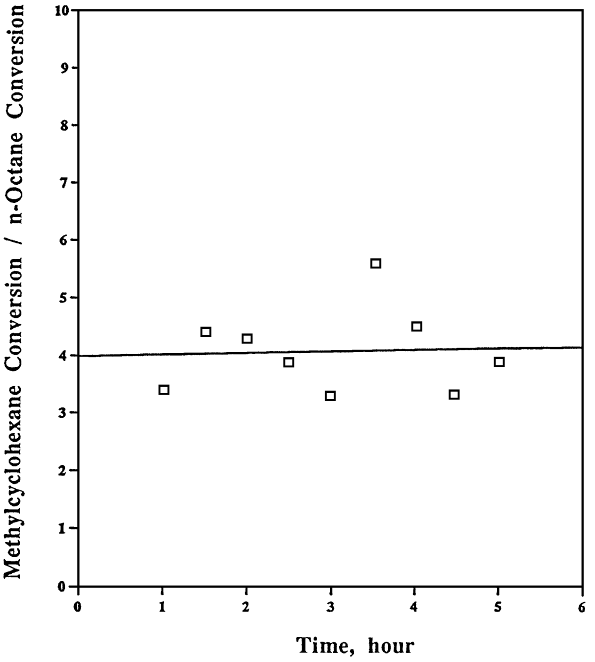

FIG. 2. The ratio of the conversion of MCH/C_8 with increasing time on stream.

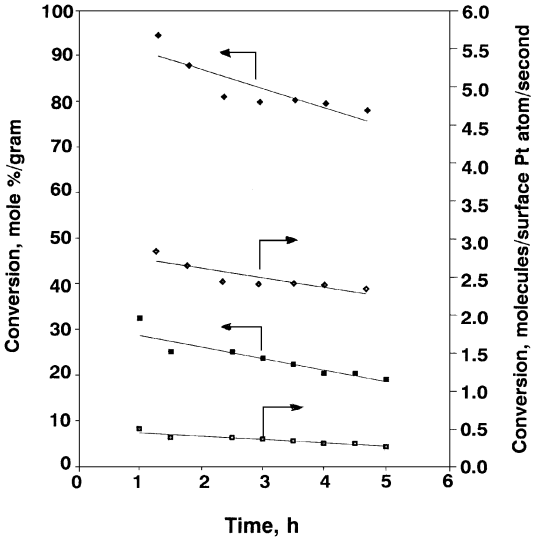

FIG. 3. The comparison of the conversion of methylcyclohexane alone (◆) (482°C; 1 atm, no added H_2; LHSV = 2.6) and in a mixture with C_8 (■) (482°C; 1 atm, no added H_2; LHSV = 1.65 (adjusted to 2.6; left axis, conversion per gram catalyst; right axis, conversion per surface Pt atom)).

During the early periods of time on stream, it appears that C_8 is converted to products other than aromatics. While the ratio of MCH/C_8 conversion is essentially constant during the entire reaction period (Fig. 2), the ratio of toluene/C_8-aromatics declines with time on stream (Fig. 4). Thus, only after about 5 h of conversion does the ratio of

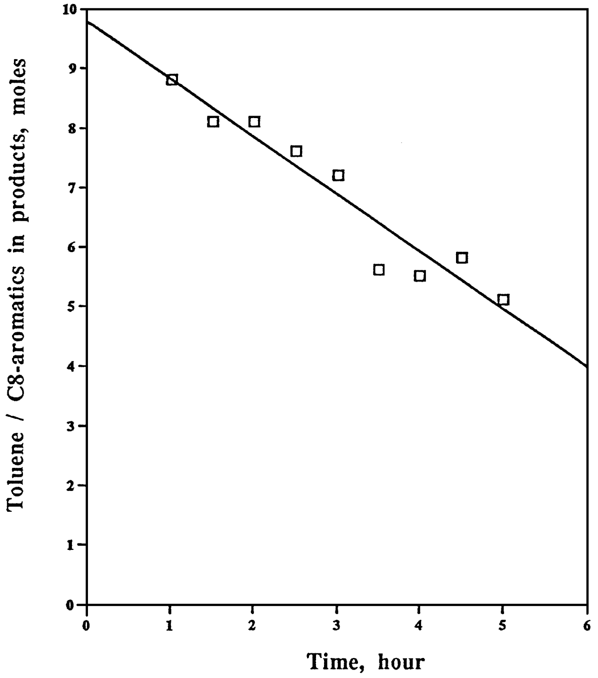

FIG. 4. Ratio of the amount of toluene and C_8-aromatics produced with increasing time on stream.

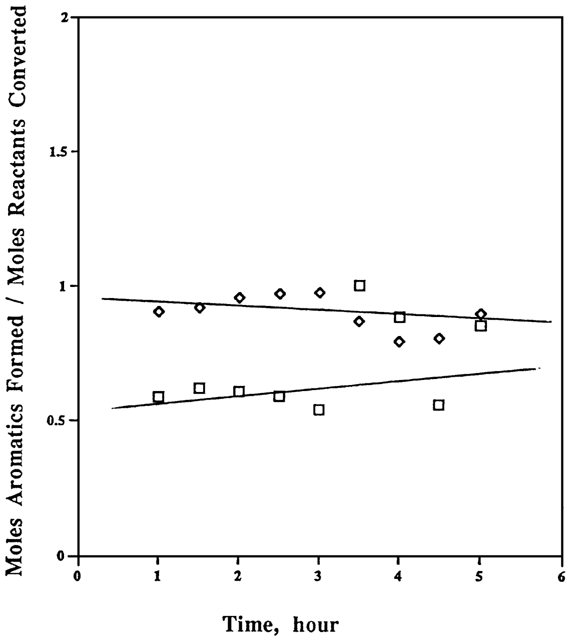

FIG. 5. The ratios for toluene formed MCH conversion (◇) and C_8-aromatics formed C_8 conversion (□) with increasing time on stream.

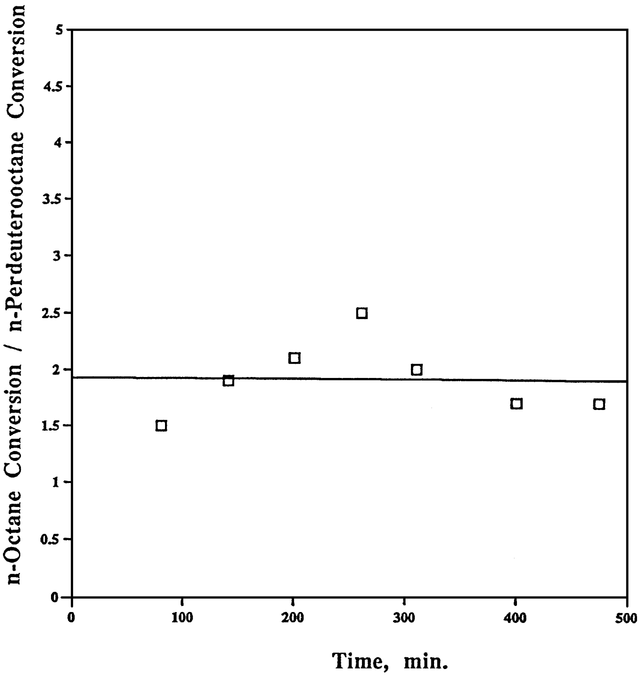

FIG. 6. The ratio for the conversion of *n*-octane-d_0 and *n*-octane-d_{18} with increasing time on stream.

toluene/C_8-aromatics approach the value of 4 that would be anticipated if the products from the conversion of both reactants produced only aromatics. The ratio of toluene produced/MCH converted remains essentially constant with a value of about 1.0 but a line through a plot of C_8 aromatics produced/C_8 converted versus time extrapolates to about 0.5 at zero time and increases toward the expected value of 1 after 5 h on stream (Fig. 5).

With platinum supported on silica or nonacidic alumina the conversion of *n*-octane produces approximately equal amounts of ethylbenzene and *o*-xylene. The addition of tin to the platinum catalyst causes the ratio of these two aromatics change from 1 for Pt–SiO_2 or Pt–Al_2O_3 to approach a value of *o*-xylene/ethylbenzene = 2 for the optimum Sn/Pt ratio (27). Samples collected during 2 to 5 h on stream show a nearly constant ratio of *o*-xylene/ethylbenzene = 1.3.

An equimolar mixture of *n*-octane-d_0 and *n*-octane-d_{18} was passed over the Pt–Mg(Al)O catalyst under the same reaction conditions as used for converting the MCH/C_8 mixture. The relative conversions of the undeuterated and deuterated isotopomers allowed a calculation of a kinetic isotope effect (k_H/k_D) of about 2 (Fig. 6). This kinetic isotope effect is considerably lower than was obtained under similar reaction conditions with a Pt–SiO_2 catalyst where this ratio was about 3.5 (28).

There is a small amount of exchange in the unconverted *n*-octane-d_0 and *n*-octane-d_{18}. The pattern of this slight amount of exchange is consistent with a sequential exchange mechanism that involves a single H(D) at a time. The exchange of *n*-octane-d_{18} is greater than in *n*-octane-d_0 even though the conversion of the former isotopomer is only about half that of the latter (Fig. 7); however, this is expected since the surface concentration of H will exceed that of D because of the difference in the conversion of

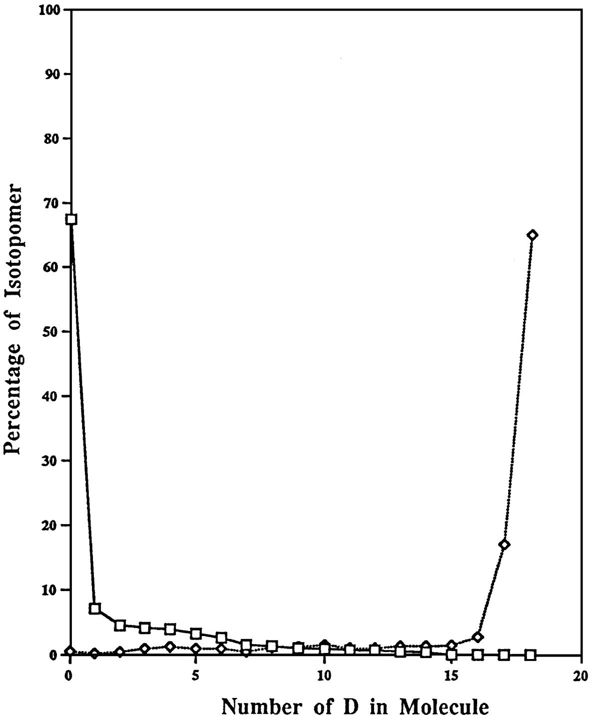

FIG. 7. The deuterium content of the unconverted *n*-octane-d_0 (□) and *n*-octane-d_{18} (◇).

the two isotopomers. The extent of exchange in both of the unconverted reactants declines monotonically; that is, the monoexchanged species is present in greater amount than the diexchanged species than the triexchanged, etc. However, the amount of H/D exchange in the unconverted C_8 is far removed from that required by isotope equilibration. If adsorption/desorption of octane is established and exchange occurred by one atom at a time, a binomial distribution would be obtained at any time during the reaction (29). However, a major conclusion of our studies (20–22, 28) is that, while adsorption of the *n*-octane is reversible at low (e.g., 300°C) temperatures, adsorption is nearly irreversible at higher temperatures (greater than 450°C). It is important to emphasize that one must not interpret the current data on the basis of a mechanism involving adsorption/desorption equilibria of the *n*-octane. Thus, in light of the nearly irreversible adsorption of *n*-octane, it is anticipated that even though the exchange occurs in a sequential manner, multiple exchange will occur prior to desorption of a small fraction of the alkane present on the Pt surface. The fact that the multiply D-labeled *n*-octane decreases so rapidly compared to the desorbed octenes and aromatics indicates that the conversion to an adsorbed species that does not again desorb as *n*-octane is rapid compared to the sequential exchange. This is not the case for the C_8-aromatics. Both ethylbenzene and *o*-xylene have the same isotope distribution (Fig. 8). Furthermore, the most dominant C_8-aromatic isotopomer is $C_8H_7D_3$; this is consistent with the surface of the Pt being enriched in the H-isotope as would be expected since about two times as much *n*-octane-d_0 is converted as *n*-octane-d_{18}. In addition, it is anticipated, based upon the relative conversion of the two *n*-octane isotopomers, that the H/D ratio on the surface would be 2 and the D content of the C_8-aromatics is consistent with this ratio provided the aromatics have equilibrated to produce a statistical isotope distribution.

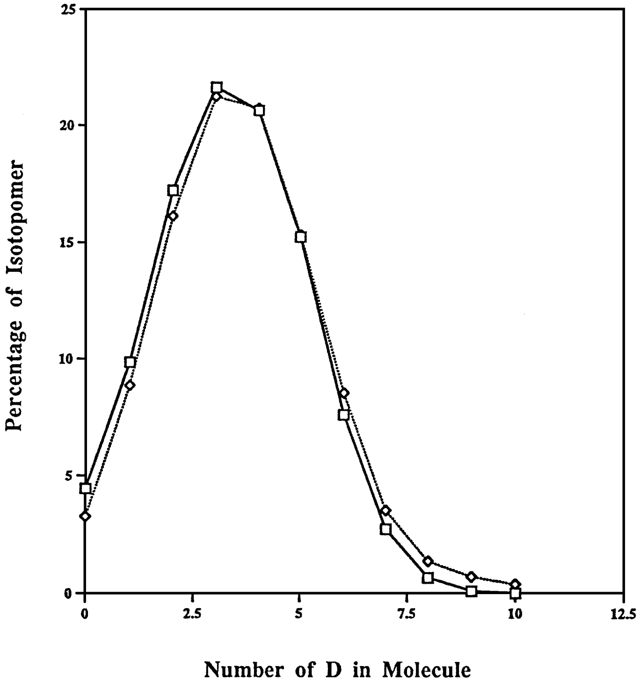

FIG. 8. The deuterium isotope distributions in ethylbenzene (◇) and *o*-xylene (□) during the conversion of an equimolar mixture of *n*-octane-d_0 and *n*-octane-d_{18}.

DISCUSSION

The catalyst used in the present study contained 0.38 wt% Pt and had a dispersion of 9.8% (determined using H_2) or 14.5% (determined using CO). Based on the dispersion obtained from hydrogen adsorption, the catalyst activity for *n*-octane dehydrocyclization falls in the range of 0.25–0.40 molecule (surface Pt atom)$^{-1}$ s^{-1}. The catalyst used in this study was prepared following the procedure given by Davis and Derouane (25). They reported as surface area of 220 m^2/g compared to the value of 250 m^2/g for our catalyst. The dispersion (ratio of H atoms/Pt atoms) reported by Davis and Derouane was 0.49 in contrast to the value of 0.098 obtained in the present study. However, the catalyst reported in Ref. (25) contained 0.88 wt% Pt compared to the 0.38 wt% Pt for the catalyst used in this study. Unless some amount of the Pt is stabilized by the support in the form that does not adsorb H, the reason for the difference in dispersion for the two catalysts is not apparent.

We estimate that the catalytic activity for *n*-hexane aromatization in Ref. (25) is about 0.09 molecules (surface Pt atom)$^{-1}$ s^{-1}. Thus, considering the easier conversion of *n*-octane to aromatics, the activity difference observed in the two studies is reasonable. Davis and Derouane (25) speculated that the basic nature of the support could influence directly the electronic properties of the metal clusters. A metal–support interaction could, according to Davis and Derouane, account for the high selectivity for the PtMg(Al)O catalyst for the aromatization of *n*-hexane. If this is the case, the extent of the metal–support interaction must be dependent upon Pt loading.

The properties of Pt–Mg(Al)O for the conversion of alkanes and cycloalkanes fall between those of supported monometallic catalyst (Pt–SiO_2 and Pt–Al_2O_3) and the bimetallic (Pt–Sn–SiO_2 and Pt–Sn–Al_2O_3). The order of activity for the conversion of alkanes at 482°C at atmospheric pressure are

$$\text{Pt–Al}_2\text{O}_3 \approx \text{Pt–SiO}_2 < \text{Pt–Mg(Al)O} < \text{Pt–Sn–SiO}_2.$$

At atmospheric pressure the total conversion of the alkane feed is about the same whether Pt is supported on acidic or nonacidic alumina. However, the selectivity for formation of aromatic products is much lower for the catalyst based on the acidic alumina due to the secondary cracking reaction that leads to lower carbon number products instead of aromatics. This is not the case at higher pressures with added hydrogen since the bifunctional cyclization pathway provides a much more rapid route for aromatics production than the direct six-carbon ring formation pathway (30).

The extent of H/D exchange in the unconverted hydrocarbon reactants is in the order of

$$\mathrm{Pt{-}SiO_2 < Pt{-}Mg(Al)O < Pt{-}Sn{-}SiO_2 < Pt{-}Al_2O_3}.$$

In considering this ranking one should remember that the alumina, either acidic or nonacidic due to the incorporation of potassium ions, is as good, or perhaps even better, catalyst for promoting the H/D catalytic exchange reaction than is the same material containing Pt (21). Our previous studies on the exchange of H/D in reactants and products combined with the determination of kinetic isotope effects have shown that the initial chemisorption step is rate determining and that this step has a large kinetic isotope effect for the conversion at temperatures above about 450°C. The data obtained in the present study combined with our earlier studies appear to require the activation energy for the desorption step be lowered so as to accommodate the observed increased exchange. Our evidence suggests that this decrease be in the order

$$\mathrm{Pt{-}SiO_2 < Pt{-}Mg(Al)O < Pt{-}Sn{-}SiO_2}.$$

Thus, it appears that the effect of Pt modification, either by an added promoter or a change in support, is to lower the activation energy of the first step in the reaction rate coordinate.

The change in the C_8-aromatic ratio of *o*-xylene/ethylbenzene from 1 to approach 2 also occurs in the order of $\mathrm{Pt{-}SiO_2 < Pt{-}Mg(Al)O < Pt{-}Sn{-}SiO_2}$. Thus, it appears that the overall rate of alkane conversion, the extent of H/D exchange and the selectivity for aromatic isomer formation are all controlled by a common factor. Extensive characterization studies have shown that essentially all of the Pt that is present in a $\mathrm{Pt{-}Sn{-}Al_2O_3}$ (Pt : Sn = 1 : 1) is present as an alloy that is dominated by the Pt : Sn = 1 : 1 alloy (32, 33). Alloy formation leads to changes in both the electronic and the geometric arrangement (ensemble effect) from that when Pt is present alone in $\mathrm{Pt{-}SiO_2}$. It therefore appears that any comparison of the silica supported Pt and Pt–Sn catalysts will involve both factors and the best that can be determined is whether one factor dominates. In this sense, electronic and ensemble effects are analogous to acid/base catalysis since it is not possible to have the acid without a conjugate base being present, and vice versa. Thus, when we describe acid catalysis, we mean the conjugate base is weak, and not that a base is not present. Without question, tin accumulates on the surface of the Pt–Sn alloy in excess of that in the bulk. This means that the alloy will have Pt surface atoms separated to a much greater extent than in the Pt only catalyst. Furthermore, the Pt–Sn alloy will have bulk electronic properties that differ from Pt alone. Thus, unless one can show that the local electronic character of a surface Pt atom surrounded by Sn atoms in the 1 : 1 alloy has the same electronic character of a surface Pt atom surrounded by Pt atoms in the Pt catalyst, electronic factors must be involved in the differences in the catalytic properties of the Pt and the Pt–Sn catalysts.

If the shape selectivity imposed by the zeolite structure can be eliminated as the source of the special selectivity of Pt for *n*-hexane conversion as indicated in Refs. (16–19), then the Pt supported on Mg(Al)O has electronic/ensemble properties that fall between those of Pt alone and Pt in a Pt–Sn alloy. For *n*-octane aromatization, the Pt–KL zeolite catalyst offers little, if any, advantage over the $\mathrm{Pt{-}SiO_2}$ or $\mathrm{-Al_2O_3}$ catalysts. Thus, unless the Pt in the Pt–Mg(Al) and Pt–KL zeolite catalysts have the same properties, the present data do not contribute to an understanding of the Pt–KL zeolite catalyst.

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