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Dehydrocyclization of *n*-Octane: H/D Exchange and Reversible Adsorption for a Pt–Sn–SiO_2 Catalyst

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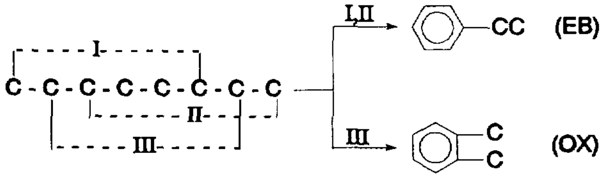
With a Pt–SiO_2 catalyst *n*-octane underwent dehydrocyclization in the presence of D_2 or with an equimolar mixture of *n*-octane-d_0 and *n*-octane-d_{18} without a measurable extent of H/D exchange in the unconverted *n*-octane. When similar experiments were conducted with a Pt–Sn–SiO_2 H/D exchange occurred. The results suggest that tin functions to decrease the strength of chemisorption of *n*-octane at 482°C so that adsorption is reversible in contrast to the irreversible adsorption for a Pt–SiO_2 catalyst. The presence of tin allows H/D exchange to occur in the unconverted *n*-octane. © 1995 Academic Press, Inc.

INTRODUCTION

One of the most widely held reaction mechanisms for the dehydrocyclization of alkanes involves the formation of aromatics in a sequential series of reactions—the alkene, diene, triene, then a cyclohexadiene intermediate, and finally the aromatic product [e.g., (1)]. Many studies involving the addition of ^{14}C-labeled compounds that were considered to be a reasonable intermediate for alkane dehydrocyclization have been reported to show results that are considered to support this type of mechanism (1–22). Data for the dependence of the conversion of an alkane upon the hydrogen partial pressure have also been considered to support the sequential dehydrogenation reaction pathway [for example, (18–23)].

On the other hand, the competitive conversions of a mixture of a cyclohexane and an *n*-alkane were consistent with a mechanism of dehydrocyclization in which either adsorption of the reactant(s) or desorption of the aromatic(s) was the rate-limiting step (24). Recently, studies have been conducted using a mixture of methylcyclohexane-d_{14}/*n*-octane-d_0, methylcyclohexane-d_0/*n*-octane-d_{18}, or methylcyclohexane-d_0/*n*-octane-d_0/D_2 (25). The results showed that essentially no H/D exchange occurred in the hydrocarbon reactants but that the alkene and aromatic products contained a H/D distribution that approached that expected for nearly an equilibration of H and D in the products and the gaseous H_2 (25). The lack of exchange in the reactants and the extent of exchange in the products were considered to show that competitive adsorption of the reactant(s) was the rate-limiting step for dehydrocyclization.

Dehydrocyclization of *n*-ocxtane can produce ethylbenzene and *o*-xylene by a mechanism that involves the direct formation of a six-member carbon ring (26):



If each of the above three steps are equally probable, the aromatic products should consist of EB : OX = 2 : 1. This ratio has been approached for Pt–SiO_2 catalysts but a ratio of EB : OX = 1 : 1 is usually obtained for Pt supported on nonacidic alumina (27). The addition of increasing amounts of tin to a Pt–nonacidic-alumina catalyst does two things: increase the catalytic activity and alters the EB : OX ratio of the aromatic products from that obtained with the tin-free catalyst (28). Thus, for a catalyst with Pt : Sn = 1 : 4, the EB : OX ratio approached 1 : 2. In one view, this change would involve an alteration of the Pt electron density as tin is added. This in turn would alter the ability of Pt to rupture the C–H bond to favor the rupture of the weaker C–H bond of the secondary hydrogens of the $-CH_2$ groups over those of the primary hydrogens of the $-CH_3$ groups. If the addition of Sn to the Pt catalyst caused the alkane to be less strongly adsorbed as the Pt/Sn ratio was increased, it is likely that H/D exchange would occur as the tin altered the catalyst properties.

The selectivity of a catalyst has been attributed to the influence of an electronic or geometric effect. Bond and Sermon (29), for example, advanced the view that very small metal crystallites may be altered by electron transfer with the support. Davis *et al.* (30) attributed the change in the aromatic distribution obtained from the dehydrocyclization of *n*-octane using catalysts with various loading of Pt on carbon to an electronic effect. It was also shown (28) that both metals, such as tin, and gaseous promoters

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could alter the aromatic product distribution for the dehydrocyclization of *n*-octane.

Davis and co-workers (28) considered the selectivity results to be determined by an electronic factor. Balandin (31) was an early proponent of the geometric effect. Biloen *et al.* (32) considered that the beneficial effect of different catalyst modifiers (such as gold, tin, sulfur, carbon) was largely due to one common cause, namely, the division of the platinum surface into very small ensembles of platinum atoms. Dautzenberg *et al.* (33) considered that the improved stability of PtSn catalysts could be the result of a change in adsorption properties due to differences in the number of adjacent platinum atoms, an ensemble effect. While it is inviting to place emphasis upon an electronic or geometric effect, just as one considers acid or base catalysis, it must be realized that the electronic and geometric effects are interrelated and cannot be varied separately, just as a reaction cannot be carried out in the presence of only an acid or a base.

EXPERIMENTAL

The reaction was carried out in a conventional flow apparatus described previously (28). Runs were effected at atmospheric pressure and a liquid hourly space velocity (LHSV) of 1.0. Liquid samples were collected at intervals and analyzed by gas chromatography using a DB-5 or SPB-5 column. The deuterium content was obtained using a GC/MS operated at 70 eV.

D_2 gas was purchased from Cambridge Isotope Laboratories and unlabeled materials and C_8D_{18} were purchased from Aldrich Chemical Co., Inc. All of the reagents used in this study were 99% pure or higher and were used without further purification.

$Pt-SiO_2$ (1 wt% Pt) was prepared by the incipient wetness technique using an aqueous solution of H_2PtCl_6 and SiO_2 (200 mesh; 300 m^2/g) obtained from W. R. Grace. For $Pt-Sn-SiO_2$ the silica was impregnated with an acetone solution containing H_2PtCl_6 and $SnCl_2 \cdot 2H_2O$ in amounts so that the final catalyst would contain 1 wt% Pt and a mole ratio Pt/Sn = 1:1. The acetone was removed using a rotovap. The dried catalyst was calcined in air at 400°C overnight and then reduced in flowing hydrogen at 482°C for at least 4 h.

RESULTS

In the initial runs, a mixture of D_2/*n*-octane (3:1 mol ratio) was passed over the $Pt-Sn-SiO_2$ and the results differed from those obtained earlier with a $Pt-SiO_2$ catalyst (25). With the $Pt-SiO_2$ catalyst there was very little exchange in the unconverted *n*-octane, but there was exchange in the ethylbenzene produced during the reaction (Fig. 1); the distribution of deuterium in *o*-xylene was essentially the same as that shown in Fig. 1. Thus, with the $Pt-SiO_2$ catalyst deuterium adsorbed on the catalyst to mix with the H produced during the conversion of *n*-octane and to exchange with surface hydrocarbon species to produce a nearly symmetrical distribution of H/D in the ethylbenzene product. However, when a $Pt-Sn-SiO_2$ catalyst was used under similar conditions, neither the *n*-octane (Fig. 2) nor the aromatic products contain significant deuterium produced (Fig. 3). The curve in Fig. 3 is for the ethylbenzene product but the *o*-xylene data were essentially the same. The conversion of *n*-octane, and the formation of aromatics for the run using the $Pt-Sn-SiO_2$ catalyst that produced the aromatics shown in Fig. 3 was about

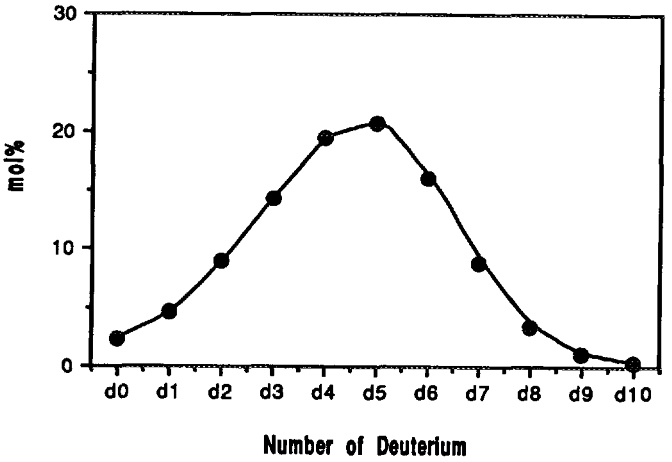

FIG. 1. Deuterium distribution in ethylbenzene produced during the conversion of a $D_2/n-C_8H_{18}$ (3:1 mol) mixture at 482°C and 1 atm with a $Pt-SiO_2$ catalyst.

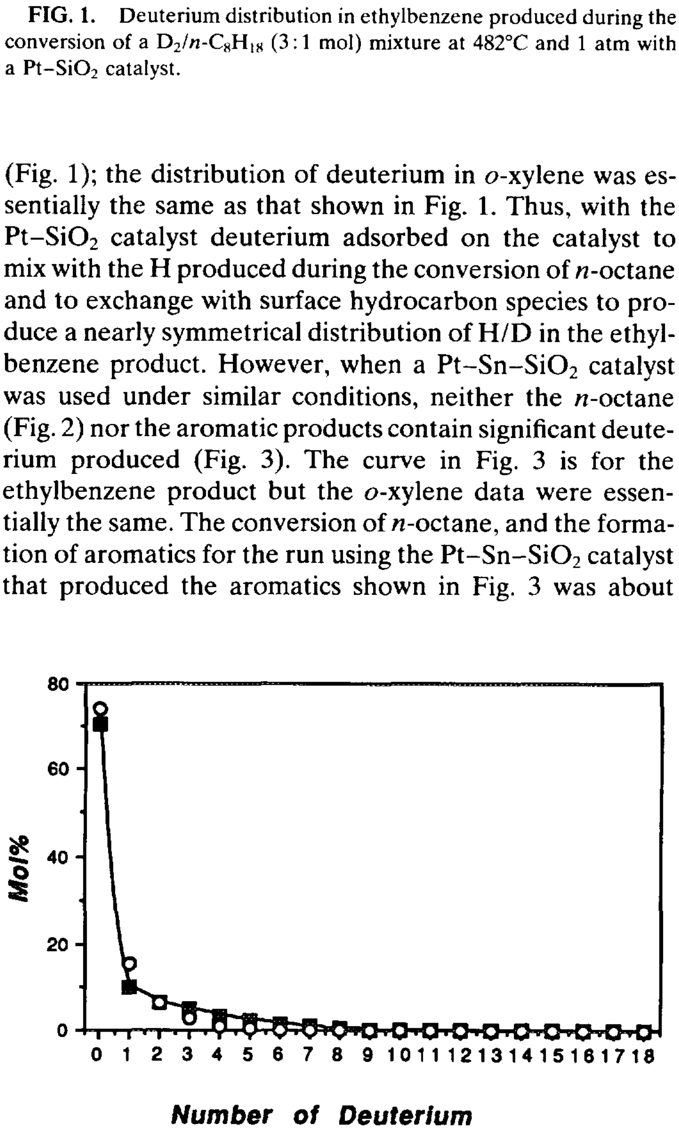

FIG. 2. Deuterium distribution in unconverted *n*-octane (reaction mixture $D_2:n-C_8H_{18}$ = 3:1) following exposure to a $Pt-SiO_2$ catalyst (■) and $Pt-Sn-SiO_2$ catalyst (○) at 482°C and 1 atm.

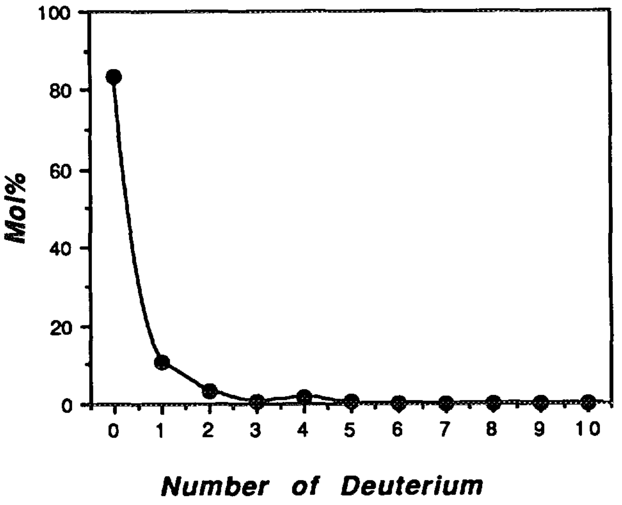

FIG. 3. Deuterium distribution in ethylbenzene produced during the conversion of a D_2/n-C_8H_{18} (3 : 1 mol) mixture at 482°C and 1 atm with a Pt–Sn–SiO_2 catalyst.

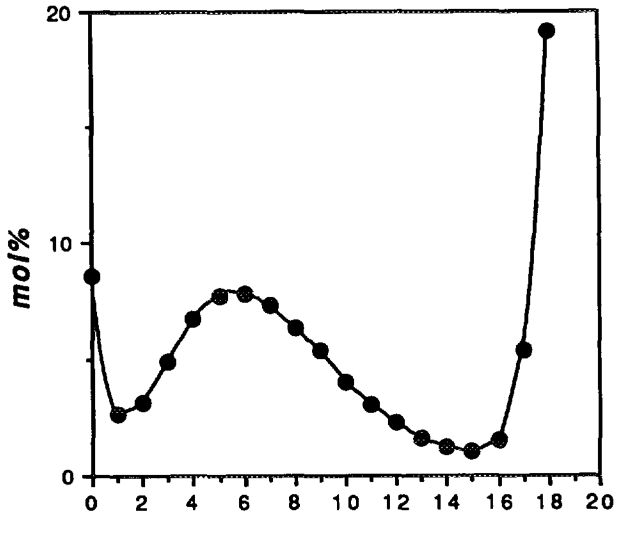

FIG. 4. Deuterium distribution in the unconverted n-octane (feed was equimolar mixture of n-C_8D_{18}/n-C_8H_{18} without added H_2 or D_2) passed over a Pt–Sn–SiO_2 catalyst at 482°C and 1 atm.

two times as great as that for the run with Pt–SiO_2 that produced the data in Fig. 1. The data in Figs. 1 and 3 show, despite the higher n-octane conversion with the Pt–Sn–SiO_2 catalyst and the resulting smaller D/H ratio, that D_2 is adsorbed to a smaller extent on the Pt–Sn–SiO_2 catalyst than it is on the Pt–SiO_2 catalyst.

The conversion of an equimolar mixture of C_8H_{18} and C_8D_{18}, without added H_2 or D_2, was carried out at 482°C and 1 atm pressure; flow rates were varied to effect n-octane conversions ranging from about 30 to 80%. For a flow rate that produces 31% conversion of n-octane, the data in Fig. 4 show that significant deuterium exchange has occurred in the unconverted n-octane when the Pt–Sn–SiO_2 catalyst was used. The data in Fig. 4 are in marked contrast to those obtained for a similar conversion level with the Pt–SiO_2 catalyst where the extent of H/D exchange in the n-octane was nearly zero (25). Furthermore, the data in Fig. 4 show that there is a kinetic isotope effect since C_8H_{18} conversion is significantly greater than that of C_8D_{18}, and the curve for the exchanged material is skewed toward the hydrogen side and attains a maximum at about d_5 rather than d_9. The two aromatic products exhibit extensive H/D exchange (Fig. 5). Again, the presence of measurable amounts of the d_0 isotopomer for both aromatics, and the much smaller amounts of the d_{10} isotopomer as well as the maximum at d_4, indicates a kinetic isotope effect.

Data are shown in Figs. 6 and 7 for the d_n isotopomer for the unconverted n-octane and for the aromatic products, respectively, for a flow that allows 86% n-octane conversion. The curves attain a maximum at d_8–d_9 for n-octane and at d_5 for both ethylbenzene and o-xylene. The data in Figs. 6 and 7 therefore show that the exchange occurs so as to approach a statistical distribution of H and D at high conversions. This observation supports the view of a kinetic isotope effect that caused the skewed isotope distributions shown in Figs. 4 and 5.

DISCUSSION

It has been established that H/D exchange does not occur in the unconverted reactant during dehydrocycliza-

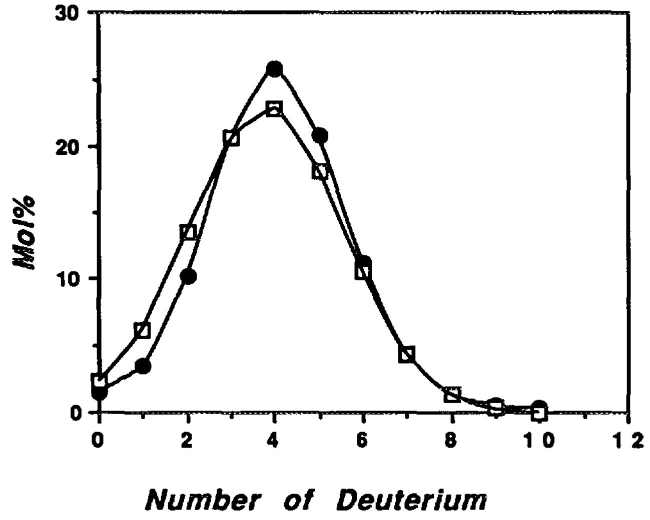

FIG. 5. Deuterium distribution in ethylbenzene (●) and o-xylene (□) produced during conversion (31%) of an equimolar mixture of n-C_8H_{18}/n-C_8D_{18} (no added H_2 or D_2) with a Pt–Sn–SiO_2 catalyst at 482°C and 1 atm.

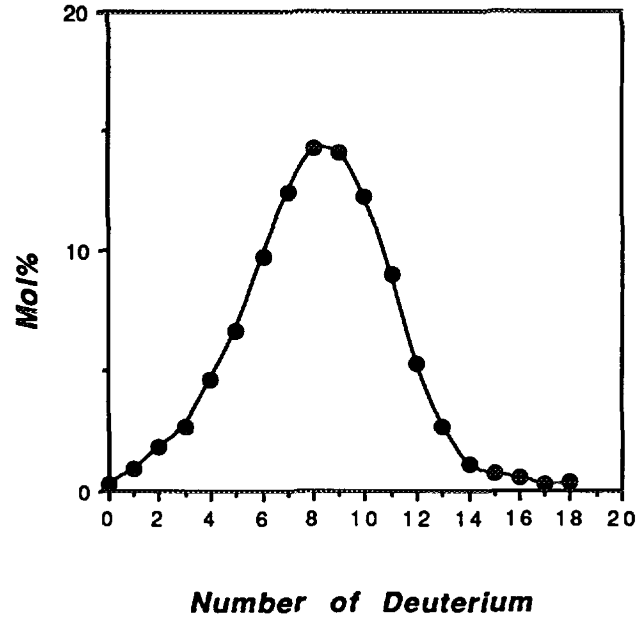

FIG. 6. Deuterium distribution in the unconverted (14% of charge) *n*-octane following contact of an equimolar mixture of $n\text{-}C_8H_{18}/n\text{-}C_8D_{18}$ (no added H_2 or D_2) with a $Pt\text{-}Sn\text{-}SiO_2$ catalyst at 482°C and 1 atm.

tion of *n*-octane at 482°C with a $Pt\text{-}SiO_2$ catalyst (25). This result and the results from the competitive conversion of alkane–cycloalkane mixtures (24) are consistent with the mechanism for alkane dehydrocyclization involving irreversible adsorption.

The present data show that tin alters the property of the platinum for alkane dehydrocyclization. Thus, reversible alkane adsorption/desorption applies for the $Pt\text{-}Sn\text{-}SiO_2$ catalyst whereas irreversible adsorption applies for the $Pt\text{-}SiO_2$ catalyst. The exchange data show that tin causes the alkane to be bound to the metal surface less tightly than when tin is absent. Furthermore, the exchange or lack of exchange in the aromatic products when gaseous D_2 is present with unlabeled *n*-octane suggest that the presence of tin also causes $D_2(H_2)$ to be adsorbed to a smaller extent and/or at a lower surface coverage. This conclusion contrasts with the recent report that the addition of tin to a $Pt\text{-}Al_2O_3$ catalyst causes an increase in hydrogen coverage (34).

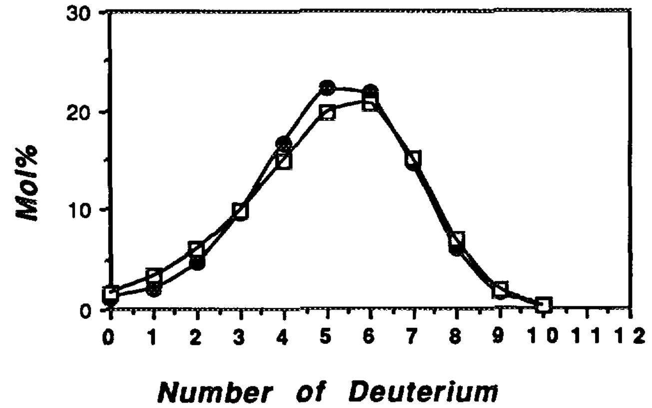

FIG. 7. Deuterium distribution in the ethylbenzene (●) and *o*-xylene (□) products following contact of an equimolar mixture of $n\text{-}C_8H_{18}/n\text{-}C_8D_{18}$ (no added H_2 or D_2) with a $Pt\text{-}Sn\text{-}SiO_2$ catalyst at 482°C and 1 atm.

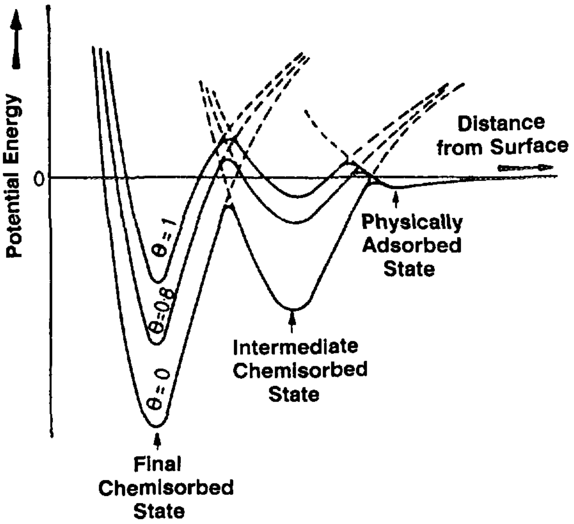

FIG. 8. Schematic of potential energy diagram showing the relative activation energies for chemisorption of intermediate and final chemisorbed states and the variation with surface coverage [from Ref. (24)].

Taylor (35) advanced the concept of activated adsorption in which a physical adsorbed precursor state precedes chemisorption at low temperatures, and this view is widely accepted. However, precursor chemisorbed states have received less coverage.

The adsorption of oxygen on nickel (36) leads to two chemisorbed states: an intermediate and a final chemisorbed state (Fig. 8). For a bare metal surface ($\theta = 0$) the activation energy for desorption is larger than that for the conversion of the intermediate state to the final chemisorbed state. However, as the surface coverage increases the relative activation energies are altered so that at $\theta = 1$, the step leading to the final chemisorbed state has a higher activation energy than desorption to the gas phase does.

The lack of H/D exchange in the unconverted *n*-octane indicates that the potential energy curve for the $Pt\text{-}SiO_2$ catalyst resembles the case of $\theta = 0$ in Fig. 8. The addition of tin to the $Pt\text{-}SiO_2$ catalyst is considered to modify the potential energy curve to resemble the one for $\theta = 1$ in Fig. 8 and this permits H/D exchange in the unconverted *n*-octane. Thus, it is proposed that the alloying of Pt with Sn alters the potential energy curve in an analogous manner.

There are extensive characterization data for Pt–Sn catalysts (37, 38). For alumina, the extent of alloy formation is more dependent on variables such as metals loading, Sn/Pt ratio, and support surface area than it is when silica is the support (37–49). The extensive characterization data for the Pt : Sn = 1 : 1 catalyst used in this study indicate that most, if not all, of the Pt is present as a Pt : Sn = 1 : 1 alloy.

Pt : Sn = 1 : 1 alloy would be expected to have a uniform surface with respect to surface Pt sites, and not one that is an arrangement of small ensembles of Pt atoms. The electronic properties of Pt in a Pt : Sn = 1 : 1 alloy will be different from that of Pt in metallic platinum particles. It is anticipated that Pt in metallic platinum will be more electron deficient than Pt in the PtSn alloy. Thus, the present H/D exchange data are consistent with that expected for adsorption that is controlled by an electronic factor rather than geometric factors, to the extent that these factors are separable.

It has been proposed that the alteration of the EB : OX ratio by the presence of tin in the catalyst was due to an alteration of adsorption to favor the weaker C–H bonds in the $-CH_2-$ group rather than the stronger bonds of the $-CH_3$ groups. However, the ready exchange of H/D in the *n*-octane reactant is not consistent with this view (19). Once the alkane adsorbs on the surface, the extensive H/D exchange indicates that the point of attachment of the alkane to the catalyst surface will also rapidly change. Thus, it appears that another explanation must be sought for the dependence of the EB : OX ratio on the presence or absence of tin. An obvious explanation is that the relative stability of the adsorbed alkene (or even diene or triene) is altered to favor the internal alkenes when tin is present; however, this stability factor must differ from the pathway that involves H/D exchange.

REFERENCES

1. Paál, Z., *in* "Catalytic Naphtha Reforming" (G. J. Antos, A. M. Aitani, and J. M. Parera, Eds.), pp. 19–44. Dekker, New York, 1995.
2. Bragin, O. V., Tovmasyan, V., Isagulyants, G., Greish, A., Kovalenko, L., and Liberman, A., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2041 (1977).
3. Iglesia, E., Baumgarten, J., and Price, G., *J. Catal.* **134,** 549 (1992).
4. Iglesia, E., Baumgarten, J., Price, G., Rose, K., and Robbins, J., *J. Catal.* **125,** 95 (1990).
5. Isagulyants, G. V., Rozengart, M. I., Derbentsev, Yu. I., Dubinskii, Yu. G., and Kazanskii, B. A., *Dokl. Akad. Naud SSSR* **191,** 600 (1970).
6. Silvestri, A. J., and Smith, R. L., *J. Catal.* **29,** 316 (1973).
7. Isagulyants, G. V., Greish, A. A., Kovalenko, L. I., Rozhdestvenskaya, N. N., and Rozengart, M. I., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 864 (1980).
8. Isagylyants, G. V., Rozengart, M., and Bryukhanov, V. G., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 870 (1980).
9. Kalechits, I. V., *Kinet. Katal.* **8,** 1114 (1967).
10. Kazanskii, B. A., Isagulyants, G. V., Rozengart, M. I., Dubinsky, Yu. G., and Kovalenko, L. I., *in* "Proceedings, 7th International Congress on Catalysis, Tokyo, 1980" (T. Seiyama and K. Tanabe, Eds.). Elsevier, Amsterdam, 1981.
11. Paál Z., and Tétényi, P., *Acta Chim. Acad. Sci. Hung.* **54,** 175 (1967).
12. Paál, Z., and Tétényi, P., *Acta Chim. Acad. Sci. Hung.* **58,** 105 (1968).
13. Isagulyants, G. V., and Balandin, A. A., *Kinet. Katal.* **2,** 737 (1961).
14. Rozengart, M. I., Mortikov, E., and Kazanskii, B. A., *Dokl. Akad. Nauk SSSR* **166,** 619 (1966).
15. Paál, Z., *J. Catal.* **105,** 540 (1987).
16. Derbentsev, Yu. I., Balandin, A. A., and Isagulyants, G. V., *Kinet. Katal.* **2,** 741 (1961).
17. Derbentsev, Yu. I., and Isagulyants, G. V., *Russ. Chem. Rev.* **38,** 714 (1969).
18. Paál, Z., and Tétényi, P., *J. Catal.* **30,** 350 (1973).
19. Paál, Z., *J. Catal.* **91,** 181 (1985).
20. Paál, Z., *Catal. Today* **12,** 297 (1992).
21. Paál, Z., *Adv. Catal.* **29,** 273 (1980).
22. Paál, Z., and Menon, P. G., *Catal. Rev.* **25,** 223 (1983).
23. Kazanskii, B. A., *in* "Symposium, Mechanisms of Hydrocarbon Reactions" (F. Márta and D. Kalló, Eds.), pp. 15–48. Elsevier, Amsterdam, 1975.
24. Davis, B. H., *J. Catal.* **23,** 365 (1971).
25. Shi, B., and Davis, B. H., *J. Catal.* **147,** 38 (1994).
26. Davis, B. H., and Venuto, P. B., *J. Catal.* **15,** 363 (1969).
27. Srinivasan, R., and Davis, B. H., *J. Mol. Catal.* **88,** 325 (1994).
28. Westfall, G. A., Pezzanite, J. O., and Davis, B. H., *J. Catal.* **42,** 247 (1976).
29. Bond, G. C., and Sermon, P. A., *Gold Bull.* **6,** 102 (1973).
30. Davis, B. H., Westfall, G. A., and Naylor, R. W., *J. Catal.* **42,** 238 (1976).
31. Balandin, A. A., *Adv. Catal.* **19,** 1 (1969).
32. Biloen, P., Helle, J. N., Verbeek, H., Dautzenberg, F. M., and Sachtler, W. M. H., *J. Catal.* **63,** 112 (1980).
33. Dautzenberg, F. M., Helle, J. N., Biolen, P., and Sachtler, W. M. H., *J. Catal.* **63,** 119 (1980).
34. Bakenkova, L. V., Szabo, S., Naidina, I. N., and Kulievskaya, Yu. G., *ACH Models Chem.* **12,** 113 (1994).
35. Taylor, H. S., *J. Am. Chem. Soc.* **53,** 578 (1931).
36. Hayward, D. O., and Trapnell, B. M. W., "Chemisorption," 2nd ed., pp. 133–135. Butterworth, Washington, 1964.
37. Davis, B. H., *in* "Selectivity in Catalysis" (M. E. Davis and S. Suib, Eds.), ACS Symp. Series, Vol. 517, p. 109. Am. Chem. Soc., Washington, DC, 1993.
38. Srinivasan, R., and Davis, B. H., *Plat. Metals Rev.* **36,** 151 (1992).
39. Srinivasan, R., DeAngelis, R. J., and Davis, B. H., *J. Catal.* **106,** 449 (1987).
40. Srinivasan, R., DeAngelis, R. J., and Davis, B. H., *Catal. Lett.* **4,** 303 (1990).
41. Li, Y. X., Stencel, J. M., and Davis, B. H., *Appl. Catal.* **64,** 71 (1990).
42. Strinivasan, R., Rice, L., and Davis, B. H., *J. Catal.* **129,** 257 (1991).
43. Srinivasan, R., and Davis, B. H., *Appl. Catal. A General* **87,** 45 (1992).
44. Srinivasan, R., Sharma, R., Su, S., and Davis, B. H., *Catal. Today* **21,** 83 (1994).
45. Russell, S. N., and Davis, B. H., *J. Catal.* **89,** 371 (1984).
46. Stencel, J. M., Goodman, J., and Davis, B. H., *in* "Proceedings, 9th International Congress on Catalysis, Calgary, 1980" (M. J. Phillips and M. Ternan, Eds.), Vol. 3, p. 1291. Chem. Institute of Canada, Ottawa, 1988.
47. Li, Y.-X., Stencel, J. M., and Davis, B. H., *React. Kinet. Catal. Lett.* **37,** 273 (1988).
48. Chiu, N.-S., Lee, W.-H., Li, Y.-X., Bauer, S. H., and Davis, B. H., *in* "Advances in Hydrotreating Catalysts" (M. Loccelli and R. G. Anthony, Eds.), p. 147. Elsevier, Amsterdam, 1989.
49. Li, Y.-X., Klabunde, K. J., and Davis, B. H., *J. Catal.* **128,** 1 (1991).