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Selective Steam Reforming of Aromatic Hydrocarbons

V. Steam Conversion and Hydroconversion of Selected Monoalkyl- and Dialkylbenzenes on Pt and Ni Catalysts

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Steam and hydrogen conversions of a series of mono- and dialkylbenzenes were studied at 713 K on variously supported platinum and nickel catalysts and compared with previous results obtained on rhodium catalysts (Duprez, D., Miloudi, A., Delahay, G., and Maurel, R., *J. Catal.* **90**, 292, 1984). Three main types of reaction were observed: dealkylation (C—C bond splitting in the side chains), dehydrogenation (into alkenylbenzenes), and degradation (i.e., ring opening). The latter reaction primarily yielded C_1 molecules and hydrogen. In the presence of steam, the monoalkylbenzenes mainly dealkylate into benzene on Pt and Ni (as on Rh). Nevertheless, Pt is characterized by a very high relative activity in dehydrogenation and by the absence of ring opening. The inverse behavior is observed on Ni. For a given metal, the activities in degradation are constant across the entire series of hydrocarbons, which suggests that ring opening occurs on specific sites. The proportion of these sites at the metal surface invariably decreases with the electronegativity of the metal. In the presence of hydrogen, the product spectra are deeply modified. Ring opening is considerably inhibited, whereas the primary C—C bond ruptures shift toward the middle and the end of the chain. Secondary reactions of realkylation, leading to toluene from benzene and CH_x fragments, are less pronounced on Ni than on Pt and Rh, which suggests that the hydrocarbon species are deeply dehydrogenated on Ni, indistinguishably from carbonaceous deposits. © 1986 Academic Press, Inc.

INTRODUCTION

In a previous paper (*1*), we reported a comparative study of the steam conversion and hydroconversion of alkylbenzenes on rhodium catalysts. The principal conclusions were the following:

(i) Dealkylation (C—C rupture on the side chain), dehydrogenation (on the side chain), and degradation (i.e., ring opening) were, on rhodium, the principal reactions of steam conversion *and* of hydroconversion: isomerization, transalkylation, and dehydrocyclization were, in general, to be discounted.

(ii) Selectivities were significantly affected by the reactant (H_2O or H_2) used for converting the hydrocarbons. For instance, in the presence of steam, benzene was the main dealkylation product, whereas hydrogen tended rather to induce C—C bond splittings in the middle or the end of the side chain.

(iii) The activity in ring opening was virtually unrelated to the alkyl group size, but was noticeably lower in hydroconversion than in steam conversion.

In the present paper, we report a comparative study of the same reactions performed on platinum and nickel catalysts. Presently available studies refer principally to hydroconversion of alkyl aromatics on platinum (*2–6*) and on nickel (*7–9*). These metals

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were also used in toluene steam dealkylation (*10, 15*) and more rarely in the steam reforming of other alkylbenzenes (*10, 16–18*). Moreover, most of the results were obtained in highly differing conditions. Therefore, in the present study, the reactions (in steam *and* in hydrogen) were performed on Pt and Ni, at the same temperature (713 K) as that used for the previous study on Rh (*1*), in order to allow direct comparison of the results in their entirety.

EXPERIMENTAL

The apparatus and methods have been described in detail in Ref. (*1*). Briefly, the reactions were performed in a flow apparatus at atmospheric pressure. The H_2O:hydrocarbon molar ratio was 6 : 1 for steam conversion, and correspondingly H_2:hydrocarbon was 4 : 1 for hydroconversion. The extrapolation method allowed the initial activities to be determined with sufficient accuracy in the case of steam conversion but not for hydrogen conversion. Turnover frequencies were then measured after 2 h on stream. The hydrocarbons processed were benzene (B), toluene (T), ethylbenzene (EtB), *iso*-propylbenzene (iPB), *tert*-butylbenzene (tBB), *n*-propylbenzene (nPB), and *o*-xylene (oX), all of which were distilled Fluka puriss. materials and had less than 0.4% impurities. Reaction products were classified as listed in Ref. (*1*).

The catalysts were prepared by means of wet impregnation with aqueous solutions of chloroplatinic acid and nickel nitrate. The supports (Al_2O_3, SiO_2, TiO_2) were identical to those used for rhodium catalysts in the previous report (*1*). Dispersions of the catalysts were measured in a pulse adsorption device, using procedures detailed elsewhere (*15, 19, 20*). Their characteristics are reported in Table 1.

As for rhodium (*1*), the main reactions were dealkylation (C—C splitting in the side chain), dehydrogenation (in the side chain), and degradation (ring opening). Minor products resulting from isomerization, transalkylation, and dehydrocyclization were proportionally more abundant in hydrogen than in steam conversion, particularly on platinum catalysts. Identification of these minor products was made by GC-MS after they were partially isolated by preparative chromatography.

Activities are systematically expressed as turnover frequencies (molecules of hydrocarbon reacted per metal site per hour) and selectivities are given in terms of molecules formed per molecule of hydrocarbon reacted.

RESULTS

1. Steam Conversion over Pt/Al_2O_3 and Ni/Al_2O_3 Catalysts

Ethylbenzene, iso-propylbenzene, and tert-butylbenzene. The product distributions reported in Fig. 1 show that, as was the case for rhodium (*1*), benzene is the chief product of dealkylation at zero conversion. Nevertheless, significant differences appear between the metals, as elaborated below.

(i) Platinum exhibits very high selectivities to dehydrogenation from the moment when these reactions may occur. For instance, the initial selectivities to styrene in EtB steam conversion (Fig. 1a) are 78 and 11% for Pt and Ni, respectively, as compared with 15% for Rh (*1*). The behavior of Pt in iPB conversion (Fig. 1b) is even more

TABLE 1

Dispersion of the Catalysts

Catalyst	Metal (%)	Dispersion (%)	Metal site concentration[a]
Pt/Al_2O_3	1.1	65	36.5
Pt/SiO_2	1.0	40	20.5
Pt/TiO_2	0.45	18	4.2
Ni/Al_2O_3	4.2[b]	4.9	35.0
Ni/SiO_2	3.9	6.4	42.5
Ni/TiO_2	3.7	0.8	5.0

[a] Site concentrations are given in μmole of surface atoms per g of catalyst.

[b] Fraction of reduced metal deduced from O_2 uptake at 773 K: 0.85.

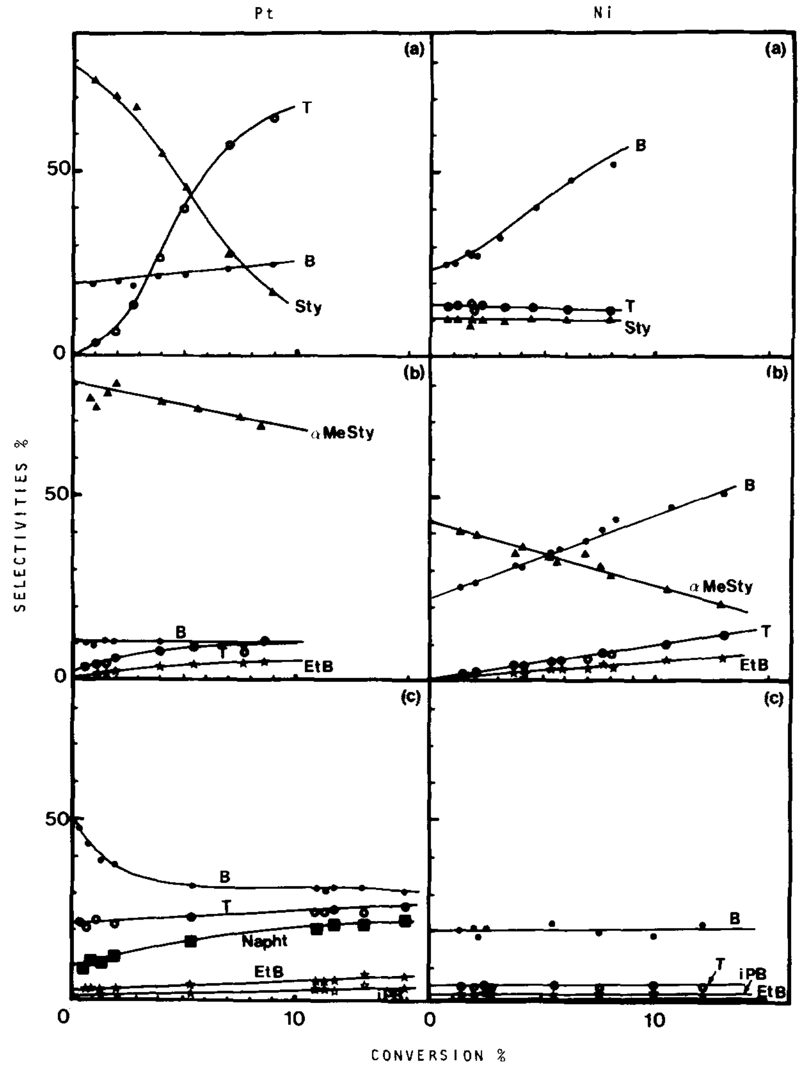

FIG. 1. Product distributions in steam conversion of (a) ethylbenzene, (b) *iso*-propylbenzene, and (c) *tert*-butylbenzene on Pt/Al_2O_3 and Ni/Al_2O_3 catalysts. Reaction conditions: 713 K, 1 bar, steam-to-hydrocarbon molar ratio = 6 : 1.

typical: the yields of dealkylation products remain confined to marginal values.

(ii) Nickel is confirmed as a poorly selective metal, whatever the starting hydrocarbon: the overall selectivity to aromatics was found to range from 30 to 50%, as compared with 90–100% for Pt and 65–85% for Rh.

(iii) Isomerization, transalkylation, and dehydrocyclization could be considered as minor reactions on rhodium (*1*). This is the case with nickel, but not with platinum. The formation of large amounts of naphthalene in *tert*-butylbenzene steam conversion (Fig. 1c) provides clear proof of the ability of platinum to promote skeletal rearrangements and dehydrocyclization.

Initial specific activities (molecules reacted per metal site per hour at zero time) are recorded in Fig. 2, including activities for benzene and toluene previously determined on the same catalysts (*15, 21*). Also represented in Fig. 2, for purposes of comparison, are the specific activities of rho-

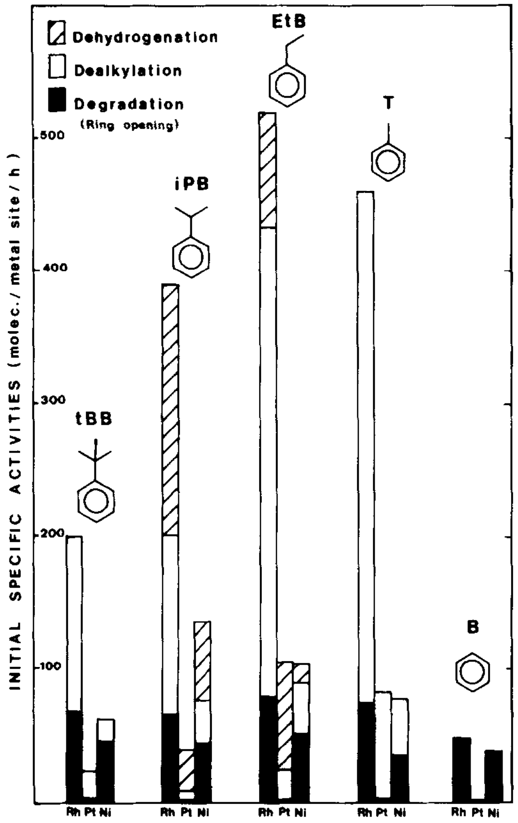

FIG. 2. Initial specific activities (per site and per hour) in steam conversion of benzene, toluene, ethylbenzene, *iso*-propylbenzene, and *tert*-butylbenzene on alumina-supported catalysts.

dium given in Ref. (*1*). For all the series of hydrocarbons processed in this study, this is very definitely the most active metal in steam dealkylation. The following general rules deduced for rhodium remain valid for platinum and nickel: (i) the activity in dealkylation decreases with the alkyl group size (T > EtB > iPB ≥ tBB); (ii) the activity in degradation (DN) appears practically unrelated to the alkyl group size. We have DN = 2–4, 35–50, and 65–85 for Pt, Ni, and Rh, respectively; (iii) on the other hand, no clear correlation with alkyl group size, valid for any metal, can be found for the activities in dehydrogenation.

n-Propylbenzene and o-xylene. The product distributions (Fig. 3) and the values of the initial activities (Table 2) are jointly presented for Pt and Ni catalysts. As for EtB and iPB, platinum exhibits very high selectivity to dehydrogenation in nPB conversion. It should be noted that styrene appears in the initial products of conversion; the same behavior was observed on Rh and was ascribed to dealkylation and subsequent dehydrogenation, in one step, of the nPB molecule. Another noteworthy result of Fig. 3a is the appearance of indane and indene (referred to as Ind) in the products of reaction. Thus, platinum even in steam conversion, is the best dehydrocyclization catalyst. One may also point out that indane and indene are secondary products and appear to result from β-methylstyrene transformation. This result is in agreement with the scheme previously proposed by Shephard and Rooney for dehydrocyclization of *n*-propylbenzene (*2*). By contrast with Rh and Pt, Ni appears to be a poorly selective catalyst for dehydrogenation. The selectivities to propenylbenzenes never exceed 25% (compared with 50% for Rh and 80% for Pt). Nickel is no better as a catalyst for dehydrocyclization: no formation of bicyclic compounds could be detected in the products. The behavior of nickel in *o*-xylene conversion also differs noticeably from that of platinum: Pt is less capable than Ni of dealkylating *o*-xylene into benzene in one step. In this respect, Ni resembles Rh which yields twice as much benzene as toluene.

II. Support Effects in Steam Reforming of Ethylbenzene

Results obtained in EtB steam conversion on silica-supported and titania-supported catalysts are recorded in Table 3. For the sake of comparison, results previously obtained on Pt/Al_2O_3 and Ni/Al_2O_3 are also reported in the table. The activity in dealkylation is virtually suppressed on platinum when supported on silica. By contrast, activity in dehydrogenation is practically constant for each platinum catalyst. In the case of nickel, no particular support effect is evident with regard to alumina-sup-

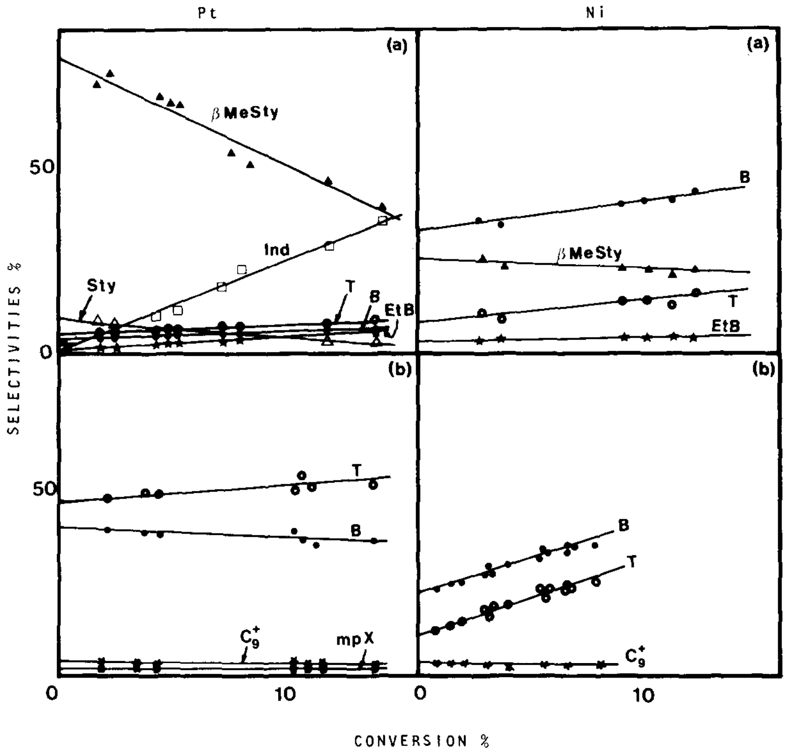

FIG. 3. Product distribution in steam conversion of (a) *n*-propylbenzene and (b) *o*-xylene on Pt/Al_2O_3 and Ni/Al_2O_3 catalysts.

ported and silica-supported catalysts. Ni/TiO_2 is relatively less active than the other nickel catalysts; nevertheless, the product distributions show that the degradation is noticeably low on Ni/TiO_2. As a result, titania may be used as a support increasing

TABLE 2

Specific Activities of Pt/Al_2O_3 and Ni/Al_2O_3 Catalysts in the Steam Conversion of *n*-Propylbenzene and *o*-Xylene at 713 K (H_2O/Hydrocarbon Molar Ratio = 6/1)

Reaction	Pt/Al_2O_3		Ni/Al_2O_3	
	Sp. act. (h^{-1})	Distribution[a] (h^{-1})	Sp. act. (h^{-1})	Distribution[a] (h^{-1})
nPB + H_2O	250	DA = 18 DH = 227 DN = 5	125	DA = 56 DH = 36 DN = 33
oX + H_2O	24	DA = 21 DN = 2 Others = 1	72	DA = 25 DN = 45 Others = 2

[a] DA, dealkylation; DH, dehydrogenation; and DN, degradation (ring opening).

TABLE 3

Support Effects in Steam Reforming of Ethylbenzene

Catalyst	Specific activity (h^{-1})	Distribution[a] (h^{-1})	
Pt/SiO_2	91	DA	1
		DH	88
		DN	2
Pt/TiO_2	98	DA	18
		DH	78
		DN	2
Pt/Al_2O_3	105	DA	21
		DH	82
		DN	2
Ni/SiO_2	97	DA	36
		DH	10
		DN	51
Ni/TiO_2	62	DA	24
		DH	16
		DN	22
Ni/Al_2O_3	107	DA	39
		DH	14
		DN	54

[a] For notation, see Table 2.

overall aromatic selectivity; in this respect, Ni/TiO_2 resembles Rh/TiO_2 (*1*).

III. Hydroconversions over Alumina-Supported Pt and Ni Catalysts

Hydrogen was used for converting ethylbenzene, *iso*-propylbenzene and *tert*-butylbenzene on Pt/Al_2O_3 and Ni/Al_2O_3 (Fig. 4). The most readily apparent differences with steam conversion are summarized in Fig. 5, which shows the following characteristics.

(i) Hydrogen decreases the selectivities to dehydrogenation products. This is not due to thermodynamic limitations; calculations show that the maximum yields of styrene and of α-methylstyrene were never reached, even in the presence of hydrogen on platinum.

(ii) Hydrogen favors C—C bond splitting in the middle and the end of the side chains: the proportion of benzene in the products of dealkylation is substantially lower than in steam conversion.

(iii) Hydrogen preserves to a larger extent the aromatic nucleus: the relative rate of ring opening invariably decreases when steam is replaced by hydrogen.

(iv) As regards C—C and C—H splitting in the side chains, differences between steam and hydrogen conversions are much less marked on nickel than on platinum and rhodium. For instance, benzene remains the chief product of dealkylation, and the selectivities to alkenylbenzenes compounds are relatively similar whatever the reactant used (H_2O or H_2).

(v) As a rule, hydrogen favors certain reactions such as isomerization and transalkylation, which were negligible in the case of steam conversions. This resulted in the presence of numerous minor hydrocarbons in the products of hydrogen conversion. In some cases, especially in tBB conversion, these products became quite important. A detailed distribution, for two levels of conversion, is recorded in Table 4.

TABLE 4

Detailed Product Distribution of *tert*-Butylbenzene Hydroconversion on Pt/Al_2O_3 and Ni/Al_2O_3 at 713 K for Two Levels of Conversion: 0% (extrapolated) and 5%

Products	Pt		Ni	
	0%	5%	0%	5%
Benzene	38	39	43	40
Toluene	0	1	9	8
Ethylbenzene	0	2	5	4
Xylenes	0	0.2	0	0
iso-Propylbenzene	25	23	21	12
α-Methylstyrene	0	2	0	0
iso-Butylbenzene	24	15	0	2
Cymenes	3	3	0.1	0.2
Methyl-*tert*-butyl benzene	6	6	10	15
Naphthalene	0	3	0	0

Note. The distributions are given as percentage selectivities (moles of product formed per 100 moles of tBB reacted).

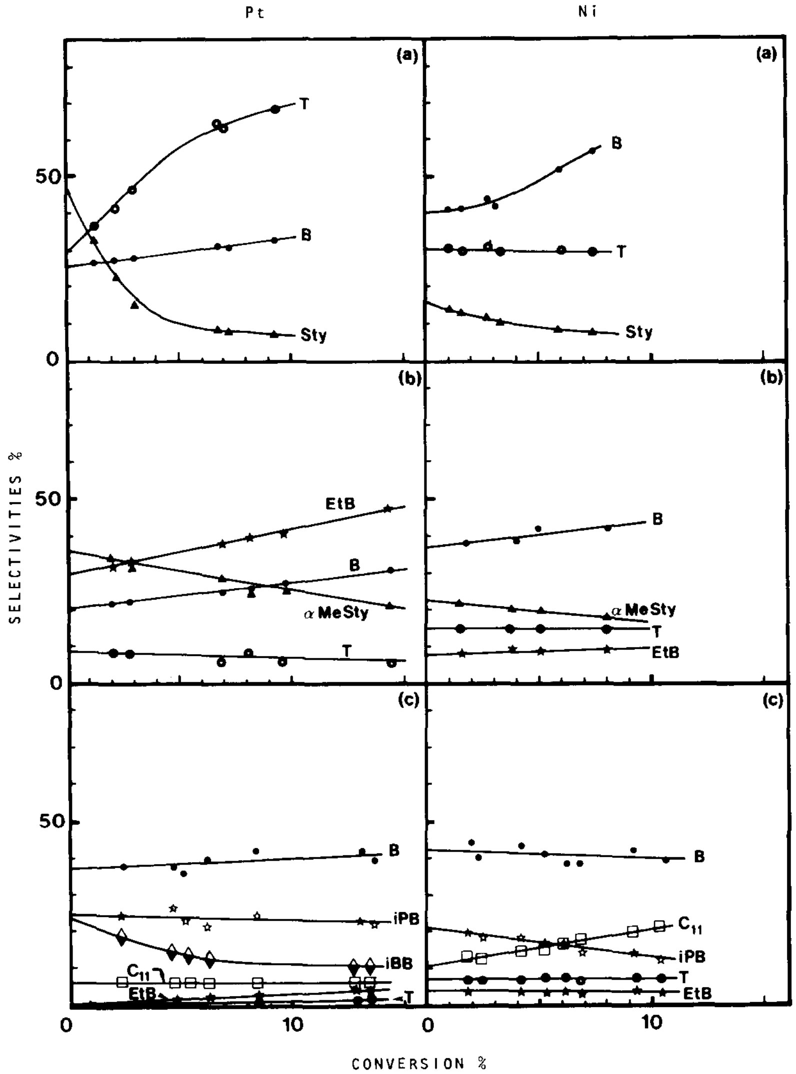

FIG. 4. Product distribution in hydrogen conversion of (a) ethylbenzene, (b) *iso*-propylbenzene, and (c) *tert*-butylbenzene on Pt/Al_2O_3 and Ni/Al_2O_3 catalysts. Reaction conditions: 713 K, 1 bar, hydrogen-to-hydrocarbon molar ratio = 4 : 1.

One should note the high selectivity to methyl-*tert*-butylbenzene (referred to as C_{11} in Fig. 4c) on Pt and Ni. Also to be noted on platinum is the substantial production of *iso*-butylbenzene (iBB). And yet, hydrogen conversion did not invariably lead to a product spectrum more complex than in steam reforming; one may note, for instance the disappearance of naphthalene in the products of tBB hydroconversion.

The activities for 2 h on stream are recorded in Table 5. The reactions of hydrogen conversion remain quite stable: virtually no deactivation was observed between 2 and 8 h on stream, and the values reported in Table 5 thereby constitute a reasonable measurement of the initial activities. On this basis, it can be concluded that (i) platinum is more active in hydrogen than in steam dealkylation, whereas nickel exhibits practically the same activity for the two reactions; and (ii) the activities in dehy-

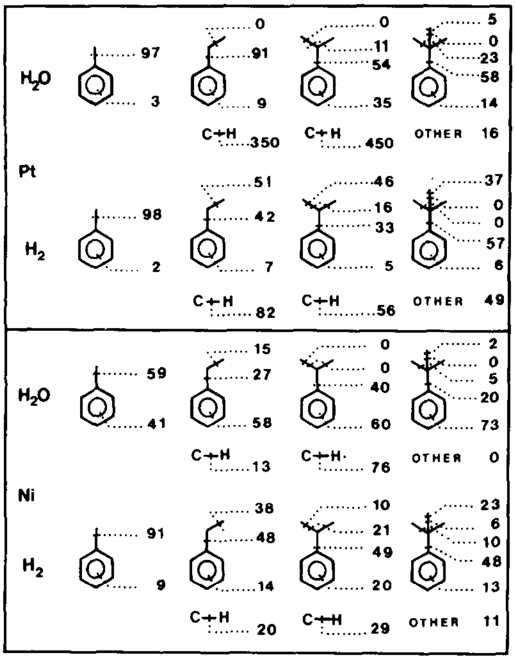

FIG. 5. Comparison of the initial selectivities of C—C splitting in steam and hydroconversion. Also given are the relative numbers of molecules reacted via C—H bond splitting per 100 molecules reacted via C—C bond ruptures. In tBB conversion, "other" reactions are isomerization, transalkylations, and dehydrocyclizations.

drogenation are lower, as a rule, in hydroconversions.

DISCUSSION

Existence of two types of sites in aromatic steam reforming. The results illustrated in Fig. 2 and Table 5 show that, for a given catalyst, the activities in ring opening are virtually constant, regardless of the size of the alkyl group. A similar result was previously obtained on Rh, and may be related to the presence of two types of sites on the metal surface. If sites I are operative for the dealkylation and the dehydrogenation reactions, sites II can effectively realize the ring opening. The rate of this reaction depends exclusively on the proportion of sites II, and is not linked to the nature of the alkyl group. The most probable intermediate is a π-arene–metal complex which can transform into σ adsorbed species. The energetic barrier of this $\pi \rightarrow \sigma$ transformation requires sites of high energy (sites II), which exist on Rh and Ni particles, exclusively.

TABLE 5

Activities of Pt/Al_2O_3 and Ni/Al_2O_3 in Hydroconversion of Some Aromatic Hydrocarbons at 713 K

Reaction	Pt		Ni	
	Overall activity[a]	Distribution[b]	Overall activity[a]	Distribution[b]
EtB + H_2	48	DA 25	38	DA 27
		DH 21		DH 7
		DN 2		DN 4
iPB + H_2	108	DA 66	49	DA 33
		DH 39		DH 11
		DN 3		DN 5
tBB + H_2	115	DA 72	28	DA 22
		TA + ISO 39		TA 3
		DN 3		DN 3

[a] Activities are given for 2 h on stream as turnover frequencies in h^{-1}.
[b] DA, dealkylation; DH, dehydrogenation; DN, degradation of the aromatic nucleus; TA, transalkylation; ISO, isomerization.

The capacity of a metal to operate C—C bond splitting in the aromatic nucleus varies in inverse proportion to its electronegativity. Hence the intermediates of ring opening require a higher availability of metal valence electrons than those of dealkylation (and dehydrogenation). A decrease of ring opening with conversion was invariably observed on Rh catalysts; this remained the case for Ni (Table 6). On Pt the variations are not representative; this metal is very selective, even at low conversion. The results on Ni and Rh could be ascribed to a favorable inhibition of ring opening by the carbon monoxide produced in the reaction (*22*). The role of CO may be explained by the electron acceptor character of this adsorbate, which lowers the Fermi level of the metal and decreases its ability to provide an electron.

Mechanisms of steam dealkylation. The results reported in Table 3 for Pt and Ni and in Ref. (*1*) for Rh decisively confirm the existence of the two types of metals which were proposed to classify the support effects in toluene steam dealkylation (*15, 23*). They are the support-sensitive metals (first group), including Rh and Pt, and the support-insensitive metals (second group), of which nickel is the most representative element.

The metals of the first group obey a bifunctional-like mechanism involving migration of hydroxyl groups from the support to the metal, where the activation of the hydrocarbon molecule occurs.

TABLE 6

Variations of the Selectivities into Ring Opening with the Overall Conversion (with Steam) on Alumina-Supported Ni and Rh Catalysts (713 K; H_2O/Hydrocarbon Molar Ratio = 6/1)

Hydrocarbon	Ni conversion		Rh conversion[a]	
	0%	10%	0%	10%
Toluene	41	30	19	14
Ethylbenzene	50	21	17	10
n-Propylbenzene	33	13	18	17
tert-Butylbenzene	71	67	33	25

[a] Calculated from data of Ref. (*1*).

The metals of the second group, such as nickel, obey a competitive mechanism, all of the determining steps being located on the metal. This mechanism is in qualitative agreement with the model developed by Jackson *et al.* (*18*) for the steam reforming of hydrocarbons over nickel/alumina catalysts. According to these authors, water is presumably adsorbed as H and OH fragments on the vacant metal sites, whereas the hydrocarbon may be adsorbed on the fraction of metal precovered with carbonaceous deposits. The oxygen species may react with the carbonaceous overlayer to yield carbon oxides and hydrogen. In the toluene steam dealkylation (*15*), hydrocarbon dissociation and surface reaction (between O-containing species and CH_x fragments) were expected to be the determining steps of the mechanism on Ni catalysts.

Selectivities to dealkylation products. Benzene is the chief initial product of dealkylation on Pt and Ni, as on Rh (*1*). Nevertheless, with increasing conversion, a systematic increase of the selectivity to toluene was observed on Rh. Two hypotheses may be invoked to explain this result, namely (i) toluene is preferentially formed by supplementary dealkylation of alkenyl benzene compounds produced in the initial stage of reaction, or (ii) toluene is essentially formed by realkylation of benzene with methyl groups, relatively abundant on the metal surface. The first hypothesis is coherent with the correlative decrease of selectivities to alkenylbenzenes accompanying the increase of selectivity into toluene. Nevertheless, the absence of alkenylbenzene compound in the product of *tert*-butylbenzene and the difficulty of imagining that both styrene (from ethylbenzene) and α-methylstyrene (from iso-propylbenzene) may dealkylate into toluene, render the second hypothesis very likely *be default.* In this respect, platinum resembles rhodium; however, except in ethylbenzene steam conversion, the increase in toluene selectivity on platinum is not as marked as on rhodium. The behavior of nickel is quite different; selectivity to toluene is relatively more stable, and even appears as slightly decreasing in the case of EtB conversion (Fig. 1). This may result from the very nature of the hydrocarbon species populating the reacting metal surface. On nickel, it now seems well established that surface carbon intermediates may be formed during ethane steam reforming (*24*). If this trend holds in the case of alkylbenzene steam reforming, it is in agreement with our results on Ni, insofar as such strongly dehydrogenated carbon species cannot easily be involved in a realkylation process of phenyl groups.

In hydrogen conversion, the spectrum of dealkylation products is generally larger than in steam conversion. Benzene remains a noticeable product; however, initial C—C splitting may occur in the middle or end of the chain. The reactions of realkylation are relatively less marked on Pt and Ni than on Rh: the selectivities into toluene show little variation with conversion, except in EtB conversion on platinum. Nevertheless, in the latter case, the alkenylbenzene hypothesis (styrene essentially yielding toluene) is all the less to be excluded in that, in iPB conversion, α-methylstyrene appears to yield EtB as a main product, which is in agreement with this hypothesis. Thus, hydrogen conversion may lead to lighter alkylbenzenes by three different routes, namely: (i) initial C—C splitting in the middle or the end of the chain, (ii) realkylation of benzene, and (iii) secondary C—C splitting preferentially on the double bond of the alkenylbenzenes produced in the initial stage of reaction. While in steam conversion the second way was predominant, the three routes are likely to be operative in hydrogen conversion. However, it is clear that the temperature of reaction may have considerable influence on the product spectrum. For instance, Beranek and Kraus (*8*) reported that hydrogen conversion of various alkylbenzenes on a nickel catalyst at 623 K leads preferentially to dealkylation of the terminal C—C bond. In our case, benzene is invariably the main product of dealkylation on Ni at 713 K. Moreover, structural factors such as metal particle size and the reduction percentage of the metallic phase may likewise alter the selectivity spectrum for a given metal (*25*). Thus, it is only with regard to similar catalysts that the results of this study may fairly be applied.

CONCLUSIONS

Steam conversion of alkylbenzenes may lead to three types of reactions: dehydrogenation (C—H cleavage in the side chain), dealkylation (C—C cleavage in the side chain), and degradation (C—C cleavage in the ring).

1. Dehydrogenation is a structure-insensitive reaction. For a given metal, its rate is practically constant; it is not linked to the structural characteristics and to the nature of the catalysts (support, particle size).
2. Dealkylation, and especially degradation, may be greatly influenced by structural factors such as particle size and support effects. Metals of the first group (Rh, Pt) are particularly sensitive to these factors.
3. As a rule, dealkylation leads to benzene as an initial product. The selectivity to toluene increases when conversion rises; this is most likely the result of a realkylation process of benzene with CH_x fragments. Nickel is relatively less capable than platinum and rhodium of inducing this realkylation reaction.
4. In the conversion of alkylbenzenes, hydrogen provokes a profound modification of the selectivity spectrum. Ring opening is lowered, and the initial C—C splitting in the alkyl group is shifted toward the end of the chain. Realkylation reactions are relatively less favored on Ni and Pt in hydrogen atmosphere.

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