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Selective Steam Reforming of Aromatic Hydrocarbons

IV. Steam Conversion and Hydroconversion of Selected Monoalkyl- and Dialkyl-Benzenes on Rh Catalysts

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Steam conversion and hydroconversion of a series of monoalkylbenzenes (C_6H_5R, R = C_2H_5, *n*-C_3H_7, *i*-C_3H_7, *tert*-C_4H_9) and of dialkylbenzenes (*o*- and *p*-xylenes) are studied at 713 K and atmospheric pressure on supported rhodium catalysts (Rh/Al_2O_3, Rh/SiO_2 and Rh/TiO_2), and compared to the toluene steam dealkylation previously studied on the same catalysts. Three types of reaction, namely dealkylation (C–C rupture on the side chain), dehydrogenation (on the side chain), and degradation (i.e., ring opening) account for virtually the whole product spectrum. Isomerization, transalkylation, and dehydrocyclization reactions may, in general, be discounted. In the presence of steam, the main initial product of monoalkylbenzene dealkylation is invariably benzene, but the splitting of the C–C bonds in the middle or end of the side chain always increases with conversion. As a rule, the specific activities (per metal site) in dealkylation decrease with the degree of substitution in the alkyl group (primary > secondary > tertiary > quaternary carbon). On the other hand, the specific activities in ring opening remain constant for all the hydrocarbons and even for the benzene. In the presence of hydrogen, multiple C–C bond splittings are invariably observed and benzene is no longer, in general, the principal initial product. The activities in ring opening are equally constant, but at a lower level than in steam conversion. These results are in overall agreement with the model of the dual active sites: sites I appear operative for dealkylation and dehydrogenation, whereas ring opening takes place at sites II with a high probability, independent of the alkyl group size. Possible adsorbed species on each type of site are described. An attempt is made to rationalize the effects of assorted selectivity-determining factors (metal particle size, support effects, selective poisons such as S and CO) in terms of electronic or geometric effects.

INTRODUCTION

As an industrial process, steam reforming is known for converting hydrocarbon fractions into hydrogen-rich gases. Over the last 10 years, *selective* steam reforming has been increasingly considered as an alternative process for the hydrotreatments of certain petroleum fractions. The starting hydrocarbon is partially gasified, in conformity with the following reaction:

$$C_xH_y + H_2O \rightarrow C_nH_m + \text{gas } (H_2, CO, CO_2, CH_4)$$

with $n < x$.

Steam dealkylation of alkylbenzenes is an example of selective steam reforming in which only the alkyl groups are gasified by water. Toluene steam dealkylation (TSDA) has been studied widely because it processes a simple molecule of potential economic interest (*1–10*). Nevertheless, selectivity was confirmed as a crucial parameter because water, as a reactant, is not as selective as hydrogen. The following sequence of selectivity to benzene in TSDA

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was reported for alumina-supported metals (*9*): Pt, Pd, 97–98%; Ir, 88%; Rh, 81%; Ni, 59%; Ru, 53%; Co, 51% whereas the selectivity to benzene in hydrodealkylation ($C_7H_8 + H_2 \rightarrow C_6H_6 + CH_4$) ranges from 90 to 100% for every metal (*11, 12*). Although selectivity is very closely linked to the nature of the metal, it was found that, for any given metal:

(i) The more dispersed that metal, the more selective is the catalyst. For instance, a well-dispersed Rh/γ-Al_2O_3 catalyst (D_0, % dispersion > 90%) exhibits an initial selectivity to benzene of 81%; this figure drops to 70% when $D_0 < 20\%$ (*9*).

(ii) The support can considerably alter the activity of the catalyst and, to a lesser extent, its selectivity (*1, 5–9*). For rhodium, the sequence of selectivity to benzene in TSDA is the following: $TiO_2 > Cr_2O_3 > Al_2O_3 > SiO_2$.

All these findings were obtained with toluene as a model molecule. Relatively few studies using other alkylbenzenes appear in the literature (*1, 13–16*). Moreover, the results of these studies generally apply to high conversion on markedly differing catalysts. Therefore, it was considered of the utmost importance to compare, on well-defined catalysts, the relative reactivities of the different C–C bonds, both in the side chains and in the aromatic nucleus. The effects of three molecular factors were specifically studied: (i) the nature of carbon in the α position of the aromatic ring (ethylbenzene, *iso*-propylbenzene and *tert*-butylbenzene series, compared to toluene and benzene), (ii) the side chain length (*n*-propylbenzene compared to ethylbenzene and toluene), and (iii) the position of a second substituent (*o*- and *p*-xylenes). The study was conducted on a well-defined Rh/γ-Al_2O_3 catalyst; in the case of ethylbenzene, comparative runs were performed on silica- and titania-supported catalysts in order to see if the strong support effect evidenced in TSDA might correctly be considered to be a widespread phenomenon. Finally, the influence of the reactant was studied by comparing the behavior of a certain number of molecules in hydrogen and steam conversion.

EXPERIMENTAL

Apparatus. The reactions are carried out in a flow reactor at 713 K and atmospheric pressure (*9*). The reactant to hydrocarbon molar ratio is about 6 for steam and 4 for hydrogen. The space velocity, in investigations on the regime of very small conversions (<2%), varied from 1 to 24 h^{-1}. Analyses are accomplished by GC, using a SE-30 glass capillary column for the hydrocarbons. The initial activities (at zero time) are determined by the "flow-rate" method, previously described for TSDA (*9, 10*): the flow-rate F_G of the gaseous products (mainly H_2, CO_2, CO, and CH_4) is assumed to be proportional to the conversion percentage τ. This is rigorously true in so far as the selectivities remain constant. Simulations made for estimating F_G as a function of the selectivities (determined *a posteriori*) show that the F_G/τ ratio is constant within ±10%. The initial conversion is consequently determined by the relation:

$$\tau_0 = \tau_t \frac{F_{G_0}}{F_{G_t}}, \qquad (1)$$

F_{G_0} being the initial gas flowrate, τ_t and F_{G_t}, respectively the conversion and the flowrate at the time-on-stream t.

This method is not applicable to hydroconversion reactions, for which the turnover number will be given for 2 h on stream.

Materials. Hydrocarbons (puriss. Fluka grade) are carefully distilled. Maximum impurity levels are generally less than 0.4%, with the exception of *p*-xylene (1% *m*-xylene impurity). Rhone-Poulenc GFS 400 γ-Al_2O_3 (BET area 210 m^2 g^{-1}, grain size 1 mm), Rhone Poulenc PBS 300 silica (BET area 260 m^2 g^{-1}, g.s. 0.3 mm), and titania (100% anatase, 10 m^2 g^{-1}, g.s. 0.3 mm) are utilized as supports. Catalysts are prepared by means of wet impregnation with an aqueous solution of rhodium chloride hy-

TABLE 1

Dispersion of the Catalysts

Name	Rh (%)	Dispersion (%)[a]
Rh/Al_2O_3	0.60	90
Rh/SiO_2	0.54	48
Rh/TiO_2	0.23	30

[a] From oxygen titration at 300 K after reduction at 773 K.

drate. Their characteristics are detailed in Table 1. Dispersion measurements are carried out in the GC pulse system previously described (*9*).

Classification of the reactions. Steam conversions of aromatics may lead, in some cases, to a high number of detectable products. Nevertheless, most of them are present in minor proportions and may be discounted in the material balance. The principal products were classified by type of reaction (see Table 2): dealkylation, dehydrogenation, and degradation of the aromatic nucleus. For instance, ethylbenzene steam conversion may imply the following reactions:

dealkylations:

$$\mathrm{EtB} + \mathrm{H_2O} \rightarrow \mathrm{T} + \mathrm{CO} + 2\mathrm{H_2} \qquad (2)$$

$$\mathrm{EtB} + 2\mathrm{H_2O} \rightarrow \mathrm{B} + 2\mathrm{CO} + 4\mathrm{H_2} \qquad (3)$$

dehydrogenation:

$$\mathrm{EtB} \rightarrow \mathrm{Sty} + \mathrm{H_2} \qquad (4)$$

TABLE 2

Classification of the Reaction Products in Alkylbenzene Steam Conversion

Hydrocarbon	Dealkylation[a] (DA)	Dehydrogenation[a] (DH)	Degradation[b] (DN)	Others[c]
Benzene (B)			Only gaseous products (H_2, CO, CO_2, CH_4)	Toluene
Toluene (T)	B	—	Only gaseous products (H_2, CO, CO_2, CH_4)	Xylenes
Ethylbenzene (EtB)	B, T	Styrene (Sty)	Only gaseous products (H_2, CO, CO_2, CH_4)	Ethyltoluene
iso-Propylbenzene (iPB)	B, T, EtB	α-Methylstyrene (αMeSty)	Only gaseous products (H_2, CO, CO_2, CH_4)	Methyl-iPB
tert-Butylbenzene (tBB)	B, T, EtB, iPB	—	Only gaseous products (H_2, CO, CO_2, CH_4)	Methyl-tBB Naphthalene
n-Propylbenzene (nPB)	B, T, EtB	β-Methylstyrene (βMeSty) Allylbenzene (AlB)	Only gaseous products (H_2, CO, CO_2, CH_4)	Indane Indene Naphthalene Methyl-nPB
Xylenes	B, T	—		Xylene isomers

[a] These reactions also yield gaseous products (H_2, for DH and H_2, CO, CO_2, CH_4 . . . for DA) not cited in the table.

[b] Degradation of the aromatic nucleus.

[c] Alkylation, transalkylation, dehydrocyclization.

degradation:

$$EtB + 8H_2O \rightarrow 8CO + 13H_2 \quad (5)$$

Ring opening and alkyl group gasification generally lead to hydrogen and C_1 molecules (CO_2, CO, CH_4). Traces of C_2–C_4 compounds are occasionally observable, particularly with *tert*-butylbenzene, in which case relatively large amounts of C_4 are obtained, in addition to C_1 compounds. Some other reactions may also intervene, such as isomerization, transalkylations, dehydrocyclization, formation of heavy hydrocarbons, and coke. In all instances, these reactions are relatively minor, especially at low conversions, and will be discounted.

RESULTS

I. Steam Conversions over Rh-γAl$_2$O$_3$

Ethylbenzene, iso-propylbenzene, and tert-butylbenzene. The product distributions in steam conversion of EtB, iPB, and tBB are listed in Fig. 1. Benzene is very definitely the chief product of dealkylation at zero conversion. However, the selectivity to toluene invariably increases with conversion, and is generally close to the selectivity to benzene near 30–40% conversion.

The dehydrogenation products are always rather abundant at low conversion. This is particularly true with iPB conversion, in which α-methylstyrene is the chief initial product. Nevertheless, with conversion, the selectivities to the dehydrogenated products rapidly decline. Thermodynamic calculations lead to maximum yield of 16% styrene and 48% α-methylstyrene, respectively, in EtB and iPB conversion at 713 K. Equilibrium is thus obviously not reached; the alkenyl compounds probably dealkylate far more quickly than the corresponding alkyl compounds.

Initial activities are recorded in Fig. 2 as turnover frequencies (molecules of hydrocarbon reacted per metal site per hour). Also noted are the initial activities for toluene and benzene previously determined in separate runs (*9, 17*). The activities recorded in Fig. 2 for the different reactions provide clear proof that (i) global activity in dealkylation decreases with the steric hindrance of the alkyl group; an inverse trend is observed for the dehydrogenation reactions, (ii) the activity in nucleus degradation is *virtually unrelated to the alkyl group size*. Details relating to this crucial finding shall be forthcoming in the Discussion section.

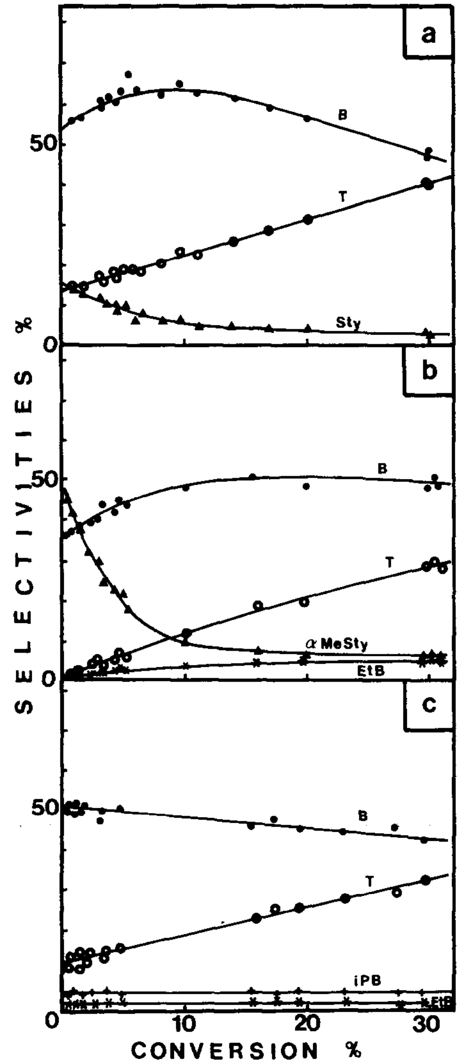


FIG. 1. Product distributions in steam conversion of ethylbenzene (a), *iso*-propylbenzene (b), and *tert*-butylbenzene (c) on Rh/Al$_2$O$_3$ catalyst. Reaction conditions: 713 K, 1 bar, steam to hydrocarbon molar ratio : 6.

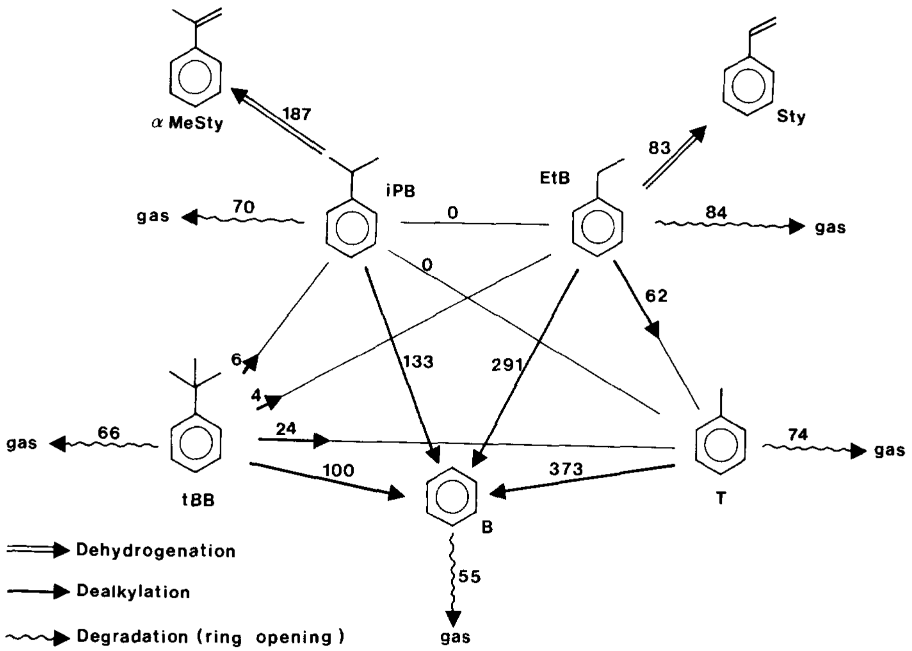


FIG. 2. Initial specific activities (per site and per hour) in steam conversion of benzene, toluene, ethylbenzene, *iso*-propylbenzene, and *tert*-butylbenzene.

n-Propylbenzene. The product distributions (Fig. 3) and the values of the initial activities (Table 3) corroborate previous conclusions. The activity in dealkylation is of the same order of magnitude as for iPB (178 versus 133 h^{-1}) and benzene is the primary product of dealkylation. One may also note the markedly elevated activity in dehydrogenation (461 h^{-1}). Formation of allylbenzene is to be observed, but β-methylstyrene is by far the most prevalent dehydrogenation product; the AlB to β-MeSty molar ratio decreases from approximately 0.1 at zero conversion to 0.05 at 30% conversion. In addition to propenylbenzenes, styrene appeared in the initial products of reaction; this implies that the molecule of nPB may dealkylate and dehy-

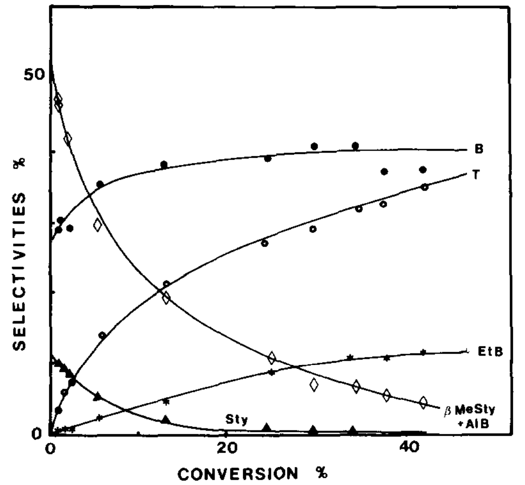


FIG. 3. Product distribution in *n*-propylbenzene steam conversion on Rh/Al_2O_3.

TABLE 3

Specific Activities of the $Rh/\gamma\text{-}Al_2O_3$ Catalyst in the Steam Conversion of *n*-Propylbenzene at 713 K (H_2O/Hydrocarbon Molar Ratio : 6)

a (h^{-1})	Distribution	
710	Dealkylation	178
	Dehydrogenation	461
	Degradation	71

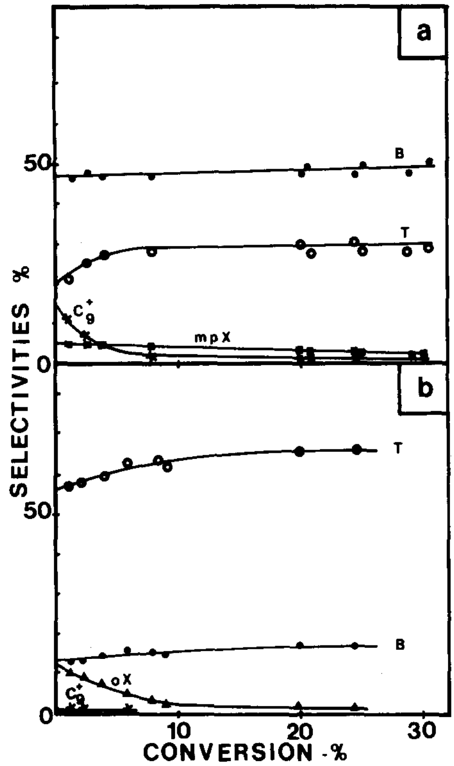


FIG. 4. Product distributions in steam conversion of *o*-xylene (a) and *p*-xylene (b) on Rh/Al_2O_3.

drogenate in a single step at the catalyst surface. It is also important to note that the degradation reaction occurs at a rate (71 h^{-1}) very close to that which was observed in the series B, T, EtB, iPB, and tBB.

Ortho- and para-xylene. Results concerning these two isomers are recorded in Fig. 4 (selectivities) and in Table 4 (activities). The most significant finding has to do with the marked difference between the two products of dealkylation; whereas *p*-xylene undergoes little more than a single C–C bond scission leading to toluene, *o*-xylene may dealkylate by relinquishing, in one step, its two methyl groups.

TABLE 4

Specific Activities of the Rh/γ-Al_2O_3 Catalyst in Steam Conversion of *o*- and *p*-Xylene at 713 K

Hydrocarbon	a (h^{-1})	Distribution	
o-Xylene	950	Dealkylation	627
		Degradation	104
		Others	219
p-Xylene	630[a]	Dealkylation	453
		Degradation	101
		Others	76

[a] Not taking account of the isomerization to *m*-xylene.

TABLE 5

Support Effects in Ethylbenzene Steam Reforming[a]

Catalyst	a (h^{-1})	Distribution (h^{-1})
Rh/SiO_2	120	DA = 12 DH = 78 DN = 30
Rh/TiO_2	150	DA = 54 DH = 87 DN = 9
Rh/Al_2O_3	520	DA = 353 DH = 83 DN = 84

[a] Overall specific activities a (expressed as molecules per metal site per hour) and distributions on variously supported Rh catalysts. DA = dealkylation, Eqs. (2 + 3); DH = dehydrogenation, Eq. (4); DN = degradation of the aromatic nucleus, Eq. (5).

II. Supports Effects in Ethylbenzene Steam Conversion

Ethylbenzene steam conversion was performed on silica- and titania-supported Rh catalysts. The distribution of the initial activities for the various reactions is provided in Table 5. For the sake of comparison, results concerning the Rh/γ-Al_2O_3 catalyst are also included in the table. On this basis, it is evident that (i) the activity in reactions involving a C–C bond splitting (DA and DN) is *strongly support sensitive,* whereas (ii) the activity in dehydrogenation is virtually unrelated to the oxide used as support. It should be noted that the differences of loading and dispersion of the various Rh catalysts may partially alter these conclu-

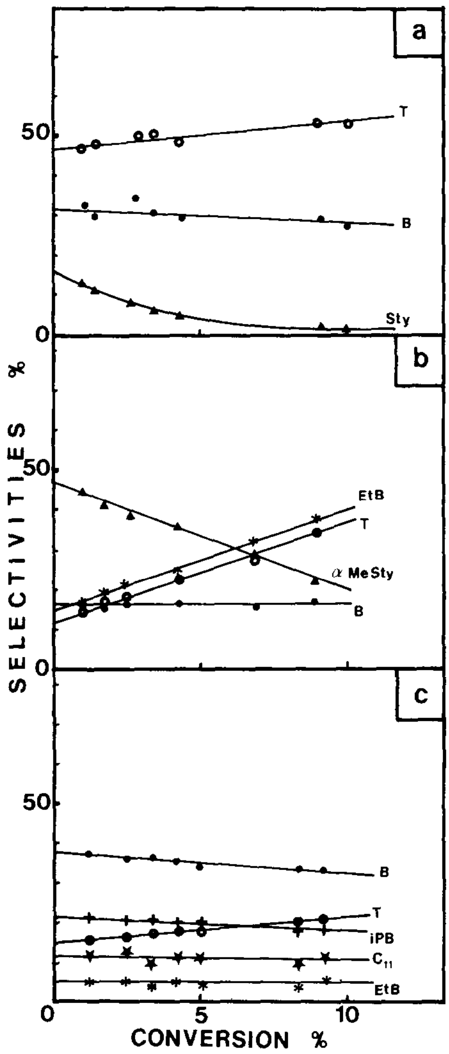


FIG. 5. Product distributions in hydroconversion of ethylbenzene (a), *iso*-propylbenzene (b), and *tert*-butylbenzene (c) on Rh/Al_2O_3. Reaction conditions: 713 K, 1 bar, hydrogen to hydrocarbon molar ratio : 4.

sions. In toluene steam dealkylation, by studying variously dispersed and loaded catalysts, we were able to bear out the existence of a true support effect on the selectivity (*9*). In particular, Rh/Al_2O_3 and Rh/SiO_2 of middle dispersion (40–50%) exhibit difference of selectivities of more than 10%. This remains probably the rule in ethylbenzene steam conversion. One may also note that titanium dioxide is, once again, the best support for purposes of preserving the aromatic nucleus. If the overall selectivities to benzene, toluene and styrene are considered, the supports may be classed as $TiO_2 > Al_2O_3 > SiO_2$, in accordance with our previous results on toluene steam dealkylation (*9*).

III. Hydroconversion over Rh/γ-Al_2O_3

Hydroconversion of ethylbenzene, *iso*-propylbenzene, and *tert*-butylbenzene were carried out on the same rhodium/alumina catalyst sample as in Part I (steam conversions). The product distributions, reported in Fig. 5, clearly demonstrate that the selectivities are strongly affected by the nature of the reactant (H_2 instead of H_2O) which reacts with the hydrocarbon. Hydroconversion preserves to a larger extent the benzene nucleus. The overall aromatic selectivity (that is to say, the sum of the selectivities of the aromatic products) is generally close to 93–96%, in comparison to 70–84% for steam conversion. Benzene has ceased to be the principal or single primary product of dealkylation and as a rule the C–C bond splitting shifts to the chain end. For instance, toluene becomes the main primary product in ethylbenzene conversion. The selectivities to dehydrogenated products are hardly affected by the change in reactant. On the other hand, hydrogen strongly favors the reactions of isomerization and of transalkylation. We may note, for instance, the fairly high selectivity to methyl-*tert*-butylbenzene (referred to as "C_{11}" in Fig. 5c) in tBB conversion.

The activities for 2 h on stream are recorded in Table 6. These values may be guardedly placed in parallel with the *initial* activities in steam conversion. Generally, these activities decrease by a factor of 2 to 3 between 0 and 2 h on stream, so that the turnover frequencies may be considered to be higher in hydroconversion than in steam conversion of aromatics on the same Rh/γ-Al_2O_3 catalyst. Nevertheless, the hydrogen to steam activity ratio is certainly lower than 10. On the basis of the data of Table 6, the following conclusions may be drawn: (i)

TABLE 6

Activities of Rh/γ-Al_2O_3 in Hydroconversion of Some Aromatic Hydrocarbons at 713 K[a]

Reaction	Overall activity[b] (h^{-1})	Distribution	
EtB + H_2	440	DA	350
		DH	65
		DN	25
iPB + H_2	310	DA	150
		DH	135
		DN	25
tBB + H_2	370	DA	305
		TA	40
		DN	25

[a] DA = dealkylation; DH = dehydrogenation; DN = degradation of the aromatic nucleus; TA = transalkylation.

[b] Activity is given for 2 hr on stream.

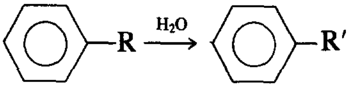
the activities in degradation of the aromatic nucleus remain constant, irrespective of the alkyl group size, (ii) the activities in dehydrogenation are roughly the same as in steam conversion, (iii) on the other hand, the activities in dealkylation appear to be a complex function of the side chain; we may note, especially, the relatively high activity in dealkylation of *tert*-butylbenzene.

DISCUSSION

Let us now explore in detail the problem of selectivity in steam conversion of aromatics. The findings of the present study and clear conclusions of research concerning toluene steam dealkylation are to be considered simultaneously. We hope thereby to engender a novel perspective on this problem.

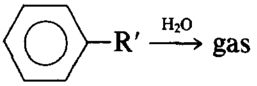
Reaction Scheme of Dealkylation

The present study clearly demonstrates that the primary reaction of steam dealkylation leads essentially to benzene, whatever the alkyl group attached to the aromatic nucleus may be:



+ gas (H_2, CO, CO_2, CH_4) (6)

Nevertheless, the degradation of the nucleus, Eq. (7):



(7)

may not be considered as an ultimate reaction converting benzene into gas when dealkylation is achieved. In fact, if (6) and (7) were consecutive reactions with R′ = H, the selectivity to benzene (or the overall selectivity to aromatics in general) would extrapolate to 100% at zero conversion. As summarized in Fig. 6, this never occurs, even in hydrodealkylation, and we may state that ring opening also occurs in the beginning of the reaction. For toluene, we would have the following triangular scheme:

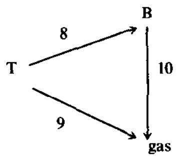


Figure 2 shows that ring opening in the benzene molecule (reaction 10) occurs at about the same rate as in the toluene molecule (reaction 9). In TSDA, reaction 10 is likely to be inhibited, toluene being more strongly bound on the metal sites than is

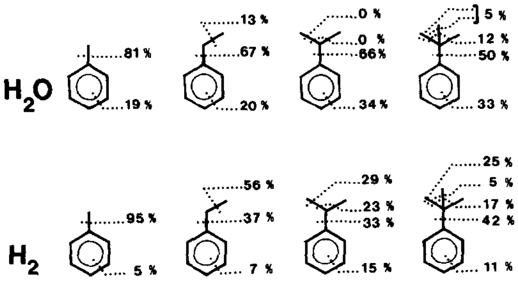


FIG. 6. Comparison of the initial selectivities of C–C splitting in steam and hydroconversion (C–H splitting, exclude from the distribution).

benzene. This hypothesis is in agreement with the results reported by Kim (*16*) on Rh-V/γ-Al_2O_3 catalysts. Competitive hydrogenation of benzene and toluene on various Group VIII metal catalysts has been similarly interpreted (*17, 18*).

Mechanism of Steam Dealkylation of Alkylbenzenes

Let us first recall the four-step mechanism proposed for the toluene steam dealkylation on Rh catalysts (*2, 7, 9*):

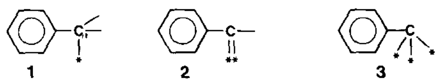
(i) adsorption and dissociation of the water molecule on the support, leading to a population of hydroxyl groups, mobile on the alumina surface.

(ii) adsorption and dissociation of the hydrocarbon on the metal. For instance, the C_6H_5–CH_3 bond scission leads to benzene and a carbene, CH_2, by hydrogen transfer between the phenyl and the methyl groups. The carbene further dehydrogenates into CH_x fragments (with x = 1 or 0) or into polymerized species C_yH_x (with $x/y < 2$).

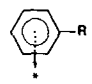
(iii) migration and transfer of the hydroxyl groups from the support to the metal, which induced us to propose a kinetic expression including the specific perimeter of the metal/support boundary (*9*).

(iv) surface reaction, on the metal, between the hydroxyl groups and the dehydrogenated fragments CH_x, leading to gaseous products H_2 and CO. Carbon dioxide and methane are produced by water gas shift (CO_2), CO methanation, or hydrodealkylation (CH_4). The reciprocal influence of toluene and carbon monoxide in these reactions has been studied in detail on Rh, Pt and RhPt catalysts (*10, 20, 21*); as soon as it is formed on the catalyst, CO competes with toluene on the metal sites, thereby inhibiting the conversion of the hydrocarbon. Nevertheless, CO was found to be far more inhibiting towards the ring opening (Eq. (9)) than toward the dealkylation (Eq. (8)). This fact has been advanced as an explanation of the slight increase of the selectivity to benzene with conversion (*19, 22*).

Let us now consider an alkylbenzene reacting with water; the four-step mechanism remains basically unchanged except for step (ii) which will depend on the hydrocarbon. To be precise, the present study has demonstrated that the specific activity of the Rh catalysts in nucleus degradation remains virtually the same, irrespective of the alkyl group. This result leads us to postulate the existence of two types of sites at the metal surface: *sites I on which dealkylation and/or dehydrogenation take place and sites II on which the aromatic nucleus will be opened with a very high probability.* Alkylbenzenes are known to exhibit, on transition metals, two basic modes of adsorption (*23, 24*): (i) mode A, corresponding to the species dehydrogenated on the alkyl group, σ-bonded with the metal, (ii) mode B, corresponding to a π-complex between the aromatic ring and the metal:



A

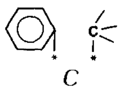


B

In the alkylbenzene series, the C_α–H bonds are the weakest CH bonds of the molecule; this α-carbon is thereby involved, with a high probability, in the metal–carbon bond. The high temperature (713 K in this study) favors the C–C bond scission, including an adjacent site, in such a way that the A species is rapidly transformed into two dissociated species (Eq. (11)):

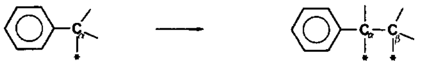
(11)

However, another possibility may be the direct dissociation upon adsorption, of the C–C_α bond (mode C):



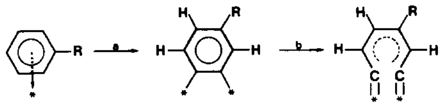
C

Mode C has been considered by Balandin (*1*) as the primary step for toluene dealkylation on Ni catalysts, and is, in fact, implicitly involved in the second step of the mechanism of toluene steam dealkylation quoted above. The fact that hydrogen does not inhibit dealkylation and that *tert*-butylbenzene can dealkylate renders the direct dissociation quite probable, given that this mode does not necessitate any preliminary hydrogen abstraction. On the other hand the mode A which may evolve into an $\alpha\beta$-diadsorbed species (Eq. (12)), accounts well for the side chain dehydrogenation and thus cannot be excluded as the first step of chemisorption:



(12)

Mode B is expected to be the precursor of the ring opening. That idea is reinforced by the fact that benzene reaction is strongly inhibited in the presence of alkylbenzenes which yield, in fact, π-alkyl–arene metal complexes more strongly bonded than those of benzene. Nevertheless, the π-species must undergo profound transformation into σ-bonded species, which corresponds to the slow step of the ring opening:



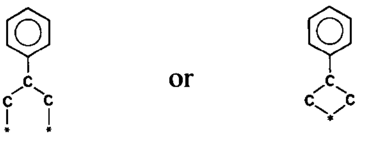
(13)

D

Once the ring is opened, all the C–C bonds are promptly cracked (virtually no C_2–C_5 molecules in the products), so that step 13 cannot be distinguished from the direct dissociation of the six C–C bonds of the ring, which may occur upon the initial chemisorption. In any event, the first C–C bond splitting in the ring only takes place on particular sites, referred above to as sites II. We will now relate these models to the experimental data concerning selectivities in alkylbenzene dealkylation.

Role of Hydrogen in Hydrodealkylation

The aromatic nucleus has been found to be much more preserved in hydrogen than in steam dealkylation (compare Fig. 2 and Table 6). Hydrogen probably inhibits the formation of the most strongly dehydrogenated species (especially the D species resulting from Eq. (13b)). This adequately explains the exceedingly low degradation of the ring in hydrodealkylation. We may now dwell upon the selectivities of C–C bond splitting along the side chain. Hydrogen, used instead of steam, tends to favor chain-end ruptures; the direct dissociation (C species) and the formation of C_α adsorbed species are thus inhibited by hydrogen. The adsorption via terminal carbons probably leads to a perpendicular position of the molecule on the metallic surface. For instance, with *iso*-propylbenzene:



Such perpendicular species adequately explain the pronounced increase of selectivity to ethylbenzene and toluene in iPB hydrodealkylation. Why hydrogen favors these species on Rh has yet to be ascertained; further studies on Ni and Pt are in progress to elucidate this point. Nevertheless, we may for the time being recall that the mechanisms of dealkylation with hydrogen and steam are basically different; in particular, hydrogen and hydrocarbon compete with the same metal sites, whereas steam is adsorbed on the support. A competitive mechanism, as in hydrodealkylation, may induce hydrocarbon to adsorb on a minimum area and thereby favor the perpendicular species. On the other hand, Ni catalysts have been found to favor competitive mechanisms, whether in hydrogen or in steam dealkylation. Preliminary results have demonstrated that selectivity differences in the two processes are relatively less pronounced on Ni than on Rh and Pt. This result corroborates our interpretation.

Factors Governing the Selectivity in Steam Dealkylation

As far as toluene steam dealkylation goes, we are dealing with factors already widely known. The influence of some such factors has been verified in ethylbenzene conversion (present study and Ref. *25*), and it may justifiably be postulated that the following series of conclusions holds, independent of the alkyl group. The selectivity with respect to benzene (to aromatics in the general case) increases with

(i) the metal dispersion (*5, 8, 9*),

(ii) the carbon monoxide coverage (*20, 21*),

(iii) the sulfur coverage (*25*), and

(iv) the effect of some special supports (*5, 9*). As stated in the Introduction, the following order of increasing selectivity was obtained:

$$TiO_2 > Cr_2O_3 > Al_2O_3 > SiO_2.$$

On the other hand, carbon coverage did not seem to be a determining factor with regard to the selectivity, which remains constant throughout the self-poisoning of the catalyst (*26*).

The general features of these factors very much tend to suggest that selectivity and, consequently, ring opening is determined either by a site ensemble effect, or by the electronic properties of the metal. In the framework of the site ensemble theory, the selective sites (sites I) would consist of a low number of rhodium atoms, probably one or two atoms: let us recall that, in poisoning experiments (*25, 26*), the residual activity of the catalyst is roughly proportional to the amount of chemisorbed hydrogen on the poisoned catalyst. On the contrary, the nonselective sites (sites II) would stem from a relatively high number of adjacent atoms (>2). This model adequately explains the higher density of sites I on small particles and the preferential poisoning of sites II by carbon monoxide and sulfur. Support effects, especially the relatively high selectivity observed on Rh/TiO_2, may be attributed to a partial precoverage of the metal by the support (for instance, coverage of Rh particles by TiO_x species). We have already demonstrated (*27*) that the SMSI effects are exceedingly sensitive to water. Nevertheless, a residual coverage by titanium oxide species most probably exists, even after a lengthy exposure of the catalyst in a steam environment. On the other hand, the site ensemble theory fails to explain the insensitivity of the selectivity to carbonaceous deposits. It should be specified that this invariability of the selectivity has been verified in a flow reactor beyond 30 min on stream, that is to say, in a carbon coverage range of 50–85%. We have very little information concerning catalyst behavior at the outset of the reaction. On the basis of a pulse reactor study, Rabinovich *et al.* (*2*) determined the selectivity on a fresh $Rh/\gamma\text{-}Al_2O_3$ catalyst. Their data yield a value of 90% upon the first pulse of toluene (8% conversion), which is quite close to the selectivity determined on an aged catalyst. We may thus suppose, for the time being, that regardless of the nature of the metallic surface, selectivity is certainly not affected by carbon.

In terms of the electronic concept, the catalyst may be viewed as displaying a maximum of selectivity when the metal particle is most electron deficient. This interpretation is supported by the fact that an electron transfer from the metal to the support is generally to be expected, and sometimes observed, in highly dispersed catalysts (*28, 29*). Likewise, electrophilic adsorbates, especially sulfur (*30*) and carbon monoxide (*31*), are believed to induce an electron transfer from the metal *d*-orbitals to the adsorbed species. On the other hand, carbonaceous deposits (i.e., C_yH_x polymeric species) are generally expected to exhibit electron donor properties similar to adsorbed unsaturated hydrocarbons (*32*). However, the electron donation is certainly weak and it is conspicuous to see that coke has no effect on the selectivity. The electronic interpretation does not succeed in providing an unquestionable explanation as to the role of the support with regard to selectivity. The metal, in the SMSI state, is believed to possess an excess electron density, resulting from a charge transfer from the reduced support to the metal. Nevertheless, as pointed out above, the steam atmosphere annihilates the SMSI effects and even seems to induce a positive charge on the metal particle (*27*). If this is the case, the electronic interpretation remains uncontested. Ring opening probably occurs from a $\pi \rightarrow \sigma$ transformation (Eq. (13)) leading to species with a number of carbon–metal bonds higher than in the intermediate species of dealkylation (A and C). Therefore, electron deficient particles are less able to realize these $\pi \rightarrow \sigma$ transformations leading to gasification of the aromatic nucleus. Most of the results obtained in toluene steam dealkylation may be explained in term of electronic effects. On the other hand, geometric or steric effects seem to be operating in the case of bulky alkyl groups. In fact, we obtained the following order for the various alkylbenzenes with respect to the dealkylation rate: toluene > ethylbenzene $\gg$ *iso*-propylbenzene ~ *tert*-butylbenzene, although the C_6H_5–CH_2R and the $C_6H_5C(R')$–H bond strengths in these hydrocarbons decrease in the reverse order (*33*). It is clear that *iso*-propyl and *tert*-butyl groups hinder the formation of the carbon–metal bond. Moreover, the primary dealkylation of *p*-xylene into benzene requires an adsorption via the two methyl groups on a relatively large surface area whereas the adsorption of *o*-xylene requires one or two metal atoms. This may explain why the selectivity to benzene was found to be quite different in the conversion of the two isomers.

To sum up, electronic effects are very likely to operate in aromatic dealkylation; the main effect is the dealkylation to ring opening ratio which increases with the electron deficiency of the rhodium particles. Nevertheless, among all the features of the reaction, only *one* (the insensitivity of the selectivity to coking) may be opposed to the geometric concept. That the ensemble effects may also operate in steam dealkylation remains a point of controversy. A necessity for further research, particularly regarding metals other than rhodium, is plainly evident. In fact, platinum and nickel are the objects of studies presently in progress.

ADDENDUM

From investigations of the propylbenzene steam dealkylation performed in his laboratory, one of the referees has remarked that the product distributions may be affected by the support porosity. This observation was interpreted on the basis of specific coking of meso- and micropores. In our case, we observed no important modification of the pore distribution in the catalyst before and after the reaction, probably because the alumina support used was not very microporous ($\bar{r}$ = 4–5 nm). As pointed out in the present paper, the product distribution is also sensitive to the dispersion state of the metal and to the nature of the carrier. This may account for slight differences observed with various Rh/Al_2O_3 samples.

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