

Effects of Dispersion and Partial Reduction on the Catalytic Properties of Rh/Al₂O₃ Catalysts in the Steam Reforming of Mono- and Bicyclic Aromatics

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The steam reforming of toluene, cumene, and methyl-1-naphthalene was studied on well-reduced Rh/Al₂O₃ catalysts of different dispersions and on partially reduced catalysts in which the dispersion of the metallic phase was maintained at $25 \pm 2\%$. The principal reactions were dehydrogenation DH (cumene \rightarrow α -methylstyrene), dealkylation DA (for instance, toluene \rightarrow benzene), naphthalene ring opening NRO (methylnaphthalene \rightarrow benzene + toluene), and degradations DN (total gasification of the molecules). Dispersion and partial reduction effects are shown to occur and can be summarized as follows: a partially reduced sample behaves catalytically as would dispersed and well-reduced catalysts. In this case, DN reactions are much inhibited, whereas DA and, to a lesser extent, NRO are relatively less affected by partial reduction. Moreover, DH is quite unaffected by these factors. The results may be expressed in terms of either electronic (DN favored on particles where the metal is more capable of donating electrons) or geometric effects (DN favored on a large ensemble of adjacent sites). These models are discussed on the basis of kinetic and XPS results, particularly those obtained on partially reduced Rh/Al₂O₃ catalyst samples. Alloy effects (selectivities modified by the presence of RhAl alloy) could also occur on a catalyst calcined and reduced at high temperatures. © 1989 Academic Press, Inc.

INTRODUCTION

Rhodium/alumina is one of the most efficient catalysts for the steam reforming of alkylbenzenes (1-7). In the course of this process, three types of reaction may occur, namely *dealkylation* (DA) leading to shorter alkylbenzenes, *dehydrogenation* (DH) producing alkenylbenzenes, and *degradation* (DN) leading to ring opening followed by transformation of the molecule into hydrogen and carbon oxides. Toluene and cumene can be chosen as probe molecules for these different reactions: toluene can dealkylate into benzene and cumene into benzene, toluene, and ethylbenzene. Each of these molecules can lead to ring

opening. Moreover, dehydrogenation occurs in cumene steam conversion which produces, at low conversion, α -methylstyrene with a relatively high selectivity (7). We have recently published a study on the steam conversion of methyl-1-naphthalene on Rh, Pt, and Ni catalysts (8, 9). In accordance with the results obtained by Kim (10), we noted that the naphthalene ring can be cleaved to give benzene and toluene on rhodium and on nickel catalysts. This reaction, called *naphthalene ring opening* (NRO), occurs at the same time as the dealkylation (methylnaphthalene \rightarrow naphthalene) and degradation, the latter being here the total gasification of *both* rings.

In the studies mentioned, steam conversions of alkylbenzenes (6, 7) and methyl-naphthalene (8, 9) were investigated on well-dispersed and well-reduced rhodium/alumina catalysts. In this paper, we give the results of further studies which show that

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the state of dispersion and of reduction of the metal induces significant changes in the catalytic behavior of rhodium/alumina catalysts. While the first parameter (particle size) is frequently invoked in studies on metal catalysts, the second parameter (reduction state) has been much more rarely studied. Yet this reduction state very probably entails significant changes in the catalytic behavior of nonnoble metal catalysts which, when supported on alumina, are not readily reducible. The effect of partial reduction on catalytic properties of cobalt (11, 12) and nickel (13) catalysts was recently reported. As far as rhodium catalysts are concerned, the determining role of Rh^{n+} species in CO/H_2 reactions was demonstrated by Watson and Somorjai (14), who used transient methods on rhodium oxide surfaces, and also by van den Berg *et al.* (15), who employed adequate promoters for Rh/SiO_2 catalysts. Rhodium/alumina catalysts present the advantage of being easily obtained with variable degrees of reduction (16, 17). The samples used in this study were selected from among a series of catalysts treated at high temperatures (air or H_2) and comprised catalysts either totally reduced with variable dispersions or dispersed at approximately 25% with varying degrees of reduction.

EXPERIMENTAL

Catalyst preparation. Rhône Poulenc GFS 300 alumina (crushed and sieved to 0.15–0.3 mm) following pretreatment at high temperatures (air 1223 K, 36 h, H_2 1273 K, 36 h, final BET area $110 \text{ m}^2 \text{ g}^{-1}$) was used as a support. Catalysts (2 and 4% Rh) were prepared by means of exchange of the support with aqueous solutions of rhodium chloride hydrate. They were dried at 393 K and subsequently calcined at a specified temperature, to be denoted $x^\circ\text{C}$ (air, 5 h), and reduced at 773 K, or else calcined at 723 K and reduced at a specified temperature, denoted $y^\circ\text{C}$ (H_2 , 14 h). The catalysts are referred to as RhAx and RhAyH , respectively.

Characterization of the catalysts. Dispersion measurements were carried out in a pulsed-flow chromatographic system described elsewhere (18). Catalyst samples (0.2 to 0.5 g) were reduced *in situ* under a flow of H_2 (total impurities <1 ppm) at 773 K for 14 h, flushed under a flow of argon (total impurities <0.5 ppm) at 773 K for 3 h, and finally cooled to room temperature. Hydrogen chemisorption (H_C) and oxygen (O_T) and hydrogen (H_T) titrations were carried out successively. The titration reaction H_T on rhodium was relatively slow and had to be carried out at 333 K so as to obtain the correct ratio $\text{H}_\text{T}/\text{O}_\text{T} = 2$. Results are given in micromoles of atoms O or H per gram of catalyst. Following H_T titration, hydrogen was thermodesorbed at 15 K min^{-1} up to 773 K. Oxygen uptakes $\text{O}_\text{C}500$ at 773 K were subsequently measured in order to evaluate the extent of metal reduction %R. On well-reduced samples, the stoichiometries O/Rh were found to be quite close to 1.5, which shows that complete oxidation of rhodium was attained at 773 K. Thus on partially reduced samples, %R can be deduced from

$$\%R = \frac{2}{3}(\text{O}_\text{C}500)/x_\text{m}, \quad (1)$$

where x_m is the rhodium content in micromoles of atoms Rh per gram.

X-ray photoelectron spectra were recorded using an AEI ES 200B spectrometer following reduction at 773 K and transfer of the sample under nitrogen into the analysis chamber of the spectrometer. Binding energies of Rh $3d_{3/2}$ and Rh $3d_{5/2}$ levels were standardized, using the Al $2p$ peak as a reference (B.E. = 74.8 eV). In partially reduced samples, four-peak spectra corresponding to the $3d$ doublets of Rh° and Rh^{3+} were observed and required a deconvolution of the spectrum for measuring accurately the kinetic energies, and hence binding energies.

Hydrocarbon/ H_2O reactions. Toluene and cumene of puriss grade were obtained from Fluka. Cumene was carefully distilled and contained less than 0.1% impurities

TABLE I

Catalyst Characteristics: Dispersion Measurements and Extent of Reduction (at 773 K)

No.	Catalyst designation	Rh (wt%)	Pretreatment		Gas uptakes				D^a (%)	R^b (%)
			Air T (K)	H_2 T (K)	H_C	O_T ($\mu\text{mol at g}^{-1}$)	H_T	O_{C500}		
1	RhA120	1.92	393	773	145	263	544	282	70	100
2	RhA450	1.93	723	773	155	271	556	281	73	100
3	RhA500H	3.53	723	773	239	376	717	507	56	100
4	RhA800H	3.74	723	1073	142	250	490	542	35	100
5	RhA900H	3.82	723	1173	113	186	392	557	25	100
6	RhA800	1.92	1073	1073	10	30	82	97	23	34
7	RhA900	1.91	1173	773	9	23	60	61	27	22

^a Dispersion of the metallic phase deduced from O_T values.^b Extent of reduction deduced from O_{C500} .

(mainly *n*-propylbenzene and trimethylbenzenes). Commercial methyl-1-naphthalene (500–800 ppm S) was desulfurized over 20% Ni/Al₂O₃, at 573 K (H_2 /Me-1-N molar ratio: 4, atm. pressure). Reaction products (30% naphthalene) were distilled (N_2 , 20 Torr) to yield methyl-1-naphthalene containing less than 5 ppm S, and approximately 5% methyl-2-naphthalene.

The reactions were carried out in a flow reactor at 713 K at atmospheric pressure. H_2O /hydrocarbon molar ratios were 5.9, 7.7, and 14.5 for toluene, cumene, and methyl-1-naphthalene, respectively. Reaction products were analyzed by GC, light hydrocarbons and carbon oxides on Porapak Q, hydrogen on a 5A molecular sieve, and aromatics on a SE30 glass capillary column. The initial activities (at zero time) were determined by the "flow-rate" method as described elsewhere (7, 19) and expressed in this study as turnover frequencies (molecules of hydrocarbon reacted per metal site and per hour). Selectivities are defined as the number of molecules formed per molecule of hydrocarbon reacted.

RESULTS

Catalyst Characteristics

The dispersion and the extent of reduction are reported in Table 1. Series 1–5 correspond to well-reduced samples with dif-

ferent dispersions while series 5–7 consist of partially reduced samples with metallic phases of comparable dispersion (~25%). High temperatures of calcination (series RhAx) induce the formation of a phase non-reducible at 773 K and even at 1073 K (catalyst 6). This result is in accordance with a report by Yao *et al.* (16), who found that air treatment inhibits the additional reduction of rhodium in alumina-supported catalysts. This nonreducible phase, resulting from a diffusion of Rh^{3+} ions in subsurface regions of the alumina matrix, does not appear to have a well-defined structure (20) and will be referred to as "diffuse oxide phase" (DOP). X-ray photoelectron spectroscopy (Table 2) confirms the dependence of binding energies on the size of the metal particles, already reported by Huizinga *et al.* (21) and by Rouco and Haller (22) for Rh catalysts. The DOP is easily characterized by XP spectra of RhA900 but disappears in spectra of RhA800 which was calcined and reduced at elevated temperatures. It may reasonably be inferred that the DOP can be either embedded in the alumina matrix or eclipsed by the metal particles. Another interesting result given in Table 2 is that the binding energy of Rh 3d in DOP is greater than that in Rh_2O_3 , which indicates that rhodium oxide in DOP is in a quite different state from that of Rh^{3+} in Rh_2O_3 .

TABLE 2

Binding Energies (in eV) of Rh 3d Doublets Deduced from XPS Measurements

No.	Catalyst designation	Rh ⁰ 3d		Rh ³⁺ 3d	
		5/2	3/2	5/2	3/2
1	RhA120	307.7	312.5		
2	RhA450	307.8	312.4		
3	RhA500H	307.7	312.5		
4	RhA800H	307.2	311.9		
5	RhA900H	307.2	311.9	No visible trace	
6	RhA800	307.1	311.8	trace	
7	RhA900	307.3	311.9	310.2	314.9
	Rh black	307.0	311.7		
	Rh ₂ O ₃			309.1	

Dispersion Effects on the Activity and on the Selectivity

Catalysts 1 and 2 were found to exhibit very similar behavior and will no longer be distinguished in what follows. Variations of the selectivities to benzene S_B in toluene steam dealkylation are given in Fig. 1. The results prove definitely that there is a promoter effect of the dispersion on the initial selectivity to benzene, extrapolated to zero conversion (Fig. 1b). The specific activities reported in Table 3 emphasize the trends of variation for each reaction, dealkylation DA and degradation DN. Even though the variations are relatively small, a continuous increase in DN with the mean particle size is apparent, while the values of DA are virtually constant. This means that the ring opening tends to be suppressed on the small particles.

The three principal reactions appearing in cumene steam reforming are dehydrogenation DH into α -methylstyrene, dealkylation DA (leading essentially to benzene B and, to a lesser extent, to toluene T), and ring degradation DN. The variations of the selectivities are shown in Fig. 2. For the sake of clarity, DH, DA, and DN are represented separately. The more dispersed catalysts are definitely more selective toward dealkylation (especially to benzene) and

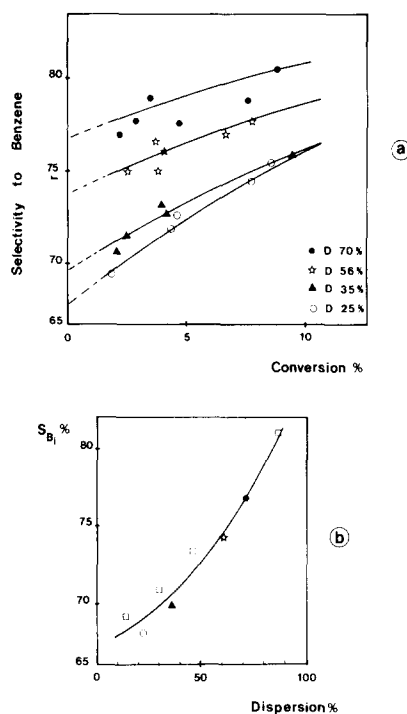


FIG. 1. Dispersion effects in toluene steam dealkylation at 713 K. (a) Variation of the selectivity to benzene with the conversion of toluene. Each symbol corresponds to differing dispersions D quoted in the figure. (b) Effect of the dispersion upon the initial selectivity to benzene. Open squares correspond to results previously obtained (27).

conserve to a greater extent the aromatic nucleus. The effect of particle size on the selectivity toward dehydrogenation is quite

TABLE 3

Activities of Variously Dispersed Rh/Al₂O₃ Catalysts in Toluene Steam Reforming^a at 713 K

Catalyst designation	D_0	a (h ⁻¹)	Distribution	
			DA	DN
RhA120	70	740	570	170
RhA500H	56	820	620	210
RhA800H	35	850	590	260
RhA900H	25	780	510	270

^a Overall specific activities a are expressed as molecules of toluene reacted per metal site per hour. DA, dealkylation to benzene; DN, degradation of the nucleus (total gasification).

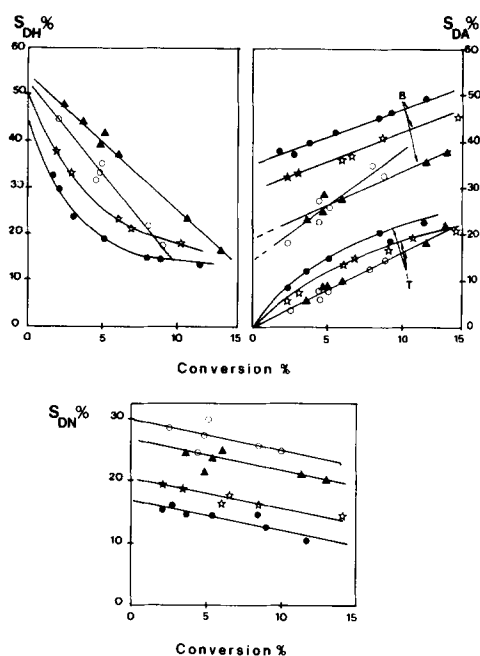


FIG. 2. Product distributions in steam conversion of cumene (713 K) on variously dispersed Rh/Al₂O₃ catalysts (same symbols as in Fig. 1). DH, dehydrogenation (α -methylstyrene); DA, dealkylation (benzene, B, and toluene, T); DN, degradation (overall gasification).

complex; this reaction appears to be relatively enhanced on RhA800H dispersed at 35%. The distribution of the specific activities (Table 4) reveals that well-dispersed Rh/Al₂O₃ catalysts are more active in cumene dealkylation, but less able to produce a ring opening, while the activity in dehydrogenation is quite unaffected by the dispersion state of the metal.

The selectivity conversion curves in methyl-1-naphthalene steam reforming plotted in Fig. 3 show that the dispersion of the metal phase favors dealkylation at the expense of degradation, whereas particle size does not appear to affect NRO. Actually, activity distributions (Table 5) demonstrate that turnover frequencies in DA and even in NRO are high on rhodium sites located on small particles; in this case, degradation is strongly inhibited. For instance, when the metal dispersion increases from 25 to 70%, the activity per metal site varies

TABLE 4

Activities of Variously Dispersed Rh/Al₂O₃ Catalysts in Cumene Steam Reforming^a at 713 K

Catalyst designation	a (h ⁻¹)	Distribution		
		DH	DA	DN
70	570	260	205	105
56	660	330	195	135
35	640	345	130	165
25	610	320	105	185

^a DH, dehydrogenation to α -methylstyrene; DA, dealkylation (benzene + toluene + ethylbenzene); DN, degradation.

by +72%, +38%, and -34% for DA, NRO, and DN, respectively.

Effect of Partial Reduction on the Activity and on the Selectivity

Catalyst samples 5-7 (Table 1) were selected for the study of the effect of partial

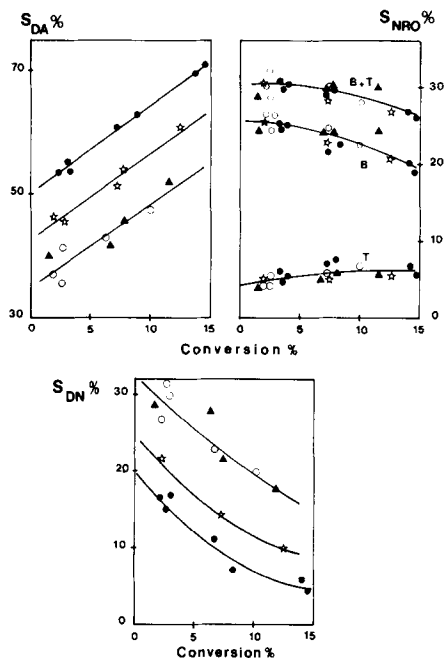


FIG. 3. Product distributions in steam conversion of methyl-1-naphthalene (713 K) on variously dispersed Rh/Al₂O₃ catalysts (same symbols as in Fig. 1). DA, dealkylation (naphthalene); NRO, naphthalene ring opening (benzene and toluene); DN, degradation (overall gasification of both rings).

TABLE 5

Activities of Various Dispersed Rh/Al₂O₃ in Methyl-1-naphthalene Steam Reforming^a at 713 K

Dispersion (%)	<i>a</i> (h ⁻¹)	Distribution		
		DA	NRO	DN
70	240	120	72	48
56	235	108	70	57
35	210	80	57	73
25	195	70	52	73

^a DA, dealkylation into naphthalene; NRO, naphthalene ring opening (into benzene + toluene); DN, degradation (total gasification of both rings).

reduction on the kinetic behavior of Rh/Al₂O₃ catalysts. With all these samples, the dispersion of the metallic phase is practically the same (about 25%); this can be considered proof of the significant role of the reduction state. The variations of the selectivity are represented in Fig. 4 (toluene), Fig. 5 (cumene), and Fig. 6 (methyl-1-naphthalene), and show that

(i) partial reduction induces significant modifications in the product spectrum. Absolute variations of selectivity are the highest in the dealkylation of methyl-1-naphthalene and in the dehydrogenation of cumene where 30% shifts of the selectivities are observed.

(ii) A partially reduced sample behaves

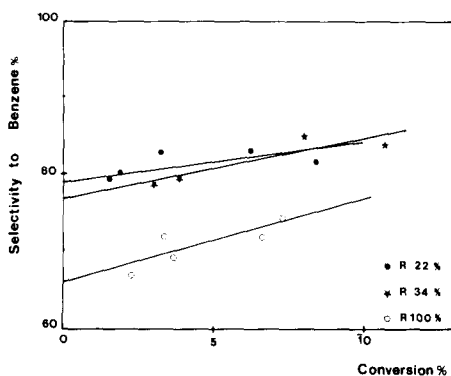


FIG. 4. Variation of the selectivity to benzene in toluene steam dealkylation on partially reduced Rh/alumina catalysts. Each symbol corresponds to differing degrees of reduction *R* quoted in this figure.

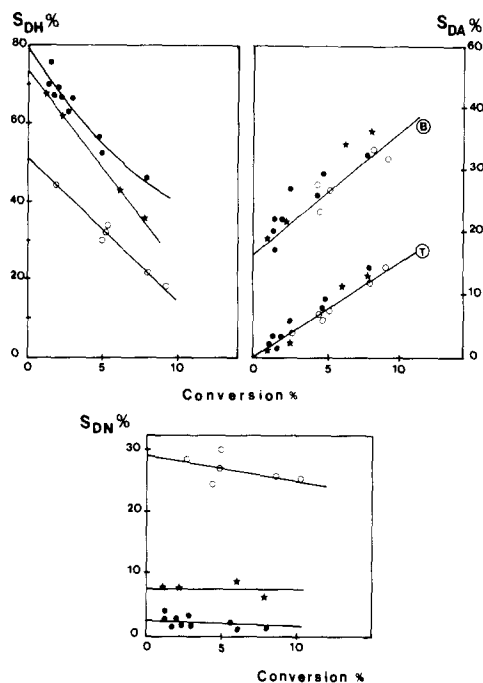


FIG. 5. Product distributions in steam conversion of cumene on partially reduced Rh/Al₂O₃ catalysts (same symbols as in Fig. 4). DH, dehydrogenation; DA, dealkylation; DN, degradation (gasification of the ring).

as would a totally reduced and better dispersed catalyst. The distribution of the specific activity is recorded in Table 6, which confirms the general trends observed for the selectivity. In every case, the degradation reactions are strongly inhibited by the presence of an unreduced phase; this is particularly so with cumene and methyl-1-naphthalene conversions. Nevertheless, it can be noted that the increase in selectivity to α -methylstyrene in cumene steam reforming is due exclusively to the inhibition of the other reactions. Actually, the dehydrogenation activity of each catalyst is virtually constant whatever the degree of reduction. Dehydrogenation is hence confirmed as a reaction which is relatively insensitive to the environment of the metal site.

DISCUSSION

The results demonstrate clearly that the effects of dispersion and of partial reduc-

TABLE 6

Activities^a of Partially Reduced Rh/Al₂O₃ Catalysts in Steam Reforming of Toluene, Cumene, and Methyl-1-naphthalene at 713 K

Extent of reduction (%)	Toluene			Cumene				Methyl-1-naphthalene			
	<i>a</i> (h ⁻¹)	DA	DN	<i>a</i> (h ⁻¹)	DH	DA	DN	<i>a</i> (h ⁻¹)	DA	NRO	DN
22	620	490	130	450	360	77	13	175	128	30	17
34	630	485	145	500	370	85	45	190	120	44	26
100	780	510	270	610	320	105	185	195	70	52	73

^a Overall specific activities *a* are given in molecules reacted per metal site per hour. DA, dealkylation; DH, dehydrogenation; DN, degradation (total gasification), NRO, naphthalene ring opening (one of the two rings).

tion are practically similar: an increase in dispersion is equivalent to a decrease in the degree of reduction. Nevertheless, the action of these factors would appear to be highly oriented: they have much more effect on the degradation reactions which lead to total gasification than on the selective reactions which give products with more than one carbon in the molecule (Ta-

ble 7). These reactions include dehydrogenation, dealkylation, and, to a lesser extent, naphthalene ring opening. The results may be interpreted by means of the three alternative models discussed below.

In the *electronic model*, selectivity would be controlled by the capacity of the metal to donate electrons. Here, degradation reactions would require a greater number of electrons than would the selective reactions, such as dealkylation and dehydrogenation. This is due to the very nature of the degradation intermediates, which would be largely dehydrogenated and multibonded to the metal (7). This model is in agreement with the analysis of the effects

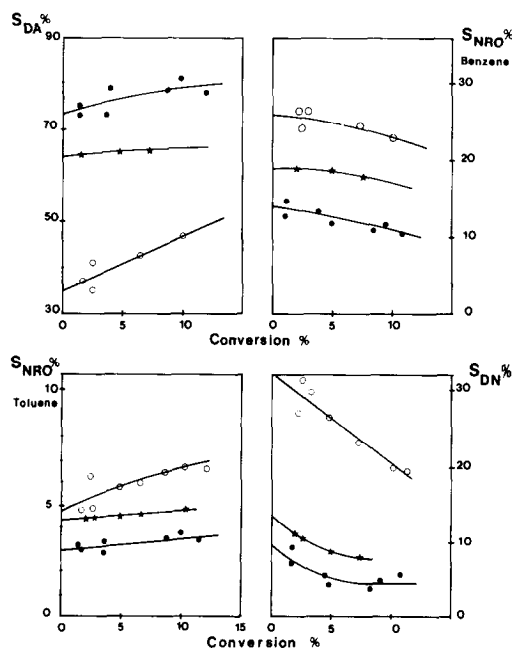


Fig. 6. Product distributions in steam conversion of methyl-1-naphthalene on partially reduced Rh/Al₂O₃ catalysts (same symbols as in Fig. 4). DA, dealkylation; NRO, naphthalene ring opening; DN, degradation (gasification of both rings).

TABLE 7

Survey of the Dispersion and the Partial Reduction Effects on the Various Reactions Involved in Aromatic Steam Reforming

Factor	Hydrocarbon	Effects on the reactions of			
		DH	DA	NRO	DN
Dispersion ^a	Toluene	-	0	-	---
	Cumene	0	-	-	---
	Me1N	-	++	---	---
Partial ^b reduction	Toluene	-	0	-	---
	Cumene	0	-	-	---
	Me1N	-	++	---	---

Note. Scale is as follows: 0, 0.9 < ratio < 1.1; +, 1.1 < ratio < 1.5; ++, 1.5 < ratio < 3; -, 0.66 < ratio < 0.9; --, 0.33 < ratio < 0.66; ---, 0.1 < ratio < 0.33; ----, 0 < ratio < 0.1.

^a Activity ratio between the best dispersed catalyst (70%) and the less dispersed one (25%).

^b Activity ratio between the less reduced catalyst (22%) and the totally reduced one.

of dispersion and of partial reduction. The work function is generally higher in small particles than in the bulk of the metal (23). This increases the electron affinity of the metal in a well-dispersed catalyst. In partially reduced samples, the diffuse oxide phase stabilized by alumina can interact with the metal particles. The dual sites $\text{Rh}^0\text{-Rh}^{3+}$, thus created, would be equivalent to positively charged species $\text{Rh}^{\delta+}$. The results obtained in this study are similar to those reported by Schwab (24). In his study of a donor-like reaction (the dehydrogenation of formic acid), Schwab showed that the presence of nickel oxide in alumina substantially increased the activity of $\text{Ni}/\text{Al}_2\text{O}_3$ catalysts. Schwab claimed that this proves that nickel is more capable of accepting an electron (and hence less able to donate an electron) in $\text{Ni-NiO}/\text{Al}_2\text{O}_3$ than in $\text{Ni}/\text{Al}_2\text{O}_3$. Nevertheless, the donor character of the formic acid decomposition depends largely on the intermediates of reaction so that the conclusions of Schwab cannot be generally accepted.

The *geometric or ensemble model* was previously developed in order to explain the kinetics of hydrogenolysis reactions (25, 26). Within the framework of this theory, the catalytic reaction depends on the occurrence of an ensemble of n adjacent sites. It is clear that the reactions requiring a large ensemble will be quite sensitive to the metal particle size and to the dilution of the surface by inactive or less active species (e.g., poisons or the added metal in bimetallic catalysts). The degradation reactions involved in the steam reforming of aromatics thus depend on an ensemble of sites larger than that of the selective reactions and, for this reason, are relatively inhibited on small particles (6, 27). If the geometric model is to be valid, the unreduced species of rhodium, catalytically inactive, must cover and dilute the metal surface randomly.

Although it would appear difficult to distinguish between the two theories, it can be noted that the XPS results can provide ar-

guments against the electronic and the geometric models. No chemical shifts of the kinetic energy of $\text{Rh}^0 3d$ were recorded in the presence of DOP (Table 2), which goes against the electronic model. However, the DOP could not be detected in the RhA800 sample either (calcined and reduced at 800°C). Even so, the variation of selectivity due to the oxide phase was recorded for this sample, which constitutes an argument against the geometric model: the DOP is deeply embedded in the alumina matrix and the presence of Rh^{3+} species on the rhodium particles is most unlikely in RhA800. Thus neither the electronic model nor the geometric model can satisfactorily explain all the results.

The *alloy model* can also be invoked to justify the results obtained on these catalysts. High-temperature treatment can lead to new chemical structures such as rhodium aluminate or rhodium-aluminum alloys which certainly have a catalytic behavior quite different from that of metallic rhodium. Actually, the formation of rhodium-aluminum alloy could be expected for the RhA800 sample which was calcined and reduced at high temperatures. Nevertheless, not only the occurrence but also the stability of new chemical structures in $\text{Rh}/\text{Al}_2\text{O}_3$ catalyst treated at elevated temperature must be confirmed. This research is currently in progress.

CONCLUSIONS

In the steam reforming of toluene, cumene, and methyl-1-naphthalene, particle size and partial reduction can modify significantly the product spectrum. The most affected reactions are the degradation (i.e., the total gasification of the molecule) and, to a lesser extent, the naphthalene ring opening and the dealkylation; the dehydrogenation of cumene to methylstyrene is practically unaffected by the factors examined in this study. The above results can be ascribed to electronic effects, the degradation being favored on metal particles which have a more marked electron-donor charac-

ter, or to geometric effects, the degradation requiring a large ensemble of adjacent metal sites. Nevertheless, a partial reduction effect is recorded even in the case where the oxide phase is no longer visible by XPS. Moreover, the binding energies of Rh⁰ are not at all affected by the presence of the oxide phase. These results seem to show that geometric and electronic effects cannot explain in every case the catalytic behavior of partially reduced Rh/Al₂O₃ catalysts, particularly when they are prepared by calcination *and* reduction at high temperatures. The formation of other rhodium-aluminum compounds could then justify the results obtained with these catalysts.

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