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Steam Dealkylation of Aromatic Hydrocarbons

II. Role of the Support and Kinetic Pathway of Oxygenated Species in Toluene Steam Dealkylation over Group VIII Metal Catalysts

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The role of the support in steam dealkylation (SDA) is studied on a series of Group VIII metal catalysts supported on alumina, silica, and titania. When possible turnover frequencies are given on the basis of the free metal fraction during the reaction. The values are generally constant with time-on-stream and represent the actual turnover frequency of the catalyst. Metals can be classified into two groups, namely, support-sensitive metals (Pt, Rh, Pd) and support-insensitive metals (Ni, Co, Ru, and to a certain extent Ir). Support sensitivity is related to the oxidizability of the metallic surface. For metals of the first group, the reaction is probably governed by a noncompetitive mechanism in which the metal coverage by the oxygenated species is negligible. Kinetic derivation leads to a rate law where there is at once intervention of the support site concentration and of the specific perimeter of the metal/support interface. One can thus explain the support effect for this metal group and the slight sensitivity to the crystallite size observed in the Rh/Al_2O_3 series. For metals of the second group, a competitive mechanism probably takes place on the metal. Kinetic derivation leads to a rate law independent of the support site concentration and accounting for the slight negative order with respect to toluene as previously reported. The conspicuous parallelism between the selectivities of the various metals in SDA, in hydrodealkylation, and in hydrogenolysis is also discussed. In addition to the metal, the support and the crystallite size are determining factors of the selectivity to benzene in SDA.

INTRODUCTION

The steam dealkylation of aromatic hydrocarbons (SDA) has been extensively studied during the last 10 years as a possible process for replacing hydrogen by water in the catalytic treatment of some petroleum fractions. The selective reaction, Eq. (1), is generally accompanied by the nonselective steam reforming, Eq. (2), and by the interconversion reactions of water–gas shift, Eq. (3), and methanation of CO, Eq. (4):

$$C_6H_5CH_3 + H_2O \rightarrow C_6H_6 + CO + 2H_2 \quad (1)$$

$$C_6H_5CH_3 + 7H_2O \rightarrow 7CO + 11H_2 \quad (2)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (3)$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O \quad (4)$$

Some other reactions can intervene, particularly the condensation of aromatic hydrocarbons which seems to be very important in regard to catalyst fouling.

The reaction over supported Group VIII metals presents the following features:

(i) On a given support, specific activities of noble metals lie within two orders of magnitude (*1–3*). Concerning Al_2O_3, Grenoble (*2*) reports the following sequence based upon the relative specific activities of the metals for benzene formation: Rh, 100; Ru, 52; Pd, 34; Pt, 21; Ir, 14; Ni, 9; Os, 3. Clearly, the noble metals show a poor specificity toward steam dealkylation.

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(ii) The specific activities of the metals depend upon the support used in association with the metal (*4–7*). Various researches devoted to rhodium catalysts lead to the following order: Cr_2O_3 130 > γ-Al_2O_3 100 > α-Al_2O_3 40–50 > Silica-alumina 15–40 > SiO_2 2–20 > C 1–2 > Rh black 0.5. It is thus obvious that the supports exhibit a specificity as great as the metal itself.

(iii) The kinetic orders with respect to toluene are close to zero; the orders with respect to water vary, but are always within the range 0–1.

These results have been interpreted in terms of a bifunctional reaction: it is assumed that a determining step, activation of water, takes place on the support. An alternative explanation might be a modification by the support of the electronic properties and especially the oxidation–reduction properties of the metal. In any case, the catalysts may be expected to show a very different sensitivity to the support, this depending upon the metal being used.

Results available in the literature on the support effect in SDA concern mainly rhodium as the active metal. In this paper, we present for the first time a comparative study of this effect with the following metals: Pt, Pd, Ir, Ru, Ni, Co, and Rh using γ-Al_2O_3 and SiO_2 as supports. In addition some data were obtained on titania (anatase) as support. The work includes the measurement of the actual turnover frequency based on the exposed fraction of the metal in aged catalysts. Metal areas are determined in fresh and aged catalysts by chemisorption, titration, and in some cases TPD techniques. Results are correlated with the relative activities of aged catalysts in benzene hydrogenation, a reaction most often considered as structure insensitive in spite of some slight discrepancies (*8*, *9*). The various metals studied here will be classified into two groups according to whether or not they are sensitive to the support in SDA. This result will be discussed in terms of metal surface oxidizability and will hence lead to a differing view concerning the kinetic pathway of the oxygenated species according to the metal group defined above.

EXPERIMENTAL METHODS

Apparatus for steam dealkylation and analysis. The steam dealkylation is carried out in a flow reactor at atmospheric pressure (*3*). The sample is reduced *in situ* at 723 K, cooled at 713 K then steamed for ¼ hr before toluene addition. The weight space velocity varies from 1 (standard value) to 12 hr^{-1} for highly metal-loaded catalysts. The partial pressures of water and toluene are 86.6 and 14.7 kPa, respectively. On account of the relative complexity of analysis and the rapid decline in conversion, initial activity (at zero time) can never be extrapolated either directly or by linear transform with sufficient accuracy. Thus the metal area was determined using the catalyst in the closest possible state that follows its activity measurement. A preliminary study showed that the most reproducible results are obtained by cooling the sample in the reaction product atmosphere, which may be purged at a temperature less than 473 K. Flushing the catalyst at 713 K in N_2 or Ar always results in a partial regeneration.

In a previous paper (*3*) we showed by calculating the catalyst efficiency and by experimental verification that there is no diffusional limitation for conversions of less than 50%. In the present work toluene conversion is typically less than 15%. Initial selectivities (at zero conversion) are determined in separate runs by varying the reactant flowrates.

Materials. The reaction has been carried out with twice-distilled water and toluene puriss. Fluka was used without further purification.

Rhone Poulenc GFS 400 γ-Al_2O_3 (BET area 210 m^2 g^{-1}, grain size 1 mm), Davison silica (BET area 350 m^2 g^{-1}, g.s. 0.3 mm), Rhone Poulenc PBS 300 silica (BET area 260 m^2 g^{-1}, g.s. 0.3 mm), and titania (anatase BET area 10 m^2 g^{-1}, g.s. 0.3 mm) were used as supports. Alumina and silica were first calcined in flowing air at 673 K for 4 hr, then treated in a stream of H_2 at 823 K for 48 hr and soaked in acidified water (HCL 0.05 *N*) for 10 hr at room temperature. Titania was treated in water, dried at 400 K, and used without further pretreatment. Catalysts were prepared by wet impregnation with aqueous solutions of metal salts, dried at 400 K, and calcined in flowing air at 673 K.

Nomenclature. Catalysts are referred to as MX where M is the metal and X the support (X = A for the γ-alumina, D for the Davison silica, P for the Rhone Poulenc silica, and T for the titania). For example, RhA is the standard catalyst 0.6% Rh/Al_2O_3. In addition some catalysts Rh/Al_2O_3 were prepared with metal of different loadings and called RhxA, where x is the Rh%. EUROPT-1 (6.2% Pt/SiO_2) is also included in the silica-supported series of catalysts.

Aged catalysts (that is, already used in SDA) are referred to as MXUt_R where MX is the name of the fresh catalyst, U signifies used, and t_R is the time-on-stream (in hours). For example, RhAU7 is the RhA catalyst used during 7 hr in steam dealkylation.

Dispersion measurements. Exposed fractions of metals are determined by the GC pulse technique (1 pulse = 0.315 cm^3). The sample (0.2 to 1 g) is previously reduced *in situ* at 723 K in flowing H_2 then purged with ultrapure Ar for 3 hr and cooled in flowing Ar at 298 K (Pt, Pd, Ru, Ni, Co) or at 333 K (Rh, Ir). Another set of experiments is carried out on fresh catalysts: after hydrogen chemisorption, the oven temperature is raised at 20 K min^{-1} to 723 K and the TPD spectra are recorded, which allows a comparison between the amounts of H_2 chemisorbed and thermodesorbed.

On Ru catalysts, oxygen titration exhibits a particular feature: a part of the chemisorbed H_2 leaves the metal surface without reacting with O_2 to give water. Nonadsorbed oxygen and hydrogen leaving the surface are separated on a 5A zeolite column prior to detection. The method for determining the exposed fraction will be given later.

Aged catalysts are characterized by their residual metal exposed fraction measured as in fresh catalysts. Nevertheless a previous study (*10*) showed that, above 573 K, reduction of RhAU catalysts in flowing H_2 results in a partial regeneration. Similar conclusions can be drawn from Fig. 1 for other catalysts. Therefore aged catalysts are uniformly reduced at 573 K prior to dispersion measurements. Highly coked and highly metal-loaded catalysts are even more sensitive to the temperature of reactivation. For these catalysts, special precautions must be taken, namely, carefully drying under ultrapure carrier gas at 473 K prior to re-reduction at this temperature. Results are then correlated with the ratio of the activities of aged and fresh catalysts in benzene hydrogenation.

Benzene hydrogenation. Apparatus and procedure. Activity is measured at 373 ± 0.5 K in a conventional flow reactor. Other conditions are: benzene (thiophen free) 2 cm^3 hr^{-1}, H_2 180 STP cm^3 min^{-1}, hydrogen to benzene molar ratio of 19. Quasilinear deactivation is very weak and activity can be easily extrapolated to zero time. Catalyst weights (16 to 200 mg) are chosen to ensure that the conversion is less than 10%. Radial heat transfer is improved by diluting

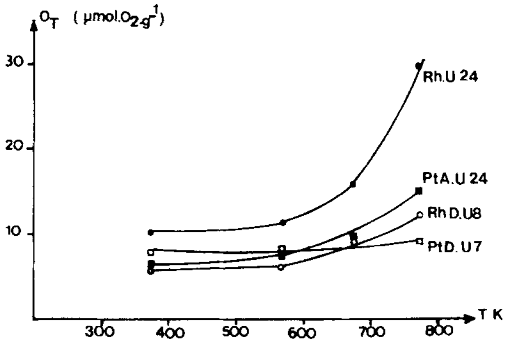

FIG. 1. Oxygen uptakes in titration of chemisorbed hydrogen on aged catalysts as a function of the temperature of reactivation.

the catalyst with carborundum (200 to 500 mg).

Runs are carried out *in situ* as follows. Reduction of aged catalysts at 573 K as in the GC pulse system, re-set of the temperature to 373 K for activity measurement, regeneration of the sample in flowing air at 573 K, reduction at 723 K, re-set to 373 K for measuring the activity of the regenerated sample which is found to be very close to that of the fresh catalyst (measured in separate runs). As a rule *in situ* regeneration was preferred to ensure that the samples are compared with the same amount of metal.

RESULTS

Dispersion of Fresh Catalysts

Chemisorption, titration, and desorption results are listed in Table 1. Stoichiometries of H and O chemisorption were assumed to be equal to unity except for O on Rh ($O/Rh_s \simeq 1.5$) and on Ru ($O/Ru_s \simeq 2$) in agreement with previous works (*10–15*). According to Wanke and Dougharty (*16*) O/Rh_s varies from 1 to 1.5 with temperature and metal loading. Fuentes and Figueras (*17*, *18*) conclude that $O/Rh_s \simeq 1$ at 298 K but this value would be very sensitive to temperature and close to 1.5 at 383 K. Under our experimental conditions (333 K, maximum partial pressure of O_2 11 kPa), the value 1.5 accounts well for the chemisorption and titration results. Numerous works have been devoted to dispersion measurement of Pt catalysts by the GC pulse technique (*19–24*). Conflicting results have been obtained, the ratio $H_C : O_T : H_T$ varying from 1 : 1 : 2 to 1 : 1.5 : 3. If chemisorption after 15 min purging is taken into consideration, H_C is close to $O_T/1.5$.

With ruthenium catalysts, titration at 298 K takes place following the two reactions:

$$\text{Ru H} + O_2 \rightarrow RuO_2 + \tfrac{1}{2} H_2 \qquad (5)$$

$$\text{Ru H} + \tfrac{5}{4} O_2 \rightarrow RuO_2 + \tfrac{1}{2} H_2O \qquad (6)$$

An example of oxygen titration on RuA at 298 K is shown in Fig. 2. If the exposed fraction of Ru titrated according to Eqs. (5) and (6) are respectively called Ru_{sa} and Ru_{sb}, then:

$$O_T = 2\ Ru_{sa} + 2.5\ Ru_{sb}. \qquad (7)$$

Ru_{sa} is obtained from the amount of hydrogen leaving the surface (peak 1) and Ru_{sb} is derived from Eq. (7). For RuA, we obtained $Ru_{sa} = 9.2\ \mu mol\ g^{-1}$ and $Ru_{sb} = 2.3\ \mu mol\ g^{-1}$: mode (5) is predominant on this catalyst. Hydrogen titration uptakes are very low at 298 K and the titration must be carried out at 473 K. These results concerning supported Ru catalysts are in agreement with those of Blanchard and Charcosset (*25*) who showed by temperature-programmed reduction that Ru/Al_2O_3 cannot be completely reduced before 473 K.

Titania-supported catalysts RhT and PtT display very small hydrogen uptakes in chemisorption compared to oxygen uptakes in titration. This result fits well with data of Tauster *et al.* (26) interpreted as a manifestation of strong metal–support interactions.

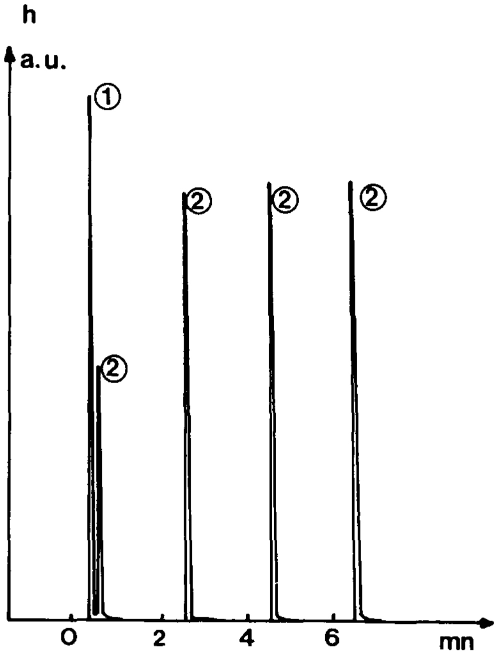

FIG. 2. Oxygen titration of chemisorbed hydrogen on RuA at 298 K; catalyst weight: 0.5 g. (1) Peak of H_2 evolved from the surface; (2) peaks of nonadsorbed O_2.

TABLE 1

Dispersion Measurements for Fresh Catalysts

Catalyst	Metal loading w%	H/M (H_C)		O/M (O_T)	H/M (H_T)	H/M (TPD)	Dispersion $D_0\%$[c]
		a	*b*				
RhA	0.6	1.02	0.93	1.92	3.75	0.89	96
Rh5A	5	0.53	0.46	0.89	1.77	0.43	45
Rh10A	10	0.161	0.136	0.275	0.53	0.134	13.7
RhD	0.6	0.37	0.35	0.78	1.41	0.33	39
RhP	0.6	0.44	0.38	0.84	1.66	0.37	42
RhT	0.3	0.031		0.41			28
PtA	1.1	0.92	0.75	1.02	1.94	0.70	68
PtD	1.1	0.49	0.41	0.58	1.06	0.40	39
PtP	1.1	0.55	0.48	0.68	1.18	0.46	45
EUROPT-1	6.2	0.76	0.65	0.82	1.68	0.63	54
PtT	0.6	0.039		0.179			16
IrA	1.15	0.93	0.85	1.28	2.44	0.81	86
IrD	1.15	0.40	0.35	0.57	1.06	0.34	38
PdA	0.6			0.49		0.28	33
PdD	0.6			0.127		0.077	8.5
NiA	5	0.043		0.180		0.037	4.3
NiD	5	0.064				0.056	6.4
NiP	5	0.039				0.033	3.9
RuA	0.6	0.19	0.18	0.42	0.68[d]	0.19	20
RuD	0.6	0.090		0.262	0.37[d]	0.07	11.3
CoA	5	0.010				0.011	1.0
CoP	5	0.014				0.014	1.4

[a] Total chemisorption.

[b] Difference between two successive chemisorptions (interval 15 min between the last pulse of the first chemisorption and the first pulse of the second one).

[c] From oxygen titration of chemisorbed hydrogen (O_T) except for Ni and Co catalysts where D_0 is given from H_C values.

[d] At 473 K; at 298 K, H_T is very low (<0.1).

Activities of Alumina-Supported Catalysts

Results are reported in Table 2 which also includes partial results on RhA, PtA, and IrA catalysts previously reported (*3*, *10*).

We define the following terms: t_R is time-on-stream in SDA (in hours); f_0 is the metal exposed fraction in fresh catalysts (i.e., $D_0/100$); f is the metal fraction still accessible in aged catalysts at $t = t_R$; r is the rate of toluene SDA at t_R and at 713 K expressed in mole of toluene reacted per mole of metal (total, not only exposed) and per hour; a_0 is specific activity based on f_0 ($a_0 = r/f_0$); a is specific activity based on f ($a = r/f$).

As r is measured at t_R, a is assumed to represent the actual turnover frequency of the toluene on the catalyst at this time. RhA, PtA, IrA, PdA, and NiA are similar from a behavioral standpoint: following a fairly rapid initial deactivation, the catalyst becomes more stable. Generally the a values are constant for a given catalyst. This fact has been interpreted as a nonselective self-poisoning by coke formation (*10*). Thus a can be assumed to represent the value of a_0 extrapolated to zero time and to be the true turnover frequency at any moment of the catalyst life.

The behavior of RuA and CoA is very different: the initial loss in activity leads to a total deactivation in less than 5 hr. This abrupt deactivation does not seem to be only due to the catalyst fouling since the

TABLE 2

Activities of Alumina-Supported Catalysts in Toluene Steam Dealkylation (713 K)

Catalyst	f_0	t_R(hr)	r(hr^{-1})	f[a]	a_0(hr^{-1})	a(hr^{-1})	Initial selectivity to benzene (%)	Selectivity at 10% conversion
RhA	0.96	2	141	0.30	147	470	81	86
		7	111	0.25	116	444		
		24	92	0.195	96	473		
		80	63	0.14	66	453		
Rh5A	0.43	6	81	0.124	189	653	74	76
Rh10A	0.137	2	9.52		72		70	74
		24	8.73	0.044	66	198		
PtA	0.68	1	28.5		42		98	98
		7	14.5	0.165	24.5	88		
		10	12		17.5			
		24	8.5	0.105	12	81		
IrA	0.86	1	21.5		25		88	91
		7	16.8	0.28	19.5	60		
		10	14		16.5			
		24	9.5	0.165	11	57		
PdA	0.33	5	20.1	0.15	61	134	97	98
		11	16.8	0.132	51	127		
NiA	0.043	1	2.17				59	70
		7	1.47	0.019	34	77		
RuA	0.20	0	12.7[b]			64[b]	53[c]	
		0.25	4.95		25			
CoA	0.010	0	0.67[b]			67[b]	51[c]	
		0.25	0.35		35			

[a] f values obtained at different times with a same catalyst correspond to separate runs.

[b] Extrapolated at zero time according to Eq. (8).

[c] Values obtained at conversion <2%, not extrapolated at zero conversion.

coke content is very low (less than 0.1%) and in addition the catalyst CoA comes out blue from the reactor which proves that the cobalt is no longer in its metallic state at the end of the run. The f values of these catalysts were not determined as the measurement itself would have inevitabily allowed the catalyst to be regenerated. Thus initial activity was estimated as follows: experimental conditions (catalyst weight, flow rates) are adjusted to allow an accurate balance to be performed at a short time-on-stream. Assuming that the selectivity remains constant, conversion is then proportional to the gaseous product flowrate F_G which may be followed from the first moment of the reaction. The initial activity r_0 is obtained by extrapolation at zero time of the actual activity r from the curve of F_G vs t_R:

$$r_0 = r_t \cdot F_{G0}/F_{Gt} \qquad (8)$$

and

$$a = (r/f_0)_{t \to 0} = r_0/f_0.$$

This measurement rests entirely on a time-constant selectivity to benzene and must be considered with care. Nevertheless, with regard to the stable catalysts, selectivity appears to be rather specific to the metal used and varies little with conversion. The slight increase which may be observed at 10% conversion has been ascribed for Rh/Al_2O_3 catalysts to the inhibitor role of CO favoring the selective reaction (*27*). For poorly selective catalysts, larger variations can be observed (see, e.g., NiA) which is not yet in excess of 10%. In the hypothesis in which such a variation in selectivity took place on RuA and CoA catalysts, r_0 might be underestimated at 18% which does not alter significantly the activities reported in Table 2.

Activities of Catalysts Supported on Silica and Titania

Results concerning both types of silica D and P and the EUROPT-1 catalyst are reported in Table 3. Initial activities of RuD and CoP were determined as for RuA and CoA.

Activity per free metal site a does not depend on the time on stream (see, e.g., catalyst RhD) and actually represents a measure of the true initial specific activity. It is also clear that a is not altered by the type of silica used in combination with the metal: if PtD, PtP, and EUROPT-1 are compared, their a values are very close to 15 hr^{-1}.

On the other hand, the relative specific activities of metals supported on alumina and silica confirm the existence of a support effect in SDA but according to the metal/support used, this effect appears to be more or less marked.

(i) Rh, Pt, Pd exhibit a lower specific activity when they are deposited on silica. By contrast, Ni, Co, Ru and to a certain extent Ir show no change with the nature of the support.

(ii) In all cases, except Pd, selectivity to benzene is found to be lower on silica as support and this is in agreement with results reported by Grenoble (*6*) on nonalumina-supported rhodium catalysts.

Titania-supported Rh appears in Table 3 as having a specific activity very close to that of the same metal supported on silica. Nevertheless it must be noted that the selectivity to benzene may be quite different (90% on Rh/TiO_2 versus 62% on Rh/SiO_2).

By contrast, platinum supported on titania exhibits a particular behavior, showing a relatively high initial activity greater than

TABLE 3

Activities of Silica-Supported and Titania-Supported Catalysts in Toluene Steam Dealkylation (713 K)

Catalyst	f_0	t_R(hr)	r(hr^{-1})	f	a_0(hr^{-1})	a(hr^{-1})	Initial selectivity to benzene (%)
RhD	0.39	8	9.7	0.107	25	91	62
RhP	0.42	7	12.2	0.128	29	95	62
PtD	0.39	6	2.75	0.181	7.0	15.2	95
PtP	0.45	7	2.15	0.145	4.8	14.8	95
EUROPT-1	0.54	7	4.42	0.30	8.2	14.7	96
IrD	0.38	1	7.0	0.155	18.4	45	62
		8	1.83	0.045	4.8	41	
PdD	0.085	2	1.19	0.022	14.0	54	97
NiD	0.064	7	1.38	0.020	21.5	69	43
NiP	0.039	7	0.82	0.0125	20.9	66	45
RuD	0.113	0	7.0[a]			62[a]	40[b]
		0.25	3.46		30.6		
CoD	0.014	0	0.90[a]			64[a]	36[b]
		0.5	0.24		17.1		
RhT	0.28	6	12.5	0.124	45	101	90
PtT	0.16	0	23.5[a]			147[a]	96[b]
		1.5	1.91		11.9		

[a] Extrapolated at zero time according to Eq. (8).

[b] Values obtained at conversion <2%, not extrapolated at zero conversion.

Pt/Al_2O_3 but followed by a sharp decrease analogous to that of Co and Ru catalysts.

Activities in Benzene Hydrogenation (BH)

Activity measurement in BH was performed on some fresh, aged, and regenerated catalysts as a second means of evaluating the free metal surface area. We define the following: b_{r_0} is the specific activity in BH of regenerated catalysts based on the exposed fraction of the fresh catalyst (per hour); b_{f_0} is the specific activity of fresh catalysts, based upon f_0; and b_{u_0} is the specific activity of aged catalysts, also based upon f_0. Results are reported in Table 4. Assuming that the activity is proportional to the free metal surface area:

$$f_0/f = a/a_0 = b_{r_0}/b_{u_0} \qquad (9)$$

and assuming the regeneration to be total,

$$b_{r_0} = b_{f_0}. \qquad (10)$$

Relation (10) has been verified with our catalysts. On the other hand, BH activities lead to a lower residual metal area: $b_{r_0}/b_{u_0} > f_0/f$. a^* values of a derived from Eq. (9) with b_{r_0}/b_{u_0} ratios are reported in Table 4. As the a^* values for a given metal supported on alumina and silica vary in the same direction, the discrepancies between a and a^* are not important enough to invalidate a comparison of the catalysts. Hereafter only a values from Tables 2 and 3 will be taken into consideration.

It is worth noting that in benzene hydrogenation Pt catalysts are support-insensitive while Rh appears as more active on alumina and Ni on silica.

TABLE 4

Activities of Rh, Pt, and Ni Catalysts in Benzene Hydrogenation (373 K)

Catalyst	b_{r_0}	b_{f_0}	b_{u_0}	b_{r_0}/b_{u_0}	f_0/f	a^*
RhA-U7	3250	3350	805	4.0	3.8	468
RhP-U7	995	980	255	3.9	3.3	112
PtA-U7	1690	1670	320	5.3	4.1	114
PtD-U6	1650	1560	385	4.2	2.2	29
EUROPT-U7	1850	1910	670	2.8	1.8	23
NiA-U7	68	67	18	3.8	2.3	127
NiD-U7	278		68	4.2	3.2	91
NiP-U7	168	178	44	3.8	3.1	81

DISCUSSION

Relative Activities of Group VIII Metals on Alumina and Silica

The following sequence of the activity of alumina-supported Group VIII metals can be derived from Table 2 for toluene conversion: Rh, 100; Pd, 28.3; Pt, 18.3; Ni, 16.7; Co, 14.5; Ru, 13.9; Ir, 12.6 and for benzene formation: Rh, 100; Pd, 33.9; Pt, 22.1; Ir, 13.7; Ni, 12.3; Co, 9.2; Ru, 9.1.

For every metal, except Ru, the results are in agreement with the relative specific activities reported by Grenoble (*2*) in spite of fairly different experimental conditions (lower water and toluene partial pressure, activities measured at 1 hr on stream and based on the initial dispersion). Grenoble points out no particular deactivation for Ru. Rabinovich and Mozhaiko (*1*) and Mori and Uchiyama (*4*) find that Ru shows a lower activity than Pd, Pt, and Ir. In his study on ethane steam reforming, Rostrup-Nielsen (*28*) obtains very close specific activities for Ru and Rh but it must be noted that these activities are determined with 10% H_2 in steam to prevent metal oxidation. In the light of these different results it seems that Ru would be very sensitive to the partial pressure of water and to the hydrogen/steam ratio in the reactive phase. This appears also the case for Co; furthermore Rostrup-Nielsen notes that the presence of 10% H_2 in steam is not sufficient to prevent the oxidation of Co.

Considering now the results given in Table 3, the following sequence is obtained for the silica-supported metals using as reference the same catalyst (RhA): in toluene conversion Rh, 20.2; Ni, 14.6; Co, 13.9; Ru, 13.4; Pd, 11.7; Ir, 9.3; Pt, 3.3, and in benzene formation Rh, 15.5; Pd, 14.2; Ni, 8.0; Ir, 7.2; Ru, 6.7; Co, 6.2; Pt, 3.8.

Results are available in the literature concerning the support effect in Rh catalysts.

The activity ratio of Rh/γ-Al_2O_3 and Rh/SiO_2 is found to be equal to 23 by Grenoble (*6*) and to 4.5 by Kochloefl (*5*). It amounts to 5 in our study. The difference lies in the relatively low activity found by Grenoble for Rh/SiO_2.

By including the other metals used in this study, the following order for the relative activity of M/Al_2O_3 and of M/SiO_2 is obtained: Pt, 5.5; Rh, 5.0; Pd, 2.4; Ir, 1.4; Ni, 1.1; Ru, 1.0; Co, 1.0. The absolute values of the activities are subject to some uncertainty but inasmuch as the order for the support sensitivity is based on *relative* activities most of the systematic errors can compensate one another.

The metals may be classified into two groups: (i) a group comprising Pt, Rh, and Pd which are support-sensitive and (ii) Ni, Ru, Co, and to a lesser extent Ir which are support-insensitive. It is worth noting that the metals of the second group are the most oxidizable metals of Group VIII. The metal oxidizability can be related to the heat of formation of the oxides, to the energy of the metal–oxygen bond or to the heat of chemisorption of oxygen on the metal. This last, more representative of the surface state, provides data which are more in correlation with a catalytic phenomenon. From the results of Brennan *et al.* (*29*), metals may be divided into two groups: (i) a first group comprising metals with a low initial heat (<400 kJ mol^{-1}) continuously decreasing with the coverage; this is the case for Pt and Pd the heats of which fall from 300 to 125 kJ mol^{-1}, and (ii) a second group comprising the metals with a larger heat (>400 kJ mol^{-1}) constant with the coverage. This group holds the majority of the metals studied by Brennan *et al.*, in particular Ni and Co. Rhodium takes up a particular place, exhibiting a large initial heat (500 kJ mol^{-1}) which decreases with the coverage (250 kJ mol^{-1} at 40% coverage). Because of its mean heat of chemisorption, rhodium may be classified in the first group.

The surface chemistry of the reactions of the metals with water is generally less well known than that of the reactions of the metals with O_2. As a rule, metals of the first group are given as relatively inert towards H_2O and the strength of interaction metal/H_2O is fairly weak (*30*). Metals of the second group are more or less oxidizable by water. Suhrmann *et al.* (*31*) report that a clean nickel surface is covered with OH groups from a temperature as low as 195 K. Alnot *et al.* (*32*) report a similar result on rhenium, a metal of the second group not studied in the present work; on rhenium at 300 K, water adsorption appears to be dissociative with a formation of H_2 and surface oxygenated species. A comparative study of Ni, Co, and Re/γ-Al_2O_3 catalysts in toluene SDA (*33*) has shown that Re was less active than cobalt and underwent a strong deactivation. Among the metals of the second group, nickel occupies a particular place: it appears to be less oxidizable by water than the other elements of the group which bears out its stability compared to that of the first group of metals.

Role of Water and Kinetic Pathway of the Oxygenated Species

The support effect previously put forward concerning the rhodium catalysts has been explained by all the authors as a direct intervention of the support in the reaction pathway (*1, 6, 35*). The most direct proof has been advanced by Dydykina *et al.* (*34*) who showed by an ir study that, in the absence of water in the reactants, toluene reacts on Rh/γ-Al_2O_3 to form CO with a correlative decrease of the OH surface density on alumina. Kochloefl (*5*) proposes a kinetic equation implying a surface reaction on the same sites. Nevertheless this equation does not exclude the fact that the support may act as a primary adsorbent for the water molecule.

The results reported in the present paper strongly support the fact that the mechanism and particularly the kinetic pathway of the oxygenated species should differ according to the group of the metal.

On the least oxidizable metals such as

Rh, Pt, and Pd, the presence of oxide or hydroxyl species in appreciable amount on the metal is very unlikely. For these metals, the noncompetitive mechanism probably predominates and can be written as follows:

(i) equilibrium of water adsorption on to the support sites (referred to as S-O-S to take into account their chemical nature)

$$H_2O + S\text{-}O\text{-}S \overset{K_w}{\rightleftharpoons} 2S\text{-}OH \tag{11}$$

(ii) adsorption and reaction of toluene on the metal site (referred to as M)

$$T + M \xrightarrow{k_T} M\text{-}CH_x + B + \frac{2-x}{2} H_2 \tag{12}$$

(iii) migration and reaction of the surface species

$$M\text{-}CH_x + 2S\text{-}OH \xrightarrow{k} S\text{-}O\text{-}S + M + (CO, H_2) \tag{13}$$

This sequence of reactions previously proposed by Grenoble has been modified in its third step to take into account the recovering of the support site.

Let us call S_0 and M_0 the respective initial concentrations of the support sites and of the metal sites (site number per unit of catalyst surface area); I_0, the total perimeter of the support/metal interface per unit of catalyst surface area; and a^* and a, the rates per unit of total surface area and per metal site, respectively.

Step (13) includes a transfer phenomenon to or through the support/metal boundary; as a consequence its rate is proportional to I_0. Thus $k = KI_0$.

Using the power transform of hyperbolic expressions, the kinetic derivation of steps (11)–(13) leads to the following expression:

$$a = \frac{a^*}{M_0} = C(S_0^2 I_0)^{1-n} P_T^{\,n} P_{H_2O}^{\,m(1-n)}. \tag{14}$$

For metals that follow the noncompetitive mechanism, Eq. (14) accounts for the support effect by the term $S_0^{2(1-n)}$ but also for the particle size effect by the term I_0^{1-n}. In the case of a homogeneous distribution of metallic particles, it has been shown that (see Appendix)

$$I_0 = \frac{A_m^2}{x_m} \cdot \frac{\beta\rho}{A} \tag{15}$$

where A_m is the metallic surface area (m^2) per g of catalyst, x_m is metal loading (%), ρ is the specific weight of the metal (g m^{-3}), A is the BET area of the catalyst (m^2 g^{-1}), and β is the coefficient depending on the particle shape (value given in Appendix). If we consider the catalysts of the Rh/Al$_2$O$_3$ series in which the metal and the support are identical, we should have:

$$\frac{(I_0)_2}{(I_0)_1} = \frac{(A_m^2/x_m)_2}{(A_m/x_m)_1} = \frac{(D_0^2 x_m)_2}{(D_0^2 x_m)_1}. \tag{16}$$

Assuming that the other terms of Eq. (14) remain unchanged, then:

$$\frac{a_2}{a_1} = (I_0)_2/(I_0)_1^{\,1-n}. \tag{17}$$

Using RhA as a reference the theoretical values a_{th} of the turnover frequency have been calculated for Rh 5A and Rh 10A catalysts taking $n = 0.1$ in Eq. (17). Results are reported in Table 5. Theoretical and experimental values are in agreement: the kinetic model developed above is in accordance with the variations of a found for the catalysts of the Rh/Al$_2$O$_3$ series. It is clear nevertheless that further experimental verifications will be necessary for bearing out this model in its generality.

From the results quoted above, the idea that the support effect might be due to a metal–support interaction appears unlikely. Nevertheless this assumption should

TABLE 5

Comparison of Experimental and Theoretical Turnover Frequencies of Rh/Al$_2$O$_3$ Catalysts

Catalyst	D_0	$D_0^2 x_m$	a_{th}	a_{exp}
RhA	96	5530		460
Rh5A	45	10100	790	653
Rh10A	13.7	1880	174	198

not be definitively excluded especially in the metal/titania series. As a matter of fact, the PtT catalyst shows an exceptionally high initial activity: the metal–support interaction which is very strong after reduction under H_2 flow, could be annihilated by water in the first moment of the reaction.

On the most oxidizable metals (Co, Ni, Ru) the presence of oxygenated species is very likely. Only a competitive mechanism may account for the absence of a support effect for these metals. Two kinetic schemes can be considered according to whether the primary activation of the water molecule takes place on the support (Scheme II) or directly on the metal (Scheme III).

Kinetic Scheme II: analogous to scheme I except that water adsorption [Eq. (11)] is followed by migration of OH groups to the metal:

$$2\text{S-OH} + \text{M} \overset{K_i}{\rightleftharpoons} \text{S-O-S} + \text{M-OH} + \tfrac{1}{2}H_2 \quad (18)$$

Scheme III:

$$H_2O + \text{M} \overset{K_w}{\rightleftharpoons} \text{M-OH} + \tfrac{1}{2}H_2 \quad (19)$$

For both schemes, Eqs. (12) and (13) remain unchanged. The kinetic derivation leads to following rate law:

$$a = \frac{k_T P_T}{1 + K} \cdot \left(1 - \frac{k_T P_T}{k M_0 K}\right) \quad (20)$$

with $K = K_i K_w P_{H_2O}/P_{H_2}^{1/2}$ for Scheme II and $K_w P_{H_2O}/P_{H_2}^{1/2}$ for Scheme III.

From this expression of the rate it appears that:

(i) The support site concentration S_0 no longer intervenes. In Scheme II, however, the constants K_i and K_w are still determined by the support whereas in Scheme III, the metal activity is completely independant of the support. Thus, Scheme III appears to be the most likely.

(ii) The analytical derivation of Eq. (20) leads to an apparent order with respect to water within the range 0 to 1 and an apparent order with respect to toluene less than one but which can become negative for the highest values of P_T. Precisely Grenoble (*2*) reports orders slightly negative for Ru, Ni, Os, and Ir supported on Al_2O_3. Inasmuch as iridium, almost support-insensitive, may be included in this group, all the metals quoted above are of the second group (Os not studied here). Thus the competitive mechanism may account for the results obtained with Ni, Co, Ru, and probably with Ir.

Selectivities to Benzene of the Catalysts

The selectivity in steam dealkylation appears to be essentially a function of the metal. Furthermore, it must be noted that the order of the metals in SDA based on their selectivities is practically identical to the order in hydrodealkylation (HDA). The selectivities (%) of the metals for benzene formation in HDA are reported by Mozhaiko *et al.* (*36*) to be: Pd, 100; Pt, 98; Rh, 97; Os, 95; Ir, 91; Re, 83. Grenoble (*37*) reports identical values with some slight variances: Pd, 100; Rh, 98; Pt, 96; Ir, 95; Ni, 94; Os, 93; Re, 85; Ru, 82 and concludes in his study that HDA and hydrogenolysis follow different mechanisms: in particular, orders with respect to H_2 are positive or slightly negative in HDA. Nevertheless, it is worth nothing that the selectivity order for the various metals in hydrogenolysis is still once more very close to that observed in SDA and HDA. Maurel and Leclercq (*38*) report the following sequence for selectivities in cyclopentane hydrogenolysis: Pd, Pt > Rh, Ir > Ni > Os > Ru > Co.

The variations of selectivity are related to the mean lifetime of the primary species leading to benzene on the metal [Eq. (12)]. For a metal to be selective it is mainly necessary that the desorption be faster than the surface reaction. Due to the rate of hydroxyl migration from the support to the metal, the overall surface reaction appears to be much slower in SDA than in HDA. Once on the metal, the hydroxyl group should be very reactive, thus magnifying the differences between the selectivities of the various metals without modifying their relative order.

The results reported in Tables 2 and 3 show that the selectivity is also dependent on the nature of the support and on the metal particle size. Metals supported on alumina or metals which are well dispersed are more selective than metals supported on silica or poorly dispersed. This is particularly the case for Rh and Ir catalysts and to a lesser extent for Pd and Pt catalysts. Thus, it may be expected that every factor capable of modifying the relative rates of the hydrocarbon surface adsorption/desorption and of the surface reaction will allow fairly large variations of selectivity. However, the influence of the support and of the crystallite size on the selectivity is not yet very clear. At this time no sure explanation can be given because this requires detailed studies of the dissociation stage of the hydrocarbon [Eq. (12)]. This will be examined in a further paper.

APPENDIX: DETERMINATION OF THE SPECIFIC PERIMETER OF THE METAL/SUPPORT INTERFACE

Let us assume there are p cubic particles (d = length of a side) per unit area of the catalyst (other terms are defined in Eq. (15)).

From the weight of rhodium in the solid, we deduce:

$$pd^3 = \frac{x_m}{100} \cdot \frac{1}{A\rho}$$

and from the metal surface area (five faces exposed per particle):

$$pd^2 = \frac{A_m}{5A}$$

and

$$I_0 = 4pd = 4\,\frac{(pd^2)^2}{pd^3} = \frac{A_m^2}{x_m} \cdot \frac{16\rho}{A}.$$

A similar reasoning gives for a hemispherical particle (diameter d)

$$I_0 = \frac{A_m^2}{x_m} \cdot \frac{400\rho}{12A} = \frac{A_m^2}{x_m} \cdot \frac{33.3\rho}{A}.$$

For a raft-type particle of square shape (length of side = D, thickness of the raft = d) we obtain:

$$I_0 = \frac{A_m^2}{x_m} \cdot \frac{400\rho}{A} \cdot \frac{e}{(1 + 4e)^2}$$

with $e = d/D$.

For a raft-type particle of cylinder shape (diameter D), the expression for I_0 is quite similar.

It is worth noting that the coefficient β of ρ/A in Eq. (15) strongly decreases only for very small values of e (β = 22.2, 20.4, 13.9, and 3.7, respectively, for e = 0.5, 0.1, 0.05, and 0.01).

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