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Coking of Pt–Ir/Al_2O_3 and Pt–Re/Al_2O_3 Catalysts in Different Pressures of Cyclopentane

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The coking reaction with cyclopentane was investigated at various pressures on bimetallic Pt–Re/Al_2O_3 and Pt–Ir/Al_2O_3 catalysts. At atmospheric pressure addition of iridium or rhenium to platinum acts in the same way on the amount of deposited coke as an increasing working pressure on pure Pt/Al_2O_3 catalysts. Such modification induces a lowering of coke content and yields more dehydrogenated carbonaceous deposits. Nevertheless, the toxicity of coke defined by its fouling effect on the pure metallic reaction of benzene hydrogenation depends on the nature of the metallic phase and the overall pressure. These toxicities are linked to the presence of light polyaromatic compounds which are precursors of graphitic coke.

INTRODUCTION

Catalytic reforming is the most important industrial application of catalysis by metals. A great improvement in this process was the introduction in 1949 of the bifunctional catalyst, platinum supported on chlorinated acidic alumina (*1*). The metallic function of the catalyst was later improved by the addition of rhenium (*2, 3*); since then many bimetallic catalysts have been studied and patented (*4*). Among the additives, Re and Ir are most frequently employed, and are known to act on the catalyst by increasing its stability when it is sulfided.

Previous studies (*5–7*) have shown that catalysts with low metal dispersions are more sensitive to autodeactivation by coke deposition than well-dispersed catalysts. This result is in agreement with that of Somorjai and co-workers (*8, 9*), who proved that coke settles more easily on planes than on corners and edges of metallic crystallites.

This beneficial effect of the high dispersion of platinum could explain the role of additives such as Re or Ir which could divide the large platinum ensembles into smaller ones, and so inhibit the coking reaction (*10–14*). On the other hand, the lower coke formation on bimetallic catalysts has also been ascribed to the ability of Re or Ir to destroy coke precursors by hydrogenolysis (*15–18*). In the same way Ir could destroy coke deposits under hydrogen (*19*).

Another explanation is given by Zhorov *et al.* (*20*) and Burch and Mitchell (*21*) who stated that Pt–Re is more suitable than Pt in hydrogenating cyclopentadiene into cyclopentene which is less active for the formation of coke precursors. In an opposite way Parera suggests that the role of Re is to decrease the dehydrogenation capacity of Pt decreasing the coke formation (*22*). Such explanations are contradictory since a good catalyst for hydrogenation has to be a good one for dehydrogenation. Yet the hydrogenation–dehydrogenation capacities of Pt and Pt–Re previously introduced are disturbed by different hydrogenolysis activities for the catalysts under consideration.

The different studies reported above show that the exact role of Re or Ir remains a topic of considerable discussion. The purpose of this paper is to study the effects of addition of Re or Ir to Pt on the coking reaction as characterized by the coke content, the coke localization (on the metal or on the support), and finally the chemical nature of the coke deposits. The different variables will be the nature of the catalyst

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and the experimental conditions such as temperature and total pressure.

EXPERIMENTAL

The supported metallic catalysts (Pt/Al_2O_3, Pt–Ir/Al_2O_3, and Pt–Re/Al_2O_3) were prepared by impregnation of alumina powder (Al_2O_3 GFS 400, 210 m^2/g, Rhône Poulenc) with aqueous solutions of the different precursor salts (H_2PtCl_6, H_2IrCl_6, NH_4ReO_4). Hydrochloric acid was added to obtain a constant chlorine content. After impregnation the catalysts were dried overnight at 383 K, then calcined under an air stream for 4 h at 773 K (Pt/Al_2O_3 and Pt–Re/Al_2O_3) or 573 K (Pt–Ir/Al_2O_3), and finally reduced under flowing hydrogen for 8 h at 773 K.

Dispersion values were determined with a gas volumetric system. A vacuum in the system of 10^{-4} Pa was created with a turbomolecular pump. Prereduced samples were reduced again for 2 h at 773 K, then outgassed at this temperature and cooled to 298 K. Metal accessibilities were obtained by the H_2–O_2 titration method (*23*) described elsewhere for Pt–Ir (*24*) and Pt–Re (*25*). The characteristics of the different catalysts are reported in Table 1.

The coking reaction was carried out at atmospheric pressure in a classical glass flow reaction. Coking at high pressure was performed in a Sotelem apparatus. The prereduced catalyst was reduced again under a flow of hydrogen at 773 K for 2 h and set at the coking temperature. Cyclopentane (Fluka, purum) was employed as a coking agent with a hydrogen : hydrocarbon molar ratio of 2.33 and a WHSV of 2.

TABLE 1

Characteristics of the Different Catalysts

Catalyst	Pt (%)	Re (%)	Ir (%)	Cl (%)	D (%)
Pt/Al_2O_3	0.60	—	—	1.2	60
Pt–Re/Al_2O_3	0.35	0.20	—	1.3	60
Pt–Ir/Al_2O_3	0.33	—	0.28	1.2	78

Analysis of coke deposition was carried out by temperature-programmed oxidation (TPO), with the temperature increasing from 298 to 823 K at 13 K min^{-1}. Oxygen diluted 1/100 in helium was used. The amounts of oxygen consumed and carbon dioxide produced were determined at intervals of 1 min by gas chromatography. Such analysis allows one to define not only the coke content (carbon wt% = percentage coke) but also the hydrogen content (H/C = hydrogen : carbon molar ratio) (*26*).

Extraction of coked catalysts was carried out with benzene for 48 h in a Soxhlet apparatus. Extractable coke was analyzed by high-performance liquid chromatography (HPLC), gas chromatography, and mass spectrometry.

The toxicity of coke for the metallic function was defined by its fouling effect on the reaction of benzene hydrogenation. This reaction was carried out at 323 K at atmospheric pressure with a hydrogen : hydrocarbon molar ratio of 19 (*6*).

RESULTS

Coking at Atmospheric Pressure

The different Pt/Al_2O_3, Pt–Ir/Al_2O_3, and Pt–Re/Al_2O_3 catalysts were coked by the cyclopentane reaction at 713 K for variable times.

Figures 1 and 2 show the variations in the amount of coke deposited as a function of time of coking. Addition of Ir or Re to Pt decreases the amount of coke deposited on the catalyst whatever the coking times there may be.

Such change in coke content induces a modification of the chemical nature of the deposits which become more dehydrogenated as Re or Ir is added to Pt (Fig. 3 and 4). This change is linked to a different localization of coke with the nature of the metallic phase: thus, the TPO curves (Fig. 5) show that the addition of Re or Ir to Pt decreases the amount of coke oxidizable at low temperature (coke deposited on the metal).

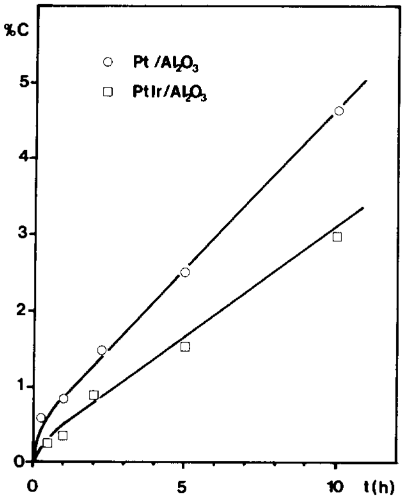

FIG. 1. Carbon percentage vs time-on-stream for Pt/Al_2O_3 and Pt–Ir/Al_2O_3 catalysts (10^5 Pa, 713 K).

Nevertheless, in spite of this decreasing coke content on the metal, the deposits are more toxic for a pure metallic reaction such as hydrogenation of benzene on Pt–Ir/Al_2O_3 than on Pt–Re/Al_2O_3 or Pt/Al_2O_3 (Table 2).

The lower activity of Pt–Re for the coking reaction corresponds to a higher activity for cyclopentane disappearance (Table 3), bearing out the great activity of Pt–Re catalysts for hydrogenolysis (*15, 27*).

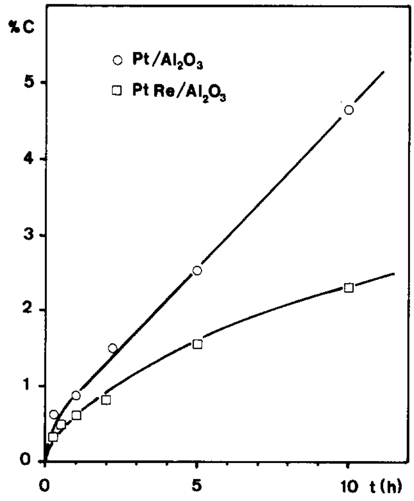

FIG. 2. Carbon percentage vs time-on-stream for Pt/Al_2O_3 and Pt–Re/Al_2I_3 catalysts (10^5 Pa, 713 K).

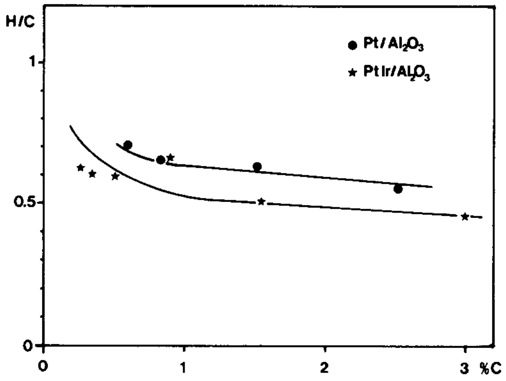

FIG. 3. H/C molar ratio vs amount of deposited coke for Pt/Al_2O_3 and Pt–Ir/Al_2O_3 catalysts (10^5 Pa, different times of coking).

Table 4 summarizes the results obtained on extraction of coked catalysts. For all catalysts, whatever the nature of the metallic phase, the amounts of extractable coke are comparable. On the other hand the analysis of extractable coke indicates that more light products (with molecular weight <202) are deposited on the Pt–Ir/Al_2O_3 catalyst.

Coking at High Pressure

The different Pt/Al_2O_3, Pt–Ir/Al_2O_3, and Pt–Re/Al_2O_3 catalysts were coked by the

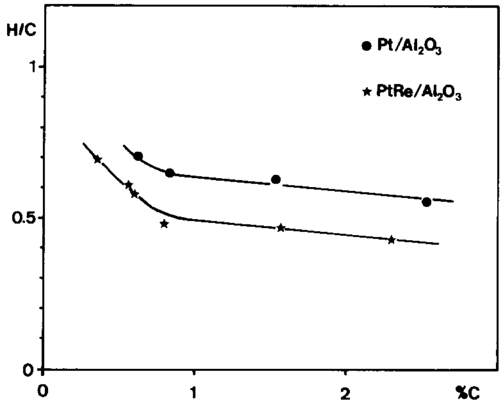

FIG. 4. H/C molar ratio vs amount of deposited coke for Pt/Al_2O_3 and Pt–Re/Al_2O_3 catalysts (10^5 Pa, different times of coking).

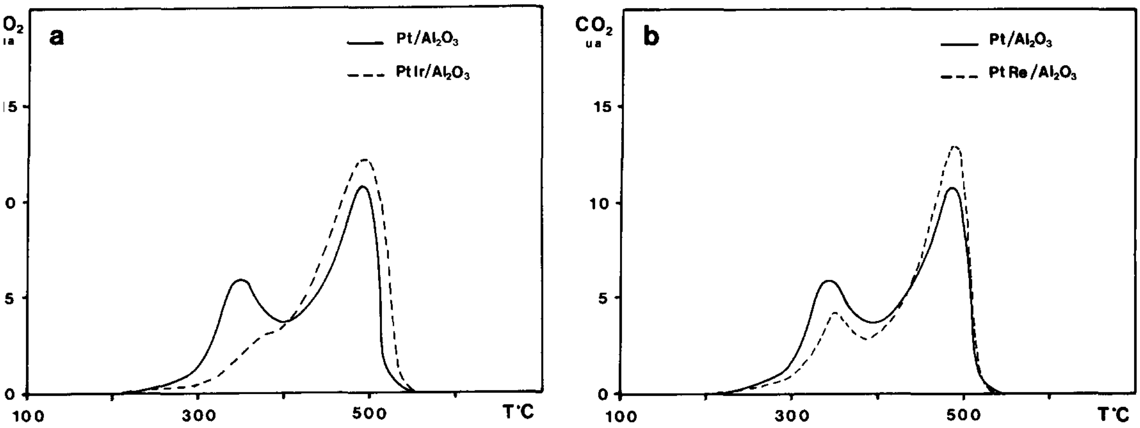

FIG. 5. (a) TPO curves of coked Pt/Al$_2$O$_3$ and Pt-Ir/Al$_2$O$_3$ catalysts (10^5 Pa, 713 K, different times of coking). (b) TPO curves of coked Pt/Al$_2$O$_3$ and Pt-Re/Al$_2$O$_3$ catalysts (10^5 Pa, 713 K, different times of coking).

cyclopentane reaction at 713 K under different overall pressures and with a constant hydrogen : hydrocarbon molar ratio of 2.33.

Table 5 shows that for all catalysts the higher the working pressure the lower the coke content. However, the order of the coking reaction as regards the overall pressure is negative and depends on the nature of the metallic phase, decreasing from Pt-Re to Pt and Pt-Ir (Table 6). Hence the inhibiting effect of high working pressure is higher on Pt-Ir/Al$_2$O$_3$ than on Pt/Al$_2$O$_3$ or Pt-Re/Al$_2$O$_3$ catalysts.

On the other hand, an increasing overall coking pressure induces a change in the toxicity of coke for the metal-catalyzed reaction of benzene hydrogenation. Comparison of the activities at the same coke coverage shows (Figs. 6 and 7) that coking at high pressure reduces the deactivation of the metallic phase of the catalyst. This effect is more important for the Pt-Ir/Al$_2$O$_3$ catalyst.

Finally Table 7 summarizes the results obtained for extraction of the different catalysts coked at 713 K under an overall pressure of 10^3 kPa. It is worth noting that extractable coke is lower on Pt-Ir/Al$_2$O$_3$ than on Pt/Al$_2$O$_3$ or Pt-Re/Al$_2$O$_3$ catalysts. The composition of the extractable coke depends also on the nature of the catalyst since the amount of light hydrocarbons (with molecular weight <202) decreases from Pt to Pt-Re and Pt-Ir. Thus, in conclusion, the more toxic coke is for the metallic function,

TABLE 2

Effect of the Nature of the Metallic Phase on the Toxicity of Coke for the Reaction of Benzene Hydrogenation[a]

Catalyst	Carbon (%)	a/a_0
Pt/Al$_2$O$_3$	1.18	0.20
Pt-Re/Al$_2$O$_3$	0.85	0.16
Pt-Ir/Al$_2$O$_3$	0.92	0.08

[a] Coke deposition at 713 K, 10^5 Pa, different times.

TABLE 3

Modification of the Selectivity of Pt Catalysts by Addition of Re for the Coking Reaction by Cyclopentane[a]

Catalyst	$<C_5$ (%)	Iso-C_5 (%)	nC_5 (%)	Cyclo-C_5 (%)	$>C_5$ (%)
Pt/Al$_2$O$_3$	3.6	6.3	11.3	71.4	7.4
Pt-Re/Al$_2$O$_3$	6.5	11.0	17.0	59.3	6.2

[a] 10^5 Pa, 713 K.

TABLE 4

Effect of the Nature of the Metallic Phase on the Graphitization of Coke Deposits[a]

Catalyst	Carbon (%)	Graphitic coke (%)	Extractable coke (%)	Products with $M < 202$ in extractable coke (%)[b]
Pt/Al_2O_3	1.18	72	28	30
$Pt–Re/Al_2O_3$	0.85	78	22	35
$Pt–Ir/Al_2O_3$	0.92	75	25	48

[a] 10^5 Pa, 713 K, variable times.
[b] M = molecular weight.

TABLE 6

Variation in the Order of the Coking Reaction (α) Relative to the Overall Pressure on the Different Catalysts[a]

Catalyst	α
Pt/Al_2O_3	−0.66
$Pt–Re/Al_2O_3$	−0.47
$Pt–Ir/Al_2O_3$	−1.07

[a] 713 K, 10 h.

the greater the amount of light hydrocarbons in the extractable coke.

DISCUSSION

During the reaction of cyclopentane at atmospheric pressure at 713 K, the addition of iridium or rhenium to platinum induces a decrease in the amount of coke deposited (Fig. 1 and 2). This change goes hand in hand with a higher hydrogenolytic activity for the bimetallic catalysts (Table 2) and agrees with the explanation of Carter *et al.* (*15*) who suggested that the addition of iridium or rhenium to platinum induces the transformation of coke precursors by hydrogenolysis. A similar explanation was given by Bertolacini and Pellet (*16*) for mechanical mixtures of Pt/Al_2O_3 and Re/Al_2O_3 catalysts.

On the other hand, such a decrease in coke deposits induces a modification of the nature of the coke, which on average becomes more dehydrogenated (Figs. 3 and 4). Nevertheless, extractions of $Pt–Ir/Al_2O_3$ catalysts coked at normal pressure show the presence of more light hydrocarbons in the extractable coke. In compensation the nonextractable coke is highly dehydrogenated. Previous works (*26, 28*) show that coke deposited on the metallic function is less dehydrogenated, implying that light extractable products are adsorbed on the metallic phase. The higher toxicity for pure metal-catalyzed reactions of coke deposited at low pressure on $Pt–Ir/Al_2O_3$ catalyst (Table 2) can be explained by assuming that the light polyaromatic compounds are accountable for the deactivation of the metallic function. This result agrees with that obtained on Pt/

TABLE 5

Variation in the Amount of Coke Deposits with the Nature of the Metallic Phase and the Overall Pressure[a]

Pressure (bar)	Carbon (%)		
	Pt/Al_2O_3	$Pt–Re/Al_2O_3$	$Pt–Ir/Al_2O_3$
1	4.65	2.3	3.0
5	—	1.6	0.50
10	1.3	1.0	0.24
15	—	0.63	—
30	0.46	0.50	—

[a] 713 K, 10 h.

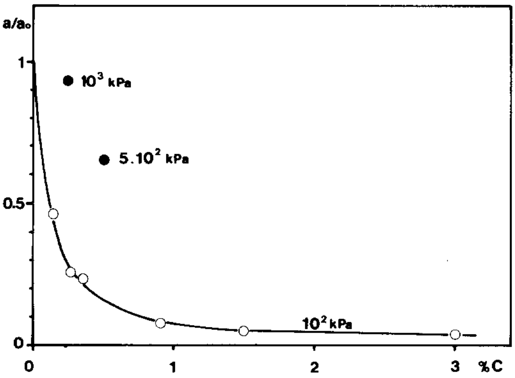

FIG. 6. Relative activity of coked catalysts for benzene hydrogenation vs coke coverage for $Pt–Ir/Al_2O_3$ catalyst at different pressures: ○, normal pressure; ●, higher pressures.

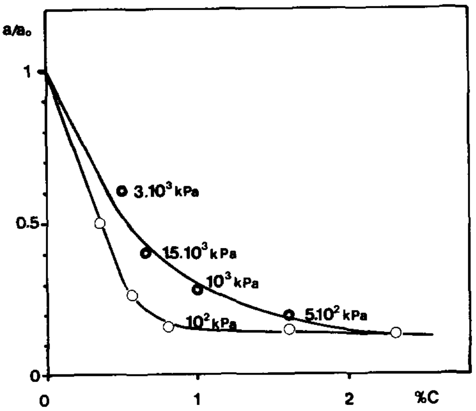

FIG. 7. Relative activity of coked catalysts for benzene hydrogenation vs coke coverage for Pt–Re/Al_2O_3 catalyst at different pressures: ○, normal pressure; ⊛, higher pressures.

Al_2O_3 catalysts of varying dispersities (*7*) for which it was shown that coke is more toxic on large platinum particles and leads to more light extractable products.

Even so, our conclusion seems to be contradictory to those of Somorjai and Blakely (*9*) and Sachtler (*13*) who suggest that adsorbed carbonaceous fragments become deleterious catalyst poisons only after atomic reorganizations resulting in graphitic structures. Such a difference can be explained by assuming that light polyaromatic products are precursors of graphitic coke and, therefore, the greater the coverage of the metallic surface with light polyaromatic fragments, the higher the amount of graphitic coke on the metallic function.

TABLE 7

Extraction of Coked Catalysts: Effect of the Addition of Re or Ir to Pt[a]

Catalyst	Carbon (%)	Graphitic coke (%)	Extractable coke (%)	Products with $M < 202$ in extractable coke (%)[b]
Pt/Al_2O_3	1.3	82	18	28
Pt–Re/Al_2O_3	1.0	84	16	4
Pt–Ir/Al_2O_3	0.24	95	5	1

[a] 713 K, 10^3 kPa.
[b] M = molecular weight.

When the overall pressure of the reactants increases (Table 5) the amount of deposited coke decreases whatever the metallic phases there may be. This effect was previously reported in the case of Pt/Al_2O_3 catalysts (*29*). Nevertheless, the effect of the working pressure is more important for Pt-Ir/Al_2O_3 catalysts for which the amount of coke deposits is very low below 3×10^3 kPa. Such a decreasing content of coke is in line with a decreasing toxicity of coke for metallic reactions and, on the other hand, with disappearance of the light polyaromatic compounds in the extractable coke. Such effects of the working pressure promoting graphitization of coke on the support were previously described for monometallic Pt/Al_2O_3 catalysts.

Finally, the total coke contents of bifunctional reforming catalysts can be decreased on the one hand by alloying Pt with Ir or Re and, on the other hand, by increasing the working pressure. For all that, the toxicities of coke for the two functions of the catalyst (metallic function and acidic function) are defined by the localization of the carbonaceous deposits and evolve independently of the coke contents.

Hence the metallic function of Pt–Ir/Al_2O_3 catalysts is more sensitive to coke deposited at low pressure than is the metallic function of Pt/Al_2O_3 catalysts. At higher working pressures, on Pt–Ir/Al_2O_3 catalysts, coke is deposited mainly on the support, thereby avoiding deactivation of the metallic phase. Such results show that an explanation of the higher performance of Pt–Ir and Pt–Re catalysts that is based only on a dilution of large platinum ensembles by Ir or Re is insufficient. It was previously pointed out for Pt/Al_2O_3 catalysts that, even at low working pressures, an increasing metallic dispersion decreases the amount of coke deposited on the metal and protects the metallic activity. It is more likely that the balance between formation, polymerization, and destruction of coke precursors on the metallic phase depends on the nature of this metallic phase and on the working pressure. At low hydrogen pressure Pt–Ir/Al_2O_3 catalysts can promote polymerization of higher polyaromatic compounds, whereas at high hydrogen pressure the same catalysts are able to destroy such coke precursors.

In conclusion, the addition of iridium or rhenium to platinum acts in the same way on the amount of deposited coke at normal pressure as does an increasing overall pressure for the coking reaction on Pt/Al_2O_3 catalysts. Such modifications induce a lowering of the coke content. Nevertheless, the toxicity of coke defined by its fouling effect on the purely metal-catalyzed reaction of benzene hydrogenation depends on the nature of the metallic phase and also on the working pressure. These toxicities are linked to the presence of light polyaromatic compounds which are the precursors of more graphitic and more toxic coke.

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