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Sulfur-Resistant Carbon-Supported Iridium Catalysts: Cyclohexane Dehydrogenation and Benzene Hydrogenation

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Carbon-supported iridium catalysts, with different metal loadings, were prepared by impregnation of a high-purity activated carbon. The dispersion of the metallic phase was studied by hydrogen and carbon monoxide chemisorption and transmission electron microscopy (TEM). The hydrogen chemisorption on the iridium crystallites supported on activated carbon was quite different from the chemisorption on an Ir/alumina catalyst. TEM observations of the catalysts show metal particles as spheres in the former case and as rafts in the latter. The cyclohexane dehydrogenation and the benzene hydrogenation were studied for both catalyst types. Both reactions are insensitive to the iridium dispersion and to the support. The thiotolerance level of the various catalysts was measured with feeds contaminated with 4 ppm of thiophene. In the case of the cyclohexane dehydrogenation, the thiotolerance level is affected neither by the support (activated carbon versus alumina) nor by the metallic dispersion of the Ir/carbon catalysts. However, in the benzene hydrogenation the carbon-supported iridium catalysts are more resistant toward the poisoning than the Ir/alumina counterpart. This behavior is interpreted as due to the different metallic microstructures produced on the two supports.

INTRODUCTION

Carbon-supported catalysts have particular applications in organic reactions and in the production of fine chemicals (*1*). In view of the presence of sulfur-containing compounds in many feedstocks, the resistance of carbon-supported metal catalysts to sulfur is of interest, yet it has been little studied. Sulfur poisoning of metals has often been reviewed (*2–4*) and noble metals have better resistance than base metals (*5*). Among the noble metals, Ir is of interest as an additive in improving the sulfur tolerance of Pt/Al_2O_3 catalysts in hydrogenolysis (*6*) and of Ni catalysts in methanation (*7*). As for supported Ir itself, it is reported (*8, 9*) that the nature of the support affects the sensitivity of the metal to poisoning. Ir/carbon catalysts, used for selective hydrogenations and production of fine chemicals (*10*), are therefore worthy of study.

The sulfur resistance of a supported metal can be changed by modifying its electronic properties, by varying the particle size, by alloying, or by changing the acid–base properties of the support (*11*). In the present work we have studied two of these effects for Ir catalysts: we have examined Ir/carbon at three different mean Ir particle sizes and for one particle size we have compared Ir/carbon with Ir/alumina. We have studied benzene hydrogenation at 298–315 K and cyclohexane dehydrogenation 500–540 K as test reactions, both of which are considered to be structure-insensitive reactions (*12, 13*). Feeds have been contaminated with thiophene to determine the sulfur tolerance of the catalyst. Gas chemisorption, X-ray diffraction, and transmission electron microscopy (TEM) have been used to characterize the catalysts.

EXPERIMENTAL

Catalyst Preparation

The support materials were a high-purity activated carbon produced at the laboratory (*14*) with a specific surface area of 690

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$m^2\ g^{-1}$ and an ash content below 0.11% and a Prolabo 13B alumina with a surface area of 100 $m^2\ g^{-1}$. The iridium-containing catalysts were prepared by the incipient wetness technique (*15*) using aqueous solutions of $H_2[IrCl_6] \cdot 6H_2O$ (Alfa Ventron). The moist materials were dried in air at 383 K for 12 h and then kept in a desiccator over P_2O_5 until use. Analysis of the metal loading was carried out by atomic absorption spectrometry (Pye Unican SP 1900). Before characterization by chemisorption and study in reaction, the catalysts were reduced in a H_2 flow (3 l h^{-1}) at 673 K for 12 h.

Catalyst Characterization

The extent of H_2 and CO chemisorptions was determined in a greaseless volumetric system (*16*). Once the catalysts were reduced, as described above, they were outgassed for 1 h at reduction temperature to a final pressure of 10^{-6} Torr (1 Torr = 133 Pa) and later cooled to 298 K, the temperature of chemisorption. The method of Benson and Boudart (*17*) and Wilson and Hall (*18*), in which the linear portion of the isotherm, determined between 40 and 240 Torr, is extrapolated to zero pressure, has been used to determine the hydrogen uptake. For the chemisorption of CO the method of Yates and Sinfelt (*19*) has been used: this consists of determining the CO isotherm at 298 K in the range 50–250 Torr, evacuating for 2 min at 298 K, and measuring a second isotherm. Subtraction of the second isotherm from the first gives the amount of CO chemisorbed on the metal. The hydrogen (99.9995%) was further purified using a Deoxo unit (Fischer Scientific) and a 0.5-nm molecular sieve. Carbon monoxide (99.97%) and helium (99.998%) were passed through a 0.5-nm molecular sieve and an Oxy-Trap (Regis Chemical Co.).

After chemisorption tests the reduced catalysts were exposed to air and further analyzed by X-ray diffraction (XRD) and transmission electron microscopy. The diffraction patterns were obtained with a Philips PW 1710 diffractometer using Cu$K\alpha$ radiation. Electron microscopy studies of the catalysts were conducted using a Jeol-200 CX instrument. Samples were dispersed in acetone and spread over self-perforated carbon microgrids. In order to obtain meaningful data at least 800 particles of iridium were measured for each catalyst. Direct magnification was 1 to 3 × 10^5, and iridium particles were measured at a final magnification of 0.4–12 × 10^6.

Catalytic Studies

Both benzene hydrogenation and cyclohexane dehydrogenation were carried out in a glass flow reactor (l = 20 cm, ϕ = 0.8 cm) containing a mixture of the catalyst (0.02–0.04 g) and powdered glass as diluent. In each experiment different batches of reduced catalysts, as above, were used. The outlet was connected to a gas chromatograph (Hewlett Packard 5890A; FID detector) with a chromatographic column (l = 1.5 m, $\phi = \frac{1}{8}$ in) containing 10% CP wax on Chromosorb WAW kept at 353 K. The H_2-containing reactant mixture was obtained from either one of four saturator–condenser systems, which contained pure benzene or cyclohexane and these products were contaminated by 4 ppm of thiophene. All hydrocarbons used were of "spectra pure" grade. The H_2 flow (60 $cm^3\ min^{-1}$) which was controlled by a mass flowmeter (Air-Liquid), was passed through a saturator maintained at 289 K. The composition obtained corresponds to a ratio H_2/hydrocarbon of 11.0 (hydrocarbon = C_6H_6 or C_6H_{12}), for both benzene hydrogenation and cyclohexane dehydrogenation. These compositions were the same for all experiments.

The reaction was performed under 101-kPa total pressure (WHSV = 24 h^{-1}). The hydrogenation of benzene was studied in the 298 to 315 K temperature range. The temperature was kept constant by a water bath and measured by a calibrated mercury thermometer. The dehydrogenation of cyclohexane was studied in the 500 to 540 K temperature range. The reaction temperature was measured by a Cr–Al thermocou-

TABLE 1

Metallic Dispersion and Mean Particle Size of Catalysts

Catalyst	D		d (nm)		
	H/Ir	CO/Ir	H_2	CO	TEM
C–0.9% Ir	1.59	1.06	0.7	1.1	1.6
C–2.8% Ir	0.68	0.48	1.6	2.3	2.6
C–6.1% Ir	0.33	0.23	3.4	4.8	3.8
Al_2O_3–2.0% Ir	0.84	0.44	1.3	2.5	2.8

ple placed in a glass pocket inside the reactor. It was verified that the reaction rate was neither limited by thermodynamics nor by diffusion processes, provided conversion was limited to values lower than 10%. Cyclohexane was practically the only product in the hydrogenation of benzene (>99 wt%). For the cyclohexane dehydrogenation, the major product was benzene, and small amounts of *n*-hexane and *n*-pentane were also detected.

RESULTS AND DISCUSSION

Catalyst Characterization

Table 1 summarizes the metallic dispersions and the mean particle sizes of the reduced iridium catalysts. The metal dispersions (*D*) have been evaluated from H_2 and CO uptakes by assuming that one hydrogen atom or one CO molecule is chemisorbed on a surface iridium atom. The average Ir particle size *d* has been calculated from the equation (*20*): $d = 1.11/D$ (nm). Table 1 also shows the mean metal particle size obtained by TEM. It is observed that the crystallite sizes as estimated by CO chemisorption data and by TEM measurements are in fair agreement. On the basis of this concordance it is assumed that one molecule of CO is adsorbed per surface iridium atom. It is noticeable from the results in Table 1 that high dispersion values are obtained for the iridium catalysts supported on activated carbon. Thus, for the 0.9% Ir/C sample a monoatomic dispersion is achieved.

However, as is evident from Table 1, the assumption that one hydrogen atom is bonded to one surface iridium atom is unrealistic, since a dispersion exceeding unity is obtained for the 0.9% Ir/C catalyst. Similar results have been reported for highly dispersed metal catalysts supported on alumina and silica (*21, 22*). A common explanation for the H/*M* ratio values above one is that part of the hydrogen is adsorbed by the support through spillover from the metal particles. However, the possibility of hydrogen spillover onto the carbon is unlikely as this process is known to be favored by the presence of surface OH groups, which do not exist in these high-temperature-treated Ir/carbon catalysts. Following Kip *et al.* (*21*), we believe that multiple hydrogen adsorption on exposed metal atoms must be the main reason for the high H/*M* values.

In order to investigate the hydrogen to iridium adsorption stoichiometry, in Fig. 1 the H/Ir ratio has been represented as a function of the CO/Ir ratio for the different catalysts. As can be seen, the catalysts supported on carbon present a H/CO ratio close to 1.5 while that supported on alumina has a H/CO value of 2.0. Hence the support has a significant effect on the number of hydrogen atoms that can be adsorbed by a surface iridium atom. This finding can be

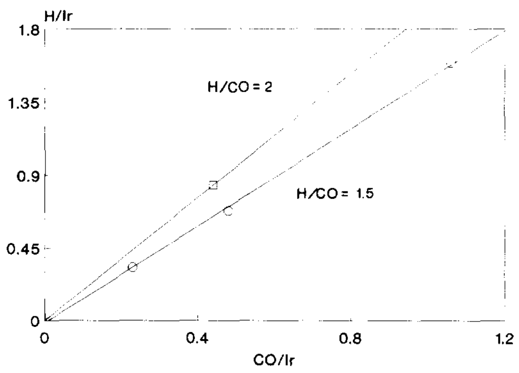

FIG. 1. Comparison of the iridium dispersion determined from hydrogen and carbon monoxide chemisorption. (○) Carbon-supported catalysts; (□) alumina-supported catalyst.

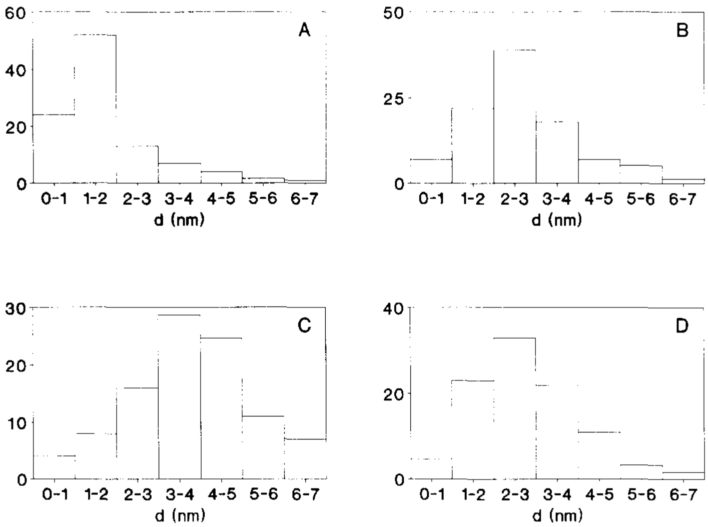

FIG. 2. Distribution of the iridium crystallite sizes determined from TEM. (A) 0.9% Ir/C, (B) 2.8% Ir/C, (C) 6.1% Ir/C, (D) 2.0% Ir/Al_2O_3.

explained if differences in support–precursor interaction are considered. It is known that carbon–metal interaction is weak, and generally spherical metal particles are produced on this support (*23*). However, in the Ir/alumina catalysts, the interaction between the support and the precursor compound during the preparation and pretreatment is stronger, which may result in metal particles with a raft structure (*24–26*). Differences in morphology have already been observed in the TEM study of the catalysts, when this observation was carefully conducted in the transmission mode. Consequently, different hydrogen chemisorption behavior of the iridium catalysts supported on activated carbon and on alumina can be attributed to a different metal crystallite structure brought about by the metal–support interaction.

The histograms with the distribution of metallic size derived from the TEM measurements are given in Fig. 2 for the various catalysts. It can be seen that in the 0.9% Ir/C sample a large quantity of iridium clusters with $d \approx 1.5$ nm is observed. As the concentration of iridium increases from 0.9 to 6.1 wt% not only a higher mean particle size but also a broader distribution of crystallite sizes is found. Since the average metal particle sizes are in general below 4 nm, in the detection limit of the XRD technique, the XRD patterns of the catalysts showed very broad peaks superimposed on the background due to the Ir metal phase. From these results, it may be concluded that iridium catalysts are well dispersed.

Catalytic Properties

In the experimental conditions used in this work, both Ir/C and Ir/Al_2O_3 catalysts underwent deactivation during the cyclohexane dehydrogenation reaction. The variation of catalytic activity during the reaction time for the 0.9% Ir/C catalyst for both pure cyclohexane as reactant or contaminated with 4 ppm of thiophene is given in Fig. 3. Similar activity–time curves were obtained for the other samples. The catalytic activity with pure cyclohexane become constant after ~90 min on-stream, and the deactivation percentage calculated by the ratio (initial activity–final activity)/initial activity is between 0.12 and 0.19 for all samples.

As noted previously, some hydrogenolysis products in addition to the dehydroge-

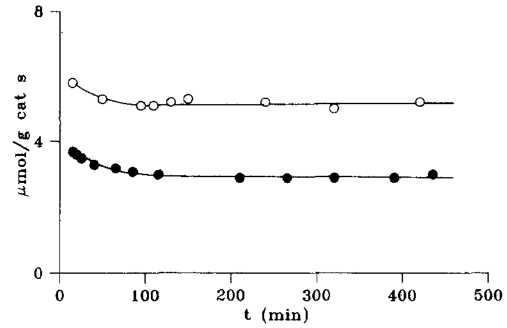

FIG. 3. Rate of C_6H_{12} dehydrogenation as a function of the time-on-stream. Sample: 0.9% Ir/C. (○) Pure cyclohexane; (●) cyclohexane with 4 ppm of thiophene.

nation product, benzene, have been detected, and the selectivity toward hydrogenolysis by-products decreases during the run time, for all the catalysts. Therefore, it is possible to explain the initial deactivation of the iridium catalysts in the cyclohexane dehydrogenation as due to coke formation during secondary hydrogenolysis reactions. This behavior of Ir catalysts is different from the one reported for platinum catalysts (*11*), which are stable during the reaction and yield only benzene as a detected product. However, a similar deactivation has been reported (*8*) for iridium catalysts. In the present work neither the metal dispersion in carbon-supported iridium nor the support (carbon vs alumina) seems to affect the deactivation process. In the following discussion the results obtained after stabilization are considered.

The apparent activation energies determined for the cyclohexane dehydrogenation are given in Table 2. The differences among the different catalysts are not large (given the actual E_a ± error values). These activation energies are comparable to others obtained on supported iridium catalysts (*8*). Table 2 also summarizes the turnover frequencies determined in the dehydrogenation of cyclohexane, at a reaction temperature of 520 K, for the various iridium catalysts. These turnover numbers are calculated assuming that an active center was defined by the chemisorption of a hydrogen atom or by a chemisorbed carbon monoxide molecule. The small differences found among the different catalysts can be explained in terms of the intrinsic limitation of the determination of number of active centers by chemisorption techniques and/or by the structure-sensitive character of the side hydrogenolysis reactions. Hence we can conclude that on the Ir/C catalysts activity is insensitive to metal dispersion and that the iridium particles deposited on carbon or alumina have similar catalytic behavior.

The cyclohexane dehydrogenation at 520 K has also been studied using cyclohexane containing 4 ppm of thiophene. The quantities of sample introduced in the reactor have been chosen in order to have the same surface iridium atoms for all experiments. After an initial deactivation the activities become constant (Fig. 3). By comparison of these stabilized activities with those obtained during the dehydrogenation of pure cyclohexane, the residual activity fractions have been calculated. These residual activities for the different iridium catalysts are shown in Fig. 4A. From this figure and from the data of Table 1, it is seen that for carbon-supported iridium an increase of dispersion by a factor of 4 does not affect the thiotolerance level of these catalysts.

TABLE 2

Turnover Frequency and Activation Energy in Cyclohexane Dehydrogenation for the Iridium Catalysts

Catalyst	TNF[a] (10^3 s^{-1})		E_a (kJ mol^{-1})
	H	CO	
C–0.9% Ir	72	108	111 ± 5
C–2.8% Ir	112	63	97 ± 14
C–6.1% Ir	100	147	100 ± 7
Al_2O_3–2.0% Ir	61	118	108 ± 11

[a] Reaction temperature: 520 K.

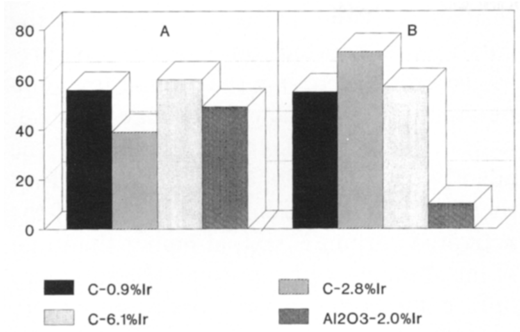

FIG. 4. Residual activities for the iridium catalysts in: (A) the dehydrogenation of cyclohexane; (B) the hydrogenation of benzene.

Also, the nature of the support, activated carbon vs alumina, does not seem to affect the thiotolerance level. These results are in agreement with other studies on supported iridium catalysts (*8*, *27*). Although influence of the acidity of the support on thioresistence has been shown in the literature (*9*, *28*), a general agreement about the support and particle size effects does not exist (*29–32*). Even though this reaction has been selected as a model reaction in many poisoning studies of platinum catalysts (*11*), in the case of iridium, the side-hydrogenolysis reactions and the subsequent catalyst deactivation by coking can complicate the interpretation of the results.

In order to determine the role of the metal dispersion in Ir/C catalysts in the sulfur poisoning and to compare with Ir/Al_2O_3, a second reaction test has been selected. This reaction was the reverse of cyclohexane dehydrogenation, that is, the hydrogenation of benzene, which is largely considered as insensitive to the structure of metal particles (*33*). Moreover, benzene hydrogenation occurs at lower temperatures, and one may expect that other deactivation processes such as carbon deposition and metallic sintering would be absent. However, in these experimental conditions the adsorption of the sulfur compound on the support might be important.

For all the studied iridium catalysts, cyclohexane is the only hydrogenation product from benzene. The variation of the catalytic activity during benzene hydrogenation for the 2.8% Ir/C catalyst, both with pure benzene as reactant or containing 4 ppm of thiophene, are shown in Fig. 5. Similar activity–time curves were obtained for the other catalysts. As shown in Fig. 5, stabilization is not achieved during the reaction. Two explanations can be advanced to describe this behavior. First, one may assume that, even at a reaction temperature close to room temperature, carbon deposition can take place (*34*). Second, the possibility of some type of contamination in the benzene might be borne in mind (*35*). Under the current conditions with benzene (Merck, reagent grade) and high-purity gases with further purification, one may find the former hypothesis as more likely. Moreover, a similar deactivation has been observed in benzene hydrogenation on various supported iridium catalysts (*8*).

In order to compare the various catalysts, the turnover number at 298 K and the apparent activation energies, after a time on-stream above 2 h, have been calculated. Table 3 summarizes the results of the calculations. As in the case of the cyclohexane dehydrogenation reaction, an active center is assumed to be a surface iridium atom, which is able to chemisorb a hydrogen atom or a carbon monoxide molecule. The differ-

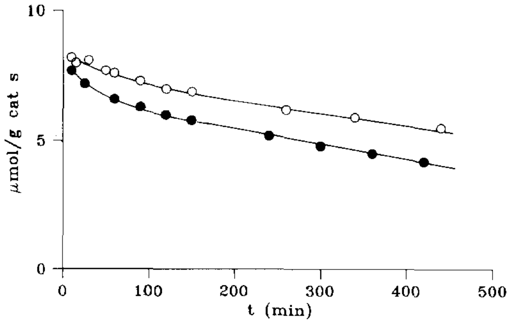

FIG. 5. Rate of C_6H_6 hydrogenation as a function of the time-on-stream. Sample: 2.8% Ir/C. (○) Pure benzene; (●) benzene with 4 ppm of thiophene.

TABLE 3

Turnover Frequency and Activation Energy for the Iridium Catalysts in Benzene Hydrogenation

Catalyst	TNF[a] (10^3 s^{-1})		E_a (kJ mol^{-1})
	H	CO	
C–0.9% Ir	46	69	43 ± 2
C–2.8% Ir	68	99	38 ± 2
C–6.1% Ir	57	83	31 ± 2
Al_2O_3–0.2% Ir	62	120	40 ± 3

[a] Reaction temperature: 298 K.

ences of apparent activation energy among the different catalysts are not large; however, a decrease with decreasing dispersion is observed for the Ir/C catalysts. This variation is often explained by a change of the reaction mechanism. However, in the present case, one should take into account the error values, the described deactivation process, and/or the possibility of variations in the reaction temperature as a consequence of the benzene hydrogenation exothermicity. Then, one may mainly consider that the variation observed in activation energy arises from these later hypotheses (or experimental phenomena). The activation energies are again comparable to reported data for the benzene hydrogenation reaction on iridium catalysts (*8*). On the other hand, there are no significant differences in the turnover number obtained for the different catalysts (Table 3). These results are consistent with the insensitivity of the benzene hydrogenation to the structure of the metallic particles.

Concerning the ability of the supported iridium to withstand sulfur poisoning, Fig. 4B shows the residual activities for hydrogenation of benzene calculated at a reaction time of 440 min, as described earlier for the case of cyclohexane dehydrogenation. It seems that metal dispersion, in Ir/C catalysts, does not affect the thiotolerance level. A noticeable difference between the Ir/C and the Ir/Al_2O_3 catalysts is found since the residual activities are fivefold higher for the catalysts supported on carbon. As previously remarked, in a reaction at low temperature (298 K), such as benzene hydrogenation, there exists the possibility of the adsorption of thiophene on the support. Furthermore, the apparent surface area of the activated carbon is sixfold higher than that of the alumina, with a porous structure very different in both supports. In order to verify this possibility, an additional experiment, with a 1 : 1 physical mixture of the carbon support and 2.0% Ir/Al_2O_3 catalyst, was performed. After the reduction treatment, the activity–time curves have been obtained both with pure benzene and with a 4 ppm thiophene-containing benzene. The curves obtained are similar to that determined when the reactor was only charged with the 2.0% Ir/Al_2O_3 catalyst. Thus the possible physical adsorption of the sulfur compound on the support does not explain the results shown in Fig. 4B.

A second series of experiments was carried out, poisoning the reduced catalysts (2.8% Ir/C and 2.0% Ir/Al_2O_3) by a pulse of thiophene (0.5 μl) added to the H_2 feed at 520 K. Under these conditions, physical adsorption of thiophene is not expected to occur. After cooling down in H_2 to room temperature, samples were subjected to the C_6H_6/H_2 mixture used for benzene hydrogenation. The residual activities after this poisoning treatment were 0.29 and 0.02, respectively, for 2.8% Ir/C and 2.0% Ir/Al_2O_3 catalysts. Taking into account that the quantity of surface iridium atoms is similar for the two experiments, we can infer that the thiophene pulse produces a stronger deactivation of the catalysts, compared with those reported in Fig. 4B. In this second series of experiments it is also demonstrated that the thiotolerance level, in benzene hydrogenation, is higher for the carbon-supported catalysts.

The complementary experiments have clearly shown that the difference of resistance to poisoning by thiophene when iridium is supported on carbon and on alumina

(Fig. 4B) cannot be attributed to a physical effect of the support. Therefore, we can speculate that this difference is produced by some kind of variation in the thiophene interaction with the iridium particles. This dissimilar interaction alters the mechanism of benzene hydrogenation but does not modify the cyclohexane dehydrogenation reaction. It must be assumed that changes in the thiophene adsorption are brought about by differences in the support properties.

Two main hypotheses are generally used to explain the changes of properties of supported metallic crystallites. The first considers possible electron transfers from or to the metal. The second contemplates that the structure of the metal crystallites can be affected by the support, and consequently, various supports give rise to different morphologies in the metal particles deposited on them. The former hypothesis has largely been used to explain the differences of thiotolerance found when metallic catalysts are supported on oxides or zeolites with diverse acidity (*8, 9, 11, 36*). However, recent theoretical studies (*37*) indicate that electron transfer by interaction of the metallic crystallites with the support requires very small metal clusters. In our case, no significant differences are observed when the iridium crystallite size for the Ir/C catalysts changes from 1 to 5 nm. Moreover, changes in the chemisorption properties are also observed when iridium is supported on carbon or on alumina, and the TEM observations seem to indicate that the morphology of the iridium crystallites is different on the two supports. Even though electron transfer cannot be excluded, we think that the difference of resistance to poisoning by thiophene is mainly due to a difference in the morphology of the metallic crystallites produced on these supports.

CONCLUSIONS

The resistance to poisoning by thiophene has been studied over carbon- and alumina-supported Ir catalysts for two reactions, i.e., benzene hydrogenation and cyclohexane dehydrogenation. The role of the metal crystallite size for the Ir/C catalysts has also been examined. Whereas for the benzene hydrogenation the Ir/C catalysts present a higher resistance to thiophene poisoning than the alumina-supported one, no significant differences are observed in the dehydrogenation of cyclohexane. Moreover, the iridium crystallite size, in the case of carbon-supported catalysts, affects neither the turnover frequencies nor the resistance to poisoning in both reactions.

An attempt to correlate the differences in catalytic behavior and the characterization of the catalysts has been carried out. This characterization includes chemisorption of H_2 and CO and TEM. It has been found that alumina-supported iridium chemisorbs hydrogen in a form different than that when supported on activated carbon. Also, the TEM observations show the raft structure of the iridium supported on alumina and the sphere morphology of iridium supported on carbon. The different resistance to poisoning found in the benzene hydrogenation between the iridium supported on carbon and on alumina has been interpreted as due to changes in the morphology of the metal crystallites.

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