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Resistance to Sulfur Poisoning of Metal Catalysts

Dehydrogenation of Cyclohexane on Pt/Al_2O_3 Catalysts

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Model Pt catalysts, containing ~0.6 wt% Pt, were prepared by deposition of dinitrodiaminoplatinum salt on a nonmicroporous alumina. The carrier has been modified by addition of K or Cl. The dispersion of the metallic phase was varied through different decomposition–reduction processes, but the final activation conditions were identical in all cases. The various catalysts have been tested in the dehydrogenation of cyclohexane which was confirmed to be a structure-insensitive reaction. The thiotolerance level of the various catalysts was measured with a feed contaminated with 0.6 ppm of thiophene. The thiotolerance level is more affected by the acidity of the support (presence of K or Cl) than by variations of Pt particle size. This has been confirmed by making sudden injections of CH_2Cl_2 or $(C_2H_5)_3N$ into the feed. On removing thiophene from the reactant mixture partial decontamination occurred and the activity recovered to ~50% of the initial value.

INTRODUCTION

The interaction between sulfur or sulfur-containing compounds and metallic surfaces has been the subject of numerous studies, most of which have been analyzed in review articles (*1–4*). Poisoning of the catalytic activity generally results from this interaction. In order to study this phenomenon, two types of approach can be used:

(i) The catalysts can be studied in the presence of a feed contaminated with a sulfur compound.

(ii) The physicochemical properties of the catalysts can be studied after adsorption of a known amount of a sulfur compound.

The first approach allows the determination of the deactivation kinetics and of the residual activity, if any (*5*). This latter, which will be referred to hereafter as the thiotolerance level, has not been systematically studied in the past. Besides the catalytic activity decrease, the presence of S may induce selectivity changes which can be explained either by the fact that S is a selective poison adsorbed on particular sites (*6*) or by considering that multiple-site-demanding reactions are suppressed before non-demanding ones (*7*).

The second and also the common way to study poisoning is based on the hypothesis that a limited contact between catalysts and sulfur compounds is sufficient to create a well-defined and permanent surface modification. Methods based on selective adsorption and methods using structure-insensitive reactions allow the determination of the metallic area remaining active after poisoning (*8*). Possible ways for regenerating the poisoned catalysts are also described (*9, 10*). A difficulty of this kind of study is that partially sulfided metals are "air sensitive" and therefore need complete *in situ* investigations (*11*).

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Generally, thioresistance of a metal can be related to an equilibrium

$$\text{Me–S} + \text{H}_2 \xrightleftharpoons{\text{sulfur compound}} \text{Me}^0 + \text{H}_2\text{S}.$$

This reaction can be shifted toward sulfur desorption either by increasing the hydrogen pressure and (or) the temperature or by decreasing the poison concentration. However, since modifications of these parameters are not always easy, other methods have been looked for in order to improve the thioresistance properties of the catalytic systems under controlled experimental conditions.

This can be done by creating a new catalyst design in which the active phase is protected either geometrically (*12*) (location inside a catalytic pellet) or chemically (*13–15*) (proximity of a compound having a higher affinity for S). In both cases, the intrinsic thioresistance of the active metal is not modified and poisoning is only delayed. Since the S–metal bond is essentially covalent, with a slight electronic transfer from the metal to the sulfur atom (*2*), the only way to alter the intrinsic thioresistance of a metal is through a modification of its electronic properties. According to literature data, this may be obtained by

alloying,
changing the metallic particle size, or
changing the acid–base properties of the carrier.

In fact, it is difficult to evaluate the relative importance of these last two parameters (*10, 16–18*).

Finally, since the presence of another electron acceptor molecule (EAM) in the feed has been described as being able to decrease the poisoning (*19*), a competitive adsorption between S and an EAM could also lessen the probability of Me–S bond formation.

The present paper is concerned with the thioresistance of Pt/Al$_2$O$_3$ catalysts in which the Pt particle size and acidity of the support have been modified. The influence of CH$_2$Cl$_2$ and (C$_2$H$_5$)$_3$N added in the feed has also been studied. The extent of these variations was followed with the help of a structure-insensitive reaction, namely, the dehydrogenation of cyclohexane either pure or containing 9 ppm of thiophene.

EXPERIMENTAL

A. Catalyst Preparation

In order to limit a non-uniform adsorption of the poison (*3*), a nonmicroporous alumina (aluminium Oxyd-C Degussa) was used as carrier. This alumina has a specific surface area of 100 m^2 g^{-1} and contains less than 30 ppm of sulfur. Due to the manufacturing procedure (flame hydrolysis) the alumina contains 0.5 wt% of Cl.

Various procedures were applied to try to decrease this initial chlorine content; acid washing or base washing (NH$_4$OH) or thermal treatment up to 773 K under flowing H$_2$ or O$_2$ were unsuccessful in this respect. However, using infrared spectroscopy, comparisons were made of the adsorption–desorption of pyridine for a chlorine free alumina (GFS 400, Rhône Poulenc) and for the Degussa alumina (*20*). The concentration of acidic sites, determined through the number of pyridine molecules adsorbed per unit area of alumina, was practically the same for both samples. The strength of the sites was lower on Degussa alumina, implying that the initial chlorine had no promoting effect on the acidity. We therefore assumed that the chlorine present in the starting material was nonreactive during the various steps of use and the corresponding catalysts will be regarded as "chlorine free" for our purposes.

For some experiments the Al$_2$O$_3$ support was modified by the addition of 1 wt% potassium hydroxide (Al$_2$O$_3$–K) or hydrochloric acid (Al$_2$O$_3$–Cl). The three types of carrier were impregnated with a chlorine-free platinum precursor, dinitrodiaminoplatinum (DNDAP), in order to obtain a platinum content comparable to the ones used for industrial catalysts. The impregnation salt was dissolved in hot water (353 K) and kept in contact with the solid during 10 h under constant stirring; the excess solvent was then evaporated under reduced pressure and the catalyst was dried at 383 K in air.

Varying the pressure or the heating rate during the activation treatment or calcining the precursor in air before activation gave rise to a number of catalysts differing in metallic surface area. In all cases a final activation under a hydrogen flow, at 773 K, was used to standardize the reduced catalysts.

B. Chemisorption Measurements

The metallic surface areas were measured by H_2 chemisorption using a conventional volumetric technique. Following activation under flowing H_2 at 773 K, the samples were outgassed at the same temperature for 1 h. Hydrogen adsorption isotherms were determined at 300 K between 1 and 20 kPa. The total chemisorbed amount $(HC)_{tot}$ was calculated from extrapolation of the linear part of the isotherm to zero pressure. After evacuating the sample for 0.5 h, a second adsorption isotherm led to the determination of $(HC)_{rev}$. The difference between the two above extrapolated values gave the amount of hydrogen irreversibly adsorbed by the catalyst under the present conditions $(HC)_{irr}$.

The values of metal surface areas measured, assuming $(HC)_{irr}/Pt_s = 1$, were in good agreement with electron microscopy determinations of particle sizes as observed on some of the catalysts.

C. Dehydrogenation of Cyclohexane

Apparatus. Prior to any catalytic activity measurement the catalysts were reactivated at 773 K for 2 h under flowing hydrogen. The reactant mixture, containing H_2, was obtained from either one of two saturator–condenser systems, S_1 or S_2; S_1 contained pure cyclohexane and S_2 contained cyclohexane contaminated by 14 ppm of thiophene.

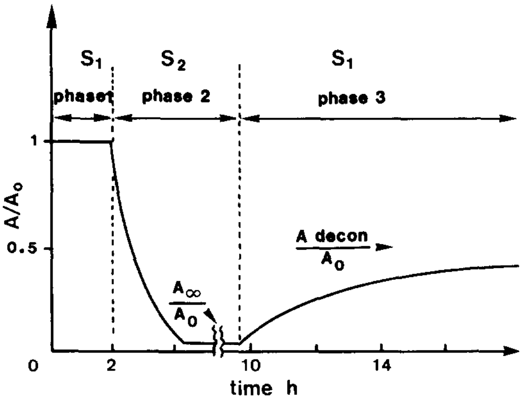

FIG. 1. Scheme of a typical catalytic run. $S_1 = C_6H_{12} + H_2$; $S_2 = C_6H_{12} + C_4H_4S + H_2$.

An injection device, upstream from the reactor, allowed the injection of small quantities of liquids which vaporized in the gas stream.

The catalyst (10 to 15 mg) was located in a quartz microreactor and was used under dynamic conditions. The composition of the reacted mixtures was analyzed by chromatography (Intersmat 120 FB) using an automatic sampling device.

All hydrocarbons used were of "spectra pure" grade.

Reaction conditions. The reaction was performed at 540 K, under 10^5 Pa total pressure, with $P_{H_2}/P_{C_6H_{12}} = 14$, and WHSV = 160 h^{-1}. 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%.

Procedure. Figure 1 represents the course of a typical experiment following the *in situ* reactivation of the sample. The experiment may be divided into three phases performed at constant temperature, 540 K. During the first phase, the catalyst was contacted with hydrogen and pure cyclohexane (S_1). For the majority of Pt catalysts, the activity stabilized very rapidly at A_0 (phase 1). After 2 h under these conditions, the catalyst was contacted with the gaseous mixture obtained from S_2 (phase 2, poison-

TABLE 1

Preparation and Adsorption Properties of the Catalysts

Catalyst	Additive	wt% Pt	Treatment before activation[a]	(HC)$_{irr}$ μmol g of cat.$^{-1}$	% Dispersion
Pt/Al$_2$O$_3$	None	0.57	—	3.8	26
		0.57	Decomposition under vacuum up to 773 K	13.0	89
Pt/Al$_2$O$_3$–K	1 wt% K	0.60	—	3.1	20
		0.60	Decomposition under vacuum up to 773 K	6.4	42
Pt/Al$_2$O$_3$–Cl	1 wt% Cl[b]		—	4.2	21
		0.78	Decomposition under vacuum up to 773 K	3.4	17
		0.78	Calcination under air up to 773 K	11.3	57

[a] Final activation was in all cases under flowing hydrogen (101 kPa) at 773 K for 2 h.

[b] Cl content was measured after the activation step.

ing phase). The activity A decreased either to zero or to a steady-state level, A_∞, different from zero, i.e., the thiotolerance level. In order to confirm the stability of the residual activity, some experiments were continued for 10 more h without noticeable change.

The third phase was the decontamination phase: the S$_2$ mixture was replaced by the S$_1$ mixture. Immediately the activity started increasing and slowly reached a new steady-state level (A_{decon}) after a period of time ranging from 5 to 12 h.

RESULTS

A. Metallic Surface Area

The symbols for the catalysts, their activation procedure, and the chemisorption results are listed in Table 1, and Fig. 2 shows a typical isotherm. Either calcination in air or decomposition under vacuum prior to the final reduction generally enhanced the dispersion of the catalysts. However, in the presence of K, the platinum dispersion obtained was at most close to 50%.

For some samples, dispersion was also calculated by H$_2$–O$_2$ titration, using H/Pt$_s$ = O/Pt$_s$ = 1 (*21, 22*). The values thus obtained were in reasonable agreement with values obtained from direct H$_2$ chemisorption.

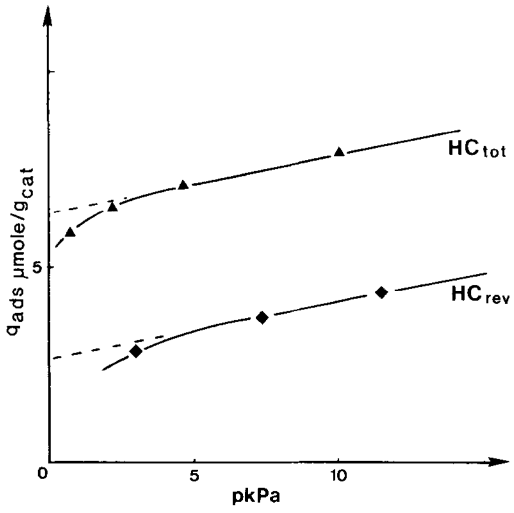

FIG. 2. Hydrogen chemisorption isotherms at 300 K for a Pt/Al$_2$O$_3$ catalyst (D = 26%).

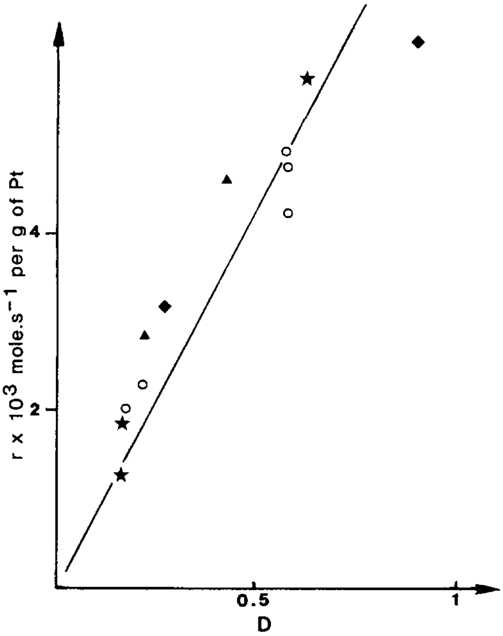

FIG. 3. Activity for cyclohexane dehydrogenation on various Pt catalysts versus metal dispersion (T = 540 K, $P_{H_2}/P_{C_6H_{12}}$ = 14, WHSV = 160 h^{-1}). ◆, Pt/Al_2O_3; ▲, Pt/Al_2O_3–K; ○, Pt/Al_2O_3–Cl; ★, Pt/Al_2O_3 (H_2PtCl_6) see Ref. (*27*).

B. Catalytic Activity

Phase 1. In the case of Pt catalysts, benzene is the only product from the dehydrogenation of cyclohexane and the reaction rate is stable. The structure insensitivity of the reaction (*23, 24*) for the catalysts of the present study was first confirmed. In Fig. 3 the specific activity is plotted versus Pt dispersion for various samples. If we take into account the precision on dispersion determinations, the average straight line may be considered satisfactory. In several cases, the apparent activation energy was measured and found to be close to 84 kJ mol^{-1}, in agreement with reported values (*25, 26*).

Phase 2. The activity versus time curves observed in the presence of the sulfur-containing reactant can be modified by many parameters. In order to compare the various catalysts, we normalized our experimental data, following Bartholomew *et al.* (*3*). For given temperature, flow rate, and thiophene content in cyclohexane, the poisoning depends on the accessible metal surface area. Figures 4–6 show the results of normalization; the relative activity, A/A_0, is plotted versus Λ which represents the number of thiophene molecules able to interact with one surface Pt atom.

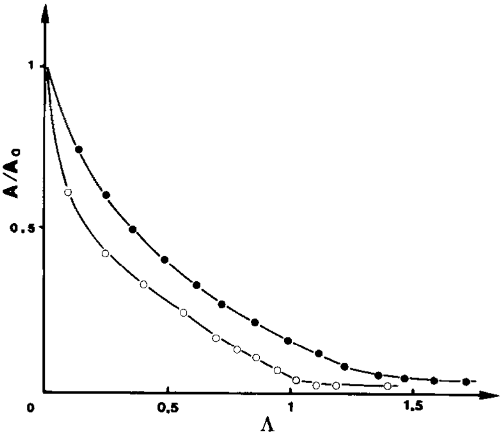

FIG. 4. Relative activity (A/A_0) versus the number of thiophene molecules flowed per surface platinum atom (Pt/Al_2O_3 catalysts). ●, D = 26%); ○, D = 89%.

Figure 4 gives the poisoning curves for two chlorine-free catalysts differing only in dispersion. The initial deactivation rate is more important for the well-dispersed catalyst. The activity stabilizes for a value A

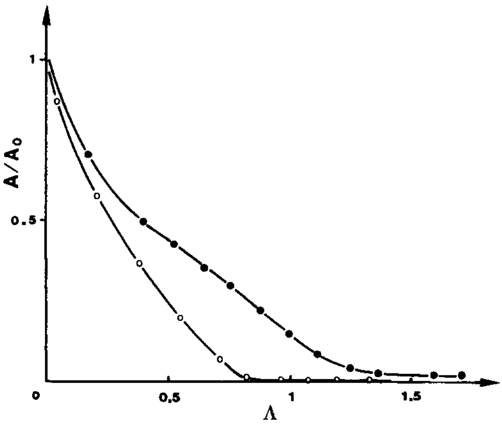

FIG. 5. Relative activity (A/A_0) versus the number of thiophene molecules flowed per surface platinum atom (Pt/Al_2O_3–K catalysts). ●, D = 20%; ○, D = 42%.

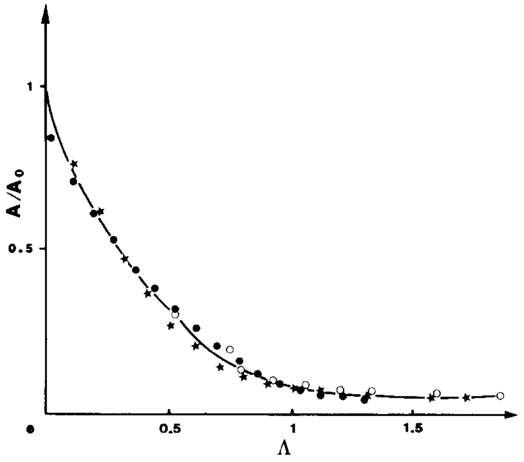

FIG. 6. Relative activity (A/A_0) versus the number of thiophene molecules flowed per surface platinum atom (Pt/Al$_2$O$_3$–Cl catalysts). ●, D = 57%; ○, D = 21%; ★, D = 17%.

different from zero when ~1.3 thiophene molecules per surface Pt atom have been injected. The thiotolerance level appears to be slightly higher for the catalyst having the larger particle size. The same types of curves are shown in Fig. 5 for potassium-containing catalysts. Again a higher dispersion leads to a faster initial deactivation rate. The thiotolerance level is zero or very low in this case. The deactivation curves for three chlorine-containing catalysts (Fig. 6) of various dispersions appear identical. The three catalysts reach a steady-state level of activity when about 1 molecule of thiophene has passed over 1 surface Pt atom. The residual activity is, for Pt/Al$_2$O$_3$–Cl, close to 5% of the initial value A_0. For the main catalysts, the relative thiotolerance level and the metallic dispersion are listed in Table 2. The results of some duplicate experiments are also reported.

Phase 3. The relative activity recoveries observed during phase 3 are also indicated in Table 2. Some of these values are given at two different times on stream, in order to illustrate the decontamination kinetics. Most catalysts recover between 40 to 50% of their initial activity.

Summarizing the preceding results, it appears that

during phase 2, the stationary state is observed after 0.8 to 1.3 molecules of thiophene have been injected for each surface Pt atom;

for chlorine-free catalysts the relative thiotolerance appears to be slightly higher when the dispersion is low;

when chlorine is present on the catalyst the influence of particle size disappears;

the addition of Cl enhances the thioresistance of the catalysts whereas the opposite is observed for K.

TABLE 2

Thiotolerance Level and Decontamination of the Various Catalysts

Catalyst	% Dispersion	$(A_x/A_0) \times 100$	$(A_{\mathrm{decon}}/A_0) \times 100$	
			400 min	600 min
Pt/Al$_2$O$_3$	26	2.4	46	51
Pt/Al$_2$O$_3$	89	1.7		49
Pt/Al$_2$O$_3$	89	1.5	34	38
Pt/Al$_2$O$_3$–K	20	1.0		42
Pt/Al$_2$O$_3$–K	42	0.5	29	39
Pt/Al$_2$O$_3$–Cl	17	4.2	44	44
Pt/Al$_2$O$_3$–Cl	21	4.6	30	42
Pt/Al$_2$O$_3$–Cl	57	4.9	48	53
Pt/Al$_2$O$_3$–Cl	57	4.6		

Attempts have been made to measure the apparent activation energy during phase 2. The values 160 to 210 kJ mol^{-1} are much higher than the values measured during phase 1.

C. Catalytic Activity following Injection of Volatile Compounds in the Feed

Injection of dichloromethane. In order to confirm the role of Cl, dichloromethane was injected at intervals into the feed (~100 molecules of dichloromethane per metal atom). Immediately following injection, catalytic activity variations were observed. Figure 7 gives an example of the phenomena occurring during independent runs when CH_2Cl_2 pulses were introduced respectively during phase 1, 2, or 3 for a Pt/Al_2O_3 catalyst with 89% dispersion.

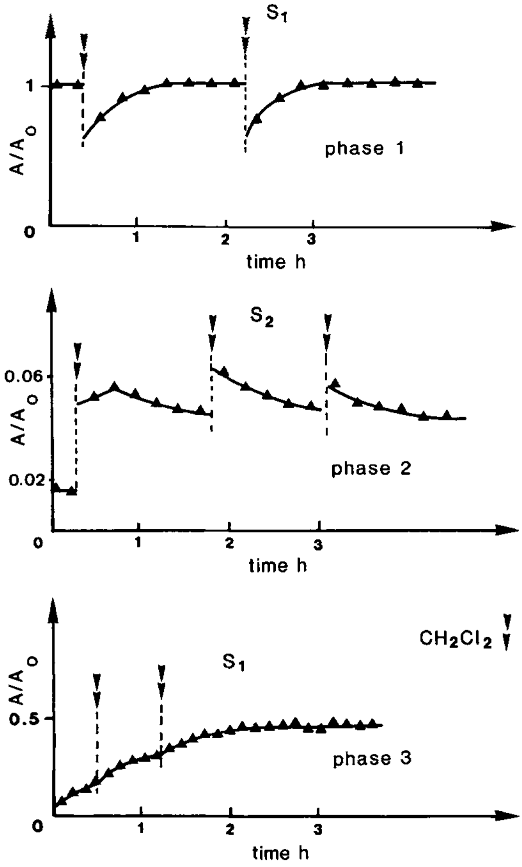

FIG. 7. Variations of the relative activity (A/A_0) of a Pt/Al_2O_3 catalyst (D = 89%) upon injections of CH_2Cl_2 (shown by arrowheads) during phase 1, phase 2, or phase 3.

TABLE 3

Influence of CH_2Cl_2 Injections on the Thiotolerance Level

Catalyst	% Dispersion	$(A_\infty/A_0) \times 100$	$(A'_\infty/A_0) \times 100$	A'_∞/A_∞
Pt/Al_2O_3-K	42	0.5	1.9	3.8
Pt/Al_2O_3	89	1.7	4.5	2.6
Pt/Al_2O_3-Cl	21	4.6	6.2	1.3
Pt/Al_2O_3-Cl	57	4.9	11.0	2.2

A transient effect was observed during phase 1 after which the initial activity was restored. If CH_2Cl_2 was contacted with the catalyst during phase 3, the decontamination speed was raised with only a negligible change of the final level of activity. Of more importance are the modifications induced during phase 2. After a positive but temporary effect the final steady-state activity is increased: it will be designated hereafter as A'_∞. A single dichloromethane injection was always sufficient for the catalysts to reach A'_∞.

In Table 3 we compare the thiotolerance levels, without or with added Cl, for some typical catalysts, and the promoting effect of chlorine addition A'_∞/A_∞.

In all cases, Cl increases the thiotolerance level and the benefit is higher when the initial A_∞/A_0 ratio is low.

Injection of triethylamine. The role of the injection of triethylamine was also investigated and the variations observed during phase 2 of the reaction are shown in Fig. 8 for a Pt/Al_2O_3 catalyst (D = 26%). Two types of phenomena were always observed: transitory and permanent. The transitory effect was always negative and could last several hours; the thioresistance level A_∞ was only slightly modified in a negative way.

DISCUSSION

A. Choice of the Reaction

For reactions occurring at low temperature, the adsorption of the sulfur compound

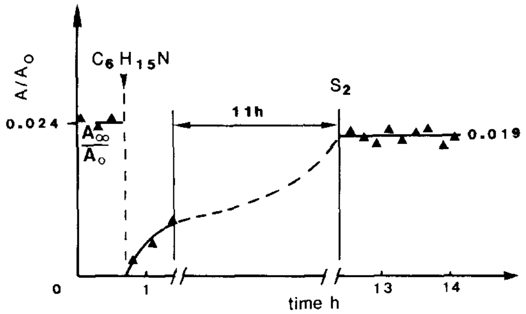

FIG. 8. Variations of the relative activity (A/A_0) of a Pt/Al$_2$O$_3$ catalyst (D = 26%) upon injection of (C$_2$H$_5$)$_3$N during phase 2.

on the carrier might be very important. Furthermore, extremely low sulfur concentrations are sufficient to completely deactivate the catalysts whatever the metallic dispersion and the nature of the additives. For high-temperature reactions, the catalysts are able to withstand higher sulfur concentration and technological problems due to a corrosive feed are more difficult to solve. Moreover, other deactivation processes such as carbon deposition and sintering may interfere. Therefore a reaction operative in a medium temperature range such as dehydrogenation of cyclohexane seems well suited for our purpose, in agreement with Minachev and Kondratev (*5*).

A second reason for our choice is that dehydrogenation of cyclohexane has been described as structure insensitive. Consequently an estimation of the unpoisoned metallic area is possible in the course of the reaction. The results obtained with the catalysts of the present study as well as with other supported Pt/Al$_2$O$_3$ catalysts (*27*) are a further confirmation of the insensitivity of this reaction to the structure of the Pt particles.

The fact that the activity during phase 1 is particularly stable is another advantage in the case of the present Pt catalysts by comparison with, for example, supported Ir catalysts (*28*). This means that during phase 2 the deactivation will result mainly from sulfur.

B. Deactivation Curves

Reference to Figs. 4–6 shows that the values of Λ, corresponding to maximum poisoning, are quite large (0.8 to 1.3 molecules of thiophene per surface Pt atom), compared to 0.7 measured by McCarty *et al.* (*29*) with H$_2$–H$_2$S mixtures. This difference could have three different explanations:

(i) Not all thiophene molecules fed with the cyclohexane are trapped during the deactivation process by the metallic phase.

(ii) An adsorption–desorption process of sulfur may exist even before reaching the thiotolerance level.

(iii) Part of the thiophene or sulfur is adsorbed on the support, besides adsorption on Pt.

In this last case the presence of Cl (*30*) or K is also liable to modify the sulfur–carrier interaction so that the contribution of the carrier cannot be merely subtracted from total sulfur adsorption.

In this first part we therefore compare the various catalysts only in a qualitative way.

It can be seen from Figs. 4 and 5 that catalysts with a higher dispersion of the metallic phase show an initial deactivation which is more rapid than with less dispersed catalysts. From literature data the effect of particle size on thioresistance is not clear. Rabo *et al.* (*16*) found that small particles were sulfur resistant whereas Echevskii *et al.* (*31, 32*) found no evidence for a particle size effect in the case of Ni, Pt and Pd deposited on different carriers. The fact that in Fig. 6 deactivation curves are more or less independent of particle size when chlorine is present on the catalyst tends to indicate that particle size is a second-order parameter for thioresistance.

Since these features of poisoning are only qualitative, it is interesting to compare the present catalysts by their thiotolerance level, from a quantitative point of view.

C. Thiotolerance Level

In Figs. 4 and 5 and from the data of Table 2 it is seen that for Pt/Al_2O_3 an increase of dispersion by a factor of 4 decreases the thiotolerance level by 1.5; in the case of Pt/Al_2O_3–K an increase by a factor of 2 of the dispersion decreases the thiotolerance level by the same factor. Finally, for Pt/Al_2O_3–Cl an increase of dispersion by 3 has no effect on the thiotolerance level. This suggests that metal dispersion has no direct relation to thiotolerance and that another property of the catalysts is more important. Using the same data, it can be seen that the thiotolerance level is much higher for Pt/Al_2O_3–Cl than for Pt/Al_2O_3 or Pt/Al_2O_3–K.

These variations of the thiotolerance level indicate that the nature of the support plays an important role and since textural properties of the present catalysts are the same, the major parameter could be the acidity.

As is well known, addition of Cl to Al_2O_3 increases the acidity (*33, 34*) whereas the presence of alkalis has the opposite effect (*35*). Influence of the acidity on thioresistance has been shown in the literature (*19, 36*). However, there is no general agreement as to the relative contribution of support acidity and particle size effects (*10, 16, 18, 31, 32, 37*).

In both cases, an electron deficiency of the metallic particles would explain the increase of thioresistance. Some preliminary experiments by XPS have shown that the presence of potassium, on a Pt/Al_2O_3 catalyst, leads to a decrease of the Pt binding energy ($4d_{5/2}$) of 0.9–1.2 eV and are indicative of an electron enrichment on Pt. However, these measurements, performed without *in situ* reduction, need further confirmation.

D. Decontamination Phase

Again, as for the deactivation curves a study of the kinetics of decontamination does not seem valuable for various reasons. Among them are the facts that

(i) the starting level of activity, A_∞, depends on the catalyst, and

(ii) the total contact time under the poisoned feed appears to modify slightly this phase.

Therefore the main feature is that, whatever the catalysts, the activity recovery, at 540 K, in the presence of pure feed, ranges from 40 to 60% of the initially unpoisoned activity, A_0. For Gallezot *et al.* (*10*), platinum catalysts poisoned by thiophene are regenerated only to 10% following a H_2 treatment at 573 K. This discrepancy may arise from the fact that the rate of decontamination is rather low and perhaps less efficient in the presence of pure hydrogen than with a mixture containing a hydrocarbon.

E. Activation Energy

The value of the apparent activation energy (84 kJ mol^{-1}) measured with pure cyclohexane is much lower than the corresponding ones (160–210 kJ mol^{-1}) measured in the presence of thiophene. Such a variation is often explained by a change of the reaction mechanism, but in the present case, modifications of the catalysts seem to be more important. Two examples follow:

(i) Temperature variations can alter not only the reaction rate but also the sulfur coverage and hence the active metal area.

(ii) Temperature variations can also probably reorganize sulfur, carbon and chlorine localization. The lack of reversibility to recover A_0 after a temperature cycle supports these hypotheses.

F. Modifications Brought about by Triethylamine or Dichloromethane Injections

In Fig. 7, it can be seen that CH_2Cl_2 gives rise to different behavior according to whether the injection was made during phase 1, 2, or 3. In phase 1 the negative transitory effect, lasting for ~1 h, could be due to competitive adsorption; this means that either chlorine or another decomposition product derived from CH_2Cl_2 is preferentially adsorbed on the metal but that the adsorption is reversible when CH_2Cl_2 is no longer present in the gas phase. The absence of permanent modification of the activity indicates that under present conditions redispersion of platinum does not occur. This is not in contradiction with literature data concerning this last phenomenon which is generally observed at a higher temperature in an oxidizing atmosphere (*38*).

In phase 2 the transitory effect is positive. By comparison with phase 3, where we observe an increase of the decontamination rate, we conclude that the addition of CH_2Cl_2 probably induces some S desorption.

The permanent effect cannot be attributed merely to a reorganization of the poison species at the surface (S, C, . . .) and is in agreement with the role of support acidity toward thioresistance. The increase of alumina acidity upon addition of organic chloride is well known (*33*, *34*).

In the case of triethylamine and for Pt/Al_2O_3 there is no permanent effect but a long-lasting inhibition is observed, probably due to a rather strong adsorption of the triethylamine or of its decomposition products. As a result, inhibition of the acidity is expected.

As for others (*39*, *40*), it appears that sulfur poisoning involves two types of S atom: (i) a strongly adsorbed form responsible for the limited decontamination and (ii) a labile form in equilibrium with the poisoned gaseous feed. The thiotolerance level results from the relative amount of these two species under experimental conditions.

The present results are in agreement with the idea that the main part of the poisoning is due to a geometrical blockage of active sites, while the differences in activity at the thiotolerance level are principally linked with the electronic properties of Pt particles interacting with the support. Even though these latter differences are relatively small, they are important since they are observed in the presence of contaminated feed, under steady-state conditions.

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