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Transformation of Carbon Compounds on Graphimet Catalysts

III. Structure and Catalytic Investigation of Pt Graphimet[1]

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The hydrogenation of cyclohexene was studied over Pt-graphimet catalysts pretreated at 298 K. The platinum atoms are situated partly on the external surface of the graphite and partly in the interlayer space. The interlayer atoms are readily accessible for hydrogen, the mass transfer resistance is greater for oxygen, and the cyclohexene cannot diffuse into the interlayer space at all. Thus, the hydrogenation of cyclohexene takes place only on the exposed atoms on the external surface of Pt graphimet, and the atoms in the interlayer space are inactive in this reaction.

INTRODUCTION

The graphite-transition-metal systems (commercially available under the name Graphimets) have numerous applications for catalytic transformations (*1–13*), but contradictory results have been reported with respect to their structures. It was previously assumed that the Graphimets contain the atomically dispersed metals inserted between the graphite layers (*14, 15*). The distance between graphite layers is 0.335 nm in graphite and 0.6–0.7 nm in Pt graphimet. The graphite layers prevent aggregation of the metal atoms into bulk metal. The high selectivity of catalytic reactions can be expected because of the fixed distances between the layers filled by metal atoms. In addition to intercalation in graphite, the distribution of metals on graphite are also reported (*7, 16–19*).

Since graphite-layered compounds are thermally unstable, under the conditions of pretreatment or catalytic hydrogenation the metal can easily move out from between the graphite layers (*20*). The metal atoms may aggregate, and three-dimensional clusters may form. This process can be observed directly on the external surface of graphite (*21, 22*). When a vast majority of the catalytically active metal is to be found on the external surface of the graphite, the graphimet catalyst becomes similar in nature to graphite-supported catalysts (*4*). For Ni-graphimet catalysts, the metal content on the surface has been found to be the determining factor in the catalytic reactions (*23*), but catalytic activity was observed only if the reduction was carried out at 673 K or higher. Treatment at such a high temperature significantly changes the original structure of the catalyst, and it is therefore difficult to draw conclusions from these investigations as to the catalytic properties of the original graphimet structure.

Oxygen chemisorbed on the surface of platinum is well known to react with hydrogen even at room temperature, and thus Pt graphimet will probably be reduced even at room temperature. Because of the low reduction temperature, the original layer structure remains intact and hence investigation of the catalytic activity of the original graphimet catalyst becomes possible.

Smith *et al.* (*18*) observed platinum is-

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lands in Pt graphimet, but the detection of residual intercalates was not the object of that work. Fürstner *et al.* (*7*) studied the structure of Pt graphimets and concluded that, independent of the method of preparation, platinum–graphite combinations consist of platinum more or less evenly distributed on graphite, and intercalation is insignificant, if it exists at all.

The aim of the present work is to investigate whether Pt graphimet behaves as a classical supported catalyst in the hydrogenation of alkenes or whether, at least partly, the metal atoms between the graphite layers are also active in the catalytic reaction.

EXPERIMENTAL

Catalysts

The 1% Pt-graphite catalyst was prepared by the Bartholomew–Boudart method (*24*). Graphite powder with 20- to 60-mesh particle size (Alfa Chemical Company) was oxidized at 873 K until it had lost 50% of its weight. The resulting support was impregnated with an ethanolic solution of H_2PtCl_6 during stirring for 31 h in a nitrogen stream. The reduction was carried out in flowing hydrogen for 2 h at 583 K, and then for 20 h at 773 K.

The Pt graphimet (1% platinum in graphite) was a product of Alfa Chemical Company. A mixture of graphite powder and platinum(IV) chloride was heated at 773 K in a chlorine stream for some days. Reduction was carried out at 223 K with lithium biphenil in a helium atmosphere. The resulting material was washed in turn with tetrahydrofuran, acetone, and water, then dried in vacuum at 413 K (*25*). Before use, the catalyst was pretreated for 2 h in hydrogen at 298 K.

The graphimet catalyst investigated contains 1% platinum, i.e., $N_t = 3.09 \times 10^{19}$ (N_t is the total number of platinum atoms per gram catalyst). Part of the platinum can be found on the external surface of the graphite in the form of crystallites (N_c is the number of crystallite platinum atoms on the surface per gram catalyst). Exposed atoms are able to adsorb hydrogen (N_e is the number of exposed crystallite platinum atoms per gram catalyst), while the atoms inside the crystallites do not adsorb hydrogen (N_u is the number of unexposed platinum atoms of surface crystallites per gram catalyst).

The rest of the platinum atoms are found inside the graphite (N_i is the number of internal platinum atoms per gram catalyst). These platinum atoms can also adsorb hydrogen, in a quantity depending on their dispersion. If platinum is present as small crystallites inside the graphite, it is only the exposed atoms that can adsorb hydrogen (N_{ie} is the number of internal exposed platinum atoms per gram catalyst), while the unexposed atoms (N_{iu}) cannot. If all these platinum atoms are intercalated, all of them are able to adsorb hydrogen ($N_{ie} = N_i$), at least in principle.

Since the catalyst contains two different types of platinum atoms able to adsorb hydrogen, different dispersion values can be determined. We calculated the total dispersion based on the total number of platinum atoms (D_t) and the dispersion corresponding to the exposed atoms (D_e),

$$D_t = (N_e + N_{ie})/N_t \qquad (1)$$

$$D_e = N_e/N_t. \qquad (2)$$

The surface dispersion (D_s) can also be determined,

$$D_s = N_e/N_c = N_e/(N_e + N_u). \qquad (3)$$

Characterization

The total surface area of the catalyst (7.1 m^2/g) was determined by N_2 adsorption at 77 K. D_s was measured by transmission electron microscopy with a Hitachi H500H instrument.

The H_2–O_2 titration provided much information about the structure of the graphimet catalyst. The measurement was carried out as follows: the catalyst covered with hydrogen was treated with oxygen at room temperature for different periods of time (Table 1) then titrated with hydrogen pulses in flowing helium at room temperature. In the knowledge of the quantity of hydrogen required for titration, we calculated the number of platinum atoms able to adsorb oxygen (N_e and N_{ie}) and divided this by the total number of platinum atoms. The resulting D value agreed with D_t or D_e, according to the experimental conditions.

Method

Catalytic transformations were observed in a static recirculation system. In the measurements, 5-mg catalyst samples were used. The flow rate was 300 $cm^3 \times min^{-1}$, and the zero time was 0.1 min. The other details of the apparatus have been described elsewhere (*26*).

Catalyst activation before measurement was performed at 298 K, and 100-Torr H_2 was used. After catalyst pretreatment, the reactor was cooled down to the reaction temperature under continuous evacuation. The reactant gas introduced into the recirculation reactor contained 13-Torr cyclohexene, 76-Torr H_2, and 671-Torr argon. The time dependence of the conversion was measured at 298, 323, and 348 K. The product distribution was determined by means of gas chromatography.

Materials

Cyclohexene (Fluka) was used after distillation and purification with Al_2O_3 under an argon atmosphere (*27*). The GC purity was found to be 100%. Hydrogen was obtained from a Matheson 8326 hydrogen generator operating with a palladium membrane.

RESULTS AND DISCUSSION

The dispersion of Pt-graphimet catalyst was determined by H_2–O_2 titration. The number of platinum atoms determined via titration was the higher, the longer the oxygen treatment (Table 1). After oxidation for 2 weeks, however, the measured number of atoms no longer increased.

A similar measurement was performed for the 1% Pt-graphite catalyst. With this catalyst, we observed that even after a 10-min oxidation period, the value of D was constant (Fig. 1).

TABLE 1

Time Dependence of the Dispersion of the Pt-Graphimet Catalyst, Calculated on the Basis of H_2–O_2 Titration

Time (min)	Dispersion (D)	$N \times 10^{-18}$ [a]
1	0.005	0.15
2	0.023	0.7
5	0.055	1.65
10	0.105	3.26
15	0.14	4.3
30	0.20	6.2
16 h	0.24	7.4
1 day	0.32	9.9
6 days	0.43	13.3
2 weeks	0.64	19.8
3 weeks	0.64	19.8

[a] Number of hydrogen adsorbing atoms/g catalyst.

This agreed with the literature finding (*28*) that a 15-min oxygen treatment was enough for full coverage of the surface of the supported platinum catalyst at 25°C.

During a shorter oxidation period, only the exposed atoms on the external surface of the Pt graphimet (N_e), and possibly the interlayer atoms close to the surface, undergo oxidation. During longer oxidation, the platinum atoms in the interlayer space (N_{ie}) are also oxidized.

The findings on the 1% Pt-graphite catalyst indicate that the total oxidation of the exposed atoms takes place in 10 min for Pt graphimet too. Thus, the values obtained after 10 min ($D_e = 0.103$ and $N_e = 3.18 \times 10^{18}$) were considered to correspond most closely to the condition under which all the exposed atoms are oxidized, but interlayer oxidation is still negligible (Fig. 2).

The constant dispersion after oxidation for 2 weeks demonstrates that at this time every interlayer atom is already oxidized. The values measured after a longer oxidation are $D_t = 0.64$ and $N_e + N_{ie} = 1.98 \times 10^{19}$. Virtually the same value was obtained when the static hydrogen chemisorption

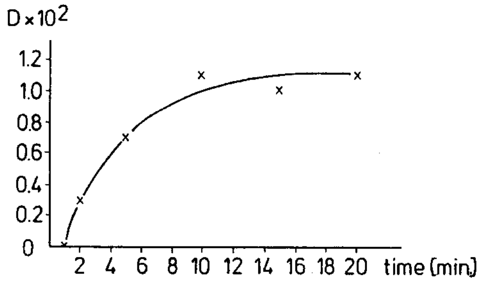

FIG. 1. Time dependence of the dispersion of the 1% Pt-graphite catalyst, calculated on the basis of H_2–O_2 titration.

method was used. If the stoichiometry of adsorption is the same for the interlayer atoms as for the exposed ones, N_{ie} can easily be calculated:

$$N_{ie} = (1.98 - 0.318) \times 10^{19} = 1.662 \times 10^{19}.$$

This value shows that, for the Pt-graphimet catalyst, more than half of the platinum is situated in the interlayer space.

On the basis of a careful EDX study, Fürstner *et al.* (*7*) reported that the intercalation of platinum is insignificant. However, it might be concluded from our results that a significant proportion of the metal is intercalated. Of course, our own investigations do not justify the existence of the coordinative interactions between the platinum and the carbon atoms. It is very likely that Pt between the layers is present as 100% dispersed clusters, because single atoms will not catalyze the titration reaction.

The surface dispersion of the Pt-graphimet catalyst was also measured directly by transmission electron microscopy. With this method, of course, it is only the surface crystallites that can be detected: small platinum particles (1.2–8 nm in size) were detected on the surface. A value of 3.26 nm was calculated for the average particle size.

Yacamán and Dominguez (*29*) have investigated Pt-graphite catalysts and found that the Pt particles have a three-dimensional cubo-octahedral structure. Burch (*30*) reported how the particle diameter is related to dispersion. For a cubo-octahedral particle shape, electron microscopic data yield $D_e = 0.24$.

From Eq. (3) the number of surface atoms that does not adsorb hydrogen (N_u) can be calculated:

$$N_u = \frac{N_e}{D_s} - N_e = 1.11 \times 10^{19}.$$

The number of interlayer atoms that does not adsorb hydrogen (N_{iu}) can also be established:

$$\begin{aligned} N_{iu} &= N_t - (N_e + N_{ie} + N_u) \\ &= 3.09 - (1.98 + 1.11) \times 10^{19} = 0. \end{aligned}$$

This means that platinum with atomic (or nearly atomic) dispersion ($N_i = N_{ie}$) is present in the interlayer space.

It is clear from Table 1 that some of the platinum atoms are hardly accessible, even for oxygen molecules. The time dependence of oxygen chemisorption may due to the diffusion process needed for oxygen to move to the inside of the Pt graphimet and to react with the inside Pt atoms. However, hydrogen reacts with the adsorbed oxygen, even during a passing pulse; i.e., the diffusion resistance is much smaller in relation to hydrogen than to oxygen (Fig. 3). The above results show that an appreciable proportion of the platinum atoms is situated inside the graphite.

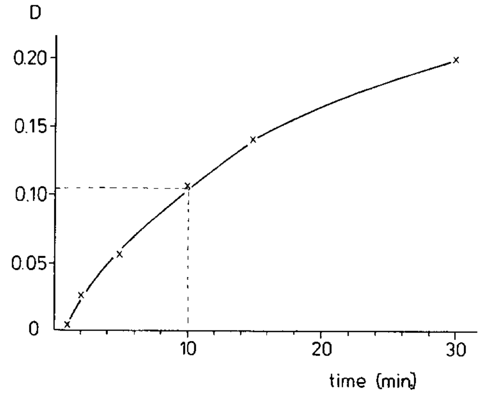

FIG. 2. Calculation of the exposed dispersion (D_e) of the Pt–graphimet catalyst.

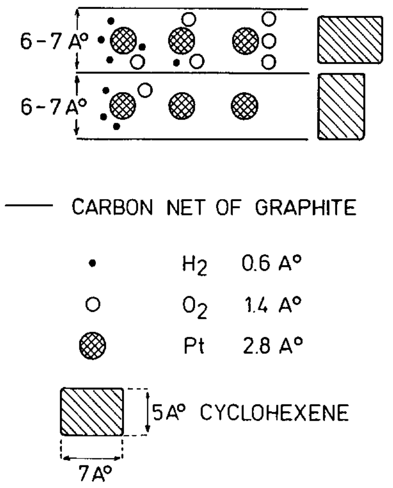

FIG. 3. Sizes of reacting molecules.

However, it has not yet been established whether only the surface crystallites of Pt graphimet are available for cyclohexene, as in the case of a classical supported metal catalyst, or, in addition to the exposed atoms of the surface metal crystallites, the role of the internal metal atoms should be taken into account.

Segal *et al.* (*31*) pointed out a structure insensitivity for cyclohexene hydrogenation in the case of Pt/SiO_2 catalysts under reaction conditions the same as those indicated above. It means that a change in dispersion has no effect on the turnover frequency. A support insensitivity was also established with respect to turnover frequency, for SiO_2 and Al_2O_3 supports (*32*). Thus, the same turnover frequency values can be expected for the different catalysts, presuming that the calculation is performed on the basis of catalytically active atoms.

The catalytic activity of Pt graphimet has been studied in the hydrogenation of cyclohexene. The time dependence of the conversion was measured at 298, 323, and 348 K, as reported in Fig. 4. Under such conditions, the hydrogenation of the reactant takes place with 100% selectivity.

It is well known that hydrogenation on Pt catalyst is of zero order with respect to the cyclohexene concentration (*31*). This is suggested equally by the constant slope of the straight lines in Fig. 4. The reaction rates were determined from the slopes, taking into consideration that the number of cyclohexene molecules present at $t = 0$ was 7.34×10^{19}. Table 2 presents the reaction rates (r) and the turnover frequencies defined by the number of cyclohexene molecules transformed per exposed platinum atoms (N_e) per second (TOF_e), or per all of

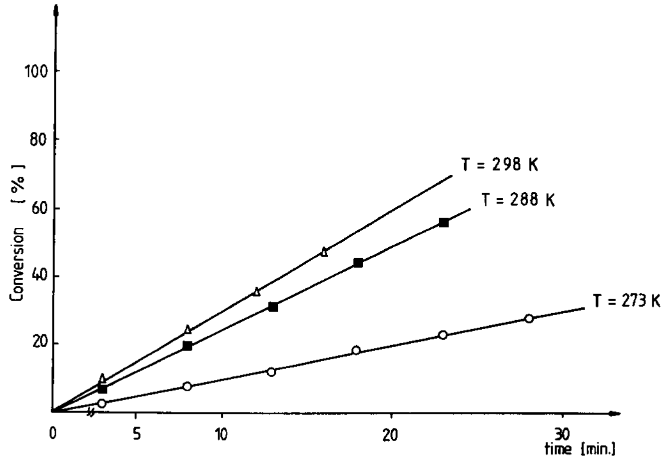

FIG. 4. Conversion of cyclohexene as a function of time at various temperatures on 1% Pt-graphimet catalyst.

TABLE 2

Hydrogenation of Cyclohexene on 1% Pt-Graphimet Catalyst

Temperature (K)	Reaction rate $(r)^a$	Turnover frequencies $(s^{-1})^a$	
		TOF_t	TOF_e
273	1.15×10^{16}	0.12	0.75
288	2.93×10^{16}	0.29	1.83
298	4.23×10^{16}	0.43	2.71

Note. Mass of catalyst, 5 mg.

[a] Number of hydrogenated molecules per second; $TOF_e = r/N_e$; $TOF_t = r/(N_e + N_{ie})$.

the atoms, adsorbing hydrogen ($N_e + N_{ie}$) per second (TOF_t). The apparent activation energy of the reaction was found to be 32 kJ mol^{-1}.

At 295 K, Segal (*31*) determined a turnover frequency of 2.65 on Pt/SiO_2 catalyst under conditions the same as those in our experiments. However, the turnover frequency (TOF_t) calculated by using the total dispersion value at 298 K (D_t, Table 2) is much smaller. At the same time, the TOF_e value (2.71) calculated on the basis of the exposed dispersion (D_e) is in very good agreement with that measured by Segal *et al.* Consequently, the hydrogenation of cyclohexene takes place only on the exposed atoms on the external surface of the graphimet, even in the case of Pt graphimet. Nevertheless, the atoms in the interlayer space are inactive, presumably because the cyclohexene molecule is too large to diffuse into the interlayer space (Fig. 3). The fact that the measured activation energy (32 kJ mol^{-1}) is also similar to the value (33.5 $kJmol^{-1}$) given by Segal *et al.* (*31*) points to the similarity with supported catalysts.

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