

Transformation of carbon compounds on graphimet catalysts. Part V. The effect of pretreatment on the structure and activity of Pt–graphimet catalyst

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Abstract

The effect of medium-temperature reduction (MTR, 573 K) on the structure and catalytic activity of Pt–graphimet was studied by transmission electron microscopy, small angle X-ray scattering, O₂–H₂ titration and sorption microcalorimetry. The test reaction was the hydrogenation of cyclohexene. MTR resulted in the migration of interlayer platinum atoms to the catalyst surface, leading to metal aggregation and the formation of additional inserted active sites responsible for increased O₂ and H₂ adsorption. The decrease in catalytic activity observed upon MTR is attributed to the encapsulation of small surface particles inside the graphite ‘host’.

Keywords: Calorimetry; Cyclohexene; Hydrogenation; Medium temperature pretreatment; O₂–H₂ titration; Pt–graphimet; Small angle X-ray scattering; Sorption microcalorimetry; Transmission electron microscopy

1. Introduction

The characteristics of transition metal–graphite intercalation compounds (graphimets) have been thoroughly examined in the past decade [1–7]. Nevertheless, information on their structure is still rather limited.

Graphite intercalation compounds are generally formed by the insertion of atomic layers of a guest species, called the intercalate, between layers of the graphite ‘host’ [8]. For graphimets, inserted metal particles may be present either in the form

of an atomic dispersion [9,10], or as small clusters [9,11]. The fixed distance between the graphite layers prevents metal aggregation. On the other hand, graphimets may also contain a considerable amount of surface metal which is of crucial importance in catalytic transformations [3,9].

Thermal treatment of graphimets is likely to increase the surface metal content via the migration of interlayer particles [12].

We have studied the effect of medium-temperature reduction (MTR, 573 K) on the structure of a Pt–graphimet sample. The catalytic activities before and after such pretreatment were also investigated.

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2. Experimental

2.1. Materials

Pt-graphimet (1% platinum in graphite) was a product of Alfa Chemical Company. Preparation of the sample included heating of a mixture of graphite powder and platinum(IV) chloride at 773 K in a chlorine stream for several days. Reduction was then carried out at 223 K with lithium biphenyl in a helium atmosphere. The product was washed in turn with tetrahydrofuran, acetone and water and then dried in vacuum at 413 K [13].

2.2. Transmission electron microscopy (TEM)

Measurements were carried out with a Zeiss 902 instrument. Prior to measurement, samples were ultrasonically dispersed in toluene [14] and then deposited on a plastic film supported by a Cu grid. Magnifications were in the range 5×10^4 – 1.4×10^5 times. The smallest detectable particle size was 0.5 nm.

2.3. Small angle X-ray scattering (SAXS)

Experiments were performed with a PW 1830 Philips generator supplied with a Kratky compact camera. Measurements were evaluated in the Guinier range, spherical symmetry being assumed for the particles. The scattering intensity I is related to the radius of gyration R according to Eq. 1:

$$\ln I = \ln I_0 - R^2 h^2 / 3 \quad (1)$$

where I_0 is the scattering intensity at zero angle and the scattering vector h is a function of half of the scattering angle expressed in radians and the X-ray wavelength λ (see Eq. 2):

$$h = 4\pi \sin \theta / \lambda \quad (2)$$

R was determined from the slope of the Guinier plot [15]. The particle radius r was obtained from Eq. 3:

$$R^2 = 3/5r^2 \quad (3)$$

2.4. O₂–H₂ titration

Measurements were performed by the conventional method [16]. O₂ was preadsorbed on Pt-graphimet for different periods of time, and subsequent titration with H₂ provided the number of active metal particles. The usual stoichiometry of Pt:H = 1:3 was applied for calculations [17]. The values of dispersions are based on the total number of platinum atoms on the catalyst.

2.5. Sorption microcalorimetry

The heat of adsorption of H₂ was determined by coupling a volumetric apparatus to the batch unit of an LKB 2107 isothermal sorption microcalorimeter. Initially, 130 mg of sample was brought into contact with 40 kPa H₂ at room temperature for 2 h. Afterwards, evacuation was performed and the sample was left at 403 K under vacuum overnight. Experiments were then carried out at 298 K. Adsorption of H₂ was accomplished by admitting small doses of H₂ gas into the calorimeter cell. Each dose produced a heat emission, which was recorded until the calorimetric baseline was attained. Desorption was effected by expansion of the gas phase in equilibrium with the adsorbate gas into a definite volume. Heat effects attributed to cell opening were corrected for by 'blank runs', He being used instead of H₂, under the same conditions. The integral molar enthalpy of chemisorption Q_{int} was determined via Eq. 4:

$$Q_{\text{int}} = Q_{p \rightarrow 0} / n_s = h^s - h^g \quad (4)$$

where $Q_{p \rightarrow 0}$ is the heat of adsorption at zero pressure derived from extrapolation of the enthalpy isotherm, n_s is the amount of adsorbed H₂ calculated from O₂–H₂ titration, and h^s and h^g are the molar enthalpies of the gas in the surface layer and the gas phase, respectively.

2.6. Catalytic test reaction

Catalytic activity was investigated via the reaction of cyclohexene hydrogenation, in a static recirculation reactor system. Details of the exper-

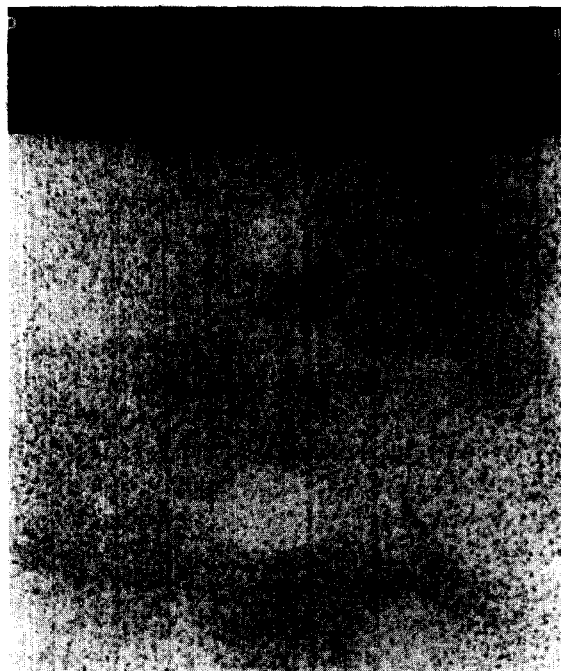


Fig. 1. TEM image of 1% Pt-graphimet (original sample).



Fig. 2. TEM image of 1% Pt-graphimet after medium-temperature reduction (MTR sample).

imental apparatus are described elsewhere [18]. The mass of catalyst used was 5 mg. Before measurements, the sample was pretreated at 298 K for 2 h under 13.3 kPa H₂. MTR of the catalyst was

effected at 573 K, under otherwise the same conditions. The reactant gas introduced into the reactor contained 1.7 kPa cyclohexene, 10.1 kPa H₂ and 89.5 kPa argon. The time dependence of the conversion was measured at different temperatures. Reaction rates were calculated from the slopes, the number of the reactant molecules present at $t = 0$ being taken as 7.34×10^{19} . The products were analyzed with a Carlo Erba gas chromatograph.

3. Results and discussion

The average particle sizes for the original Pt-graphimet and that treated by MTR were determined from TEM and SAXS measurements. TEM experiments on the original sample suggested the presence of small, evenly distributed particles, ranging in size from 1.2 to 14 nm (Fig. 1). For the MTR sample, however, the formation of large aggregates was observed in addition to the original small particles (Fig. 2).

After pretreatment at 573 K, the particle size range was found to be 2–270 nm. The number of aggregates was substantially lower than that of the small particles.

Guinier plots obtained from SAXS experiments are displayed in Fig. 3.

Table 1 shows the mean particle diameters from both SAXS and TEM measurements. The agreement appears to be completely satisfactory.

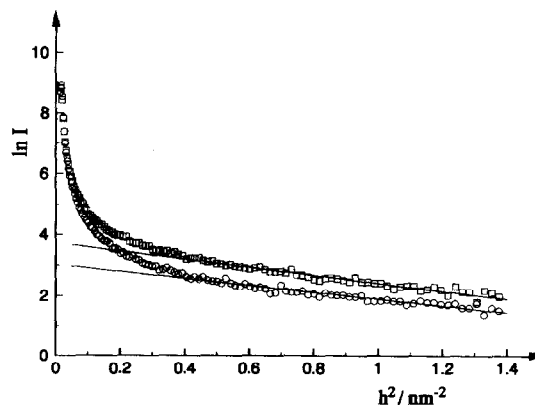


Fig. 3. Guinier plots of 1% Pt-graphimet. Circles: original sample; squares: MTR sample.

Table 1
SAXS and TEM data determined for Pt-graphimet before and after MTR

Sample	SAXS			TEM
	Slope	R/nm	d/nm	d/nm
original	-0.9532	1.69	4.36	4.67
MTR	-1.1741	1.88	4.85	5.39

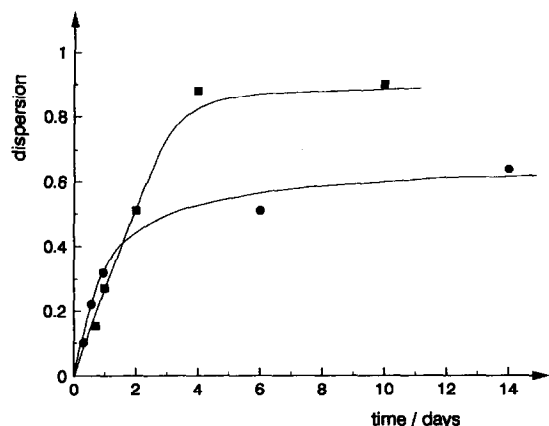


Fig. 4. Dispersion of 1% Pt-graphimet as a function of oxidation time, obtained from O_2 - H_2 titration. Circles: original sample; squares: MTR sample.

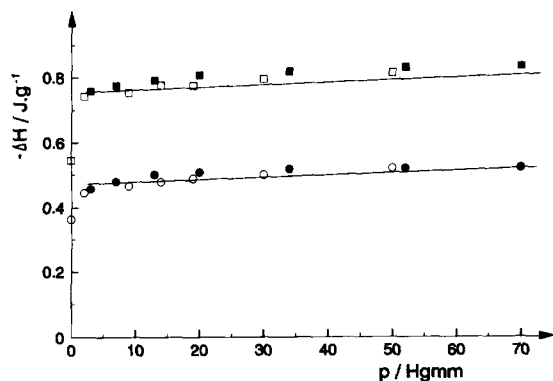


Fig. 5. Integral enthalpy isotherm of adsorption of H_2 on 1% Pt-graphimet at 298.15 K. Circles: original sample; squares: MTR sample. Solid symbols: adsorption; open symbols: desorption. Mass of sample: 0.1300 g.

In both cases, only a slight increase in the average particle size can be detected following medium-temperature pretreatment, despite the formation of large aggregates observed by TEM. Previous experiments [19] prove that for Pt-graphimet, more than half of the total amount of metal is situated in the interlayer space. Similarly to the

intraparticulate atomic model described earlier [20], sintering may occur by the transport of inserted metal atoms to the surface. The additional metal atoms may gather together to form large surface aggregates. On the other hand, MTR caused no significant change in the size of the finely distributed surface metal atoms observed in the original sample. The occurrence of sintering at 573 K points to an important difference between the structure of Pt-graphimet and that of supported platinum catalysts. In fact, despite the original presence of surface metal, Pt-graphimet is much more 'fragile' than a supported sample, for the layered structure of the graphite 'host' undergoes deformation even under relatively mild conditions. For supported platinum catalysts, sintering is generally observed above 773 K [20]. In some cases a much higher temperature is required for an appreciable change in structure [21,22]. Therefore, the role of interlayer metal should be taken into account in investigations of Pt-graphimet as a catalyst.

Fig. 4 depicts the change in platinum dispersion as a function of oxidation time. For the original sample, it took 2 weeks of oxidation for the highest dispersion possible to be reached. For the pretreated sample, however, the number of active particles no longer increased after merely 4 days of oxidation. Moreover, the maximum dispersion value found after MTR ($D=0.90$) was significantly higher than before ($D=0.64$). This suggests easier access for O_2 gas to the platinum atoms available for adsorption.

The results of sorption microcalorimetry experiments are illustrated in Fig. 5.

Apart from the first step (chemisorption), adsorption is found to be reversible (physisorption) for both the original and the MTR sample. The heat of chemisorption *per unit mass of catalyst* remarkably increased after MTR. The integral molar enthalpies of adsorption ($-29.9 \text{ kJ mol}^{-1}$ and $-33.8 \text{ kJ mol}^{-1}$, before and after MTR, respectively) are in good agreement with data published on supported Pt catalysts, ranging from -25 kJ mol^{-1} to -97 kJ mol^{-1} [23]. For such samples, the integral molar heats of adsorption

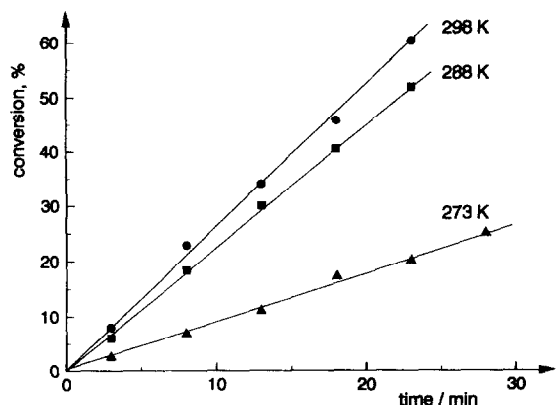


Fig. 6. Cyclohexene conversion plotted against reaction time at different temperatures for 1% Pt-graphimet catalyst pretreated at 298 K (original sample). Mass of catalyst: $5 \cdot 10^{-3}$ g. Partial pressures: cyclohexene: 1.7 kPa; H₂: 10.1 kPa; argon: 89.5 kPa.

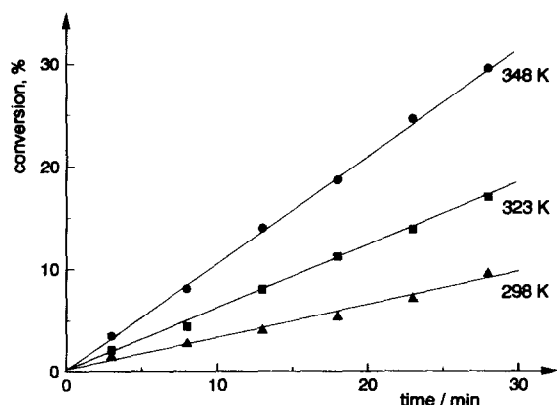


Fig. 7. Cyclohexene conversion plotted against reaction time at different temperatures for 1% Pt-graphimet catalyst pretreated at 573 K (MTR sample). Mass of catalyst: $5 \cdot 10^{-3}$ g. Partial pressures: cyclohexene: 1.7 kPa; H₂: 10.1 kPa; argon: 89.5 kPa.

have been reported to be independent of the Pt crystallite size [23,24].

Both sorption microcalorimetry and O₂-H₂ titration clearly indicate an increased amount of platinum metal available for H₂ and O₂ adsorption. As has already been pointed out, both O₂ and H₂

are able to penetrate between the graphite layers to some extent [19]. The enhancement in the number of active sites for O₂ and H₂ chemisorption may be due to the migration of interlayer metal atoms that were previously completely inaccessible. That is, besides surface aggregates, migration might lead to the formation of further inserted platinum atoms between the graphite layers, these being available for O₂ and H₂ adsorption.

The catalytic activity of Pt-graphimet was investigated in the reaction of cyclohexene hydrogenation. Under the present experimental conditions, cyclohexane formation took place with 100% selectivity.

Figs. 6 and 7 display plots of conversion vs. reaction time at various temperatures. After reduction at 573 K, somewhat higher reaction temperatures were required to obtain fair conversions. Table 2 presents the reaction rates and turnover frequencies (TOF) for both samples. Dispersions obtained from the O₂-H₂ titration mentioned above were used in the calculations.

The TOF values indicate that MTR resulted in a considerable loss of activity, the TOF being about one order of magnitude smaller than before. The decrease in catalytic activity suggests the encapsulation of active platinum atoms inside the graphite 'host'. After MTR, a considerable number of surface atoms may become covered with graphite. This makes no difference for either O₂ or H₂ adsorption, as such particles may also appear between the graphite layers, still accessible for simple gases like O₂ and H₂. As the size of the cyclohexene molecule practically rules out the possibility of its penetrating between the graphite

Table 2
Reaction rates and turnover frequencies for Pt-graphimet before and after MTR

Original sample $D=0.64$, $E_a=32.11$ kJ mol ⁻¹			MTR sample $D=0.90$, $E_a=26.52$ kJ mol ⁻¹		
T/K	$r \times 10^{-16}$ [molecule/s]	TOF	T/K	$r \times 10^{-15}$ [molecule/s]	TOF
273	1.148	0.116	298	3.093	0.022
288	2.929	0.297	323	8.972	0.065
298	4.243	0.431	348	14.590	0.105

layers [19], Pt–graphimete may be regarded as a supported metal catalyst for cyclohexene hydrogenation.

The hydrogenation of cyclohexene on supported platinum catalysts is well known to be a structure-insensitive reaction [25]. This confirms the decrease in the number of accessible surface atoms as a possible reason for the significantly lower TOF values after MTR.

The Arrhenius activation energies were calculated to be 32.1 kJ mol^{-1} and 26.5 kJ mol^{-1} for the samples reduced at room temperature and at 573 K, respectively. These values are in good agreement with the activation energy of 33.5 kJ mol^{-1} published for Pt/SiO₂ [26].

4. Conclusions

Unlike traditional supported catalysts, Pt–graphimete displayed a remarkable change of structure even upon MTR, i.e. under relatively mild conditions. The formation of large surface aggregates at 573 K, observed by TEM, is attributed to the migration of inserted platinum atoms to the surface of the catalyst. Nevertheless, aggregation did not influence the average particle size to an appreciable extent. Thus, no significant sintering effect on the fine platinum particles of the original sample can be established in response to MTR.

However, the increased platinum dispersion observed after MTR, and also the integral enthalpy isotherms of adsorption, indicate an enhanced number of active sites available for both H₂ and O₂ adsorption. Such active sites may be formed through the further migration of inserted metal atoms between the layers of the graphite ‘host’.

On the other hand, encapsulation of active surface atoms into graphite explains the loss in the number of adsorbed cyclohexene molecules after MTR.

Briefly, the effects of MTR on the structure and activity of Pt–graphimete were as follows:

1. the migration of interlayer platinum atoms to the surface, leading to metal aggregation;
2. the migration of further metal atoms between other graphite layers situated next to the surface, providing increased O₂ and H₂ adsorption;
3. the encapsulation of small surface particles, decreasing the amount of adsorbed cyclohexene molecules.

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