Catalysis Letters 35 (1995) 119–123

The surface characterization of Pt-graphimet

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Received 12 January 1995; accepted 30 June 1995

The distribution of active sites in Pt-graphimet was investigated before and after medium-temperature reduction (MTR). 1-butene titration was employed for characterization. The effects of interlayer platinum migration and surface recrystallization were established. MTR indicated that the site densities of Pt-graphimet are similar to those of supported platinum catalysts.

Keywords: catalysis; Pt-graphimet; 1-butene titration; single turnover method

1. Introduction

Transition metal–graphite intercalation compounds (graphimets) have been investigated intensively in the past few years [1–7]. Graphite intercalation compounds are formed by the insertion of a guest species, the intercalate, between layers of the graphite host [8]. Accordingly, an important proportion of the metal component of graphimets is situated between the graphite layers. For Pt-graphimet, more than half the platinum is found in the interlayer space [9]. However, the catalytic activity of graphimets has been mostly attributed to the presence of surface metal aggregates [10–12]. Thermal treatment of graphimets results in the migration of interlayer metal on the surface, even under relatively mild conditions [13,14]. As a consequence, the catalytic behaviour is influenced considerably. The medium-temperature reduction (MTR, 573 K, 1 h) of Pt-graphimet gives rise to an appreciable decrease of catalytic activity [14]. In order to obtain more information on the reactivity of the active sites, 1-butene titration was employed for further investigations. The single turnover (STO) procedure developed initially for supported metal catalysts [15,16] enabled us to distinguish between hydrogenation and isomerization active sites. We have studied the effects of MTR on the structure and reactivity of Pt-graphimet in comparison with supported platinum catalysts.

2. Experimental

2.1. CATALYSTS

Pt-graphimet (1% platinum in graphite) was a product of Alfa Chemical Company. The sample was prepared by heating a mixture of graphite powder and platinum(IV) chloride at 773 K in a chlorine stream for several days. Reduction was carried out with lithium biphenyl at 223 K in a He atmosphere. The product was washed with tetrahydrofuran, acetone and water and then dried in vacuum at 413 K [17]. MTR of Pt-graphimet was performed in flowing H_2 at 573 K for 1 h. The flow rate was 30 cm^3/min. Dispersions were determined by H_2 titration at 298 K. For the original and the pretreated sample, the dispersions obtained were 64 and 90%, respectively [9,14].

1% Pt/graphite catalyst was prepared according to the Bartholomew–Boudart method [18]. Graphite powder of 20–60 mesh particle size (a product of Alfa Chemical Company) was burnt off until 50% of its weight had been lost. The sample was impregnated with H_2PtCl_6 during stirring for 31 h in a N_2 stream. Reduction was carried out in flowing H_2 for 2 h at 583 K, and then for 20 h at 773 K. The dispersion of this sample was found to be 6.8%.

3% Pt/Cab-O-Sil was prepared by impregnation of a BDH Cab-O-Sil support with an aqueous solution of H_2PtCl_6. The mixture was stirred for 1 h and water was then removed with a rotary evaporator. The solid was dried at 403 K for 16 h. Reduction was first started at room temperature in a H_2 stream. The temperature was then elevated to 483 K and maintained there for 3 h. Finally, the sample was heated to 673 K and exposed to H_2 for another 4 h. Cooling was performed in a N_2 stream. Dispersion from H_2 titration was 10%.

2.2. CHARACTERIZATION

The experimental apparatus included a flow reactor system connected to a Hewlett-Packard 5890 series II gas chromatograph. The 1-butene was a Linde product and its purity was 99.3%. The carrier gas used was 99.996% pure He. H_2 was obtained from a Matheson 8326 generator operating with a palladium membrane. 1-butene was introduced into the reactor via a 25 μl loop. The product isomers were separated on a Chrompack fused silica gel column with a stationary phase of Al_2O_3/KCl. The mass of catalyst was 20 mg.

Isothermal reductions were performed at 298 K by flushing the sample with O_2-free He for 30 min, H_2 for 1 h and He again for 30 min. Reductions at 323 K were carried out by purging the sample at room temperature for 30 min in He and then heating it to the reduction temperature. After attainment of this temperature, the gas stream was switched to H_2 and the sample was exposed for 1 h. Subsequently, the gas stream was switched back to He and the reactor was purged for another 30 min at 323 K and then cooled to room temperature. Excess reactive hydrogen was removed by adding successive pulses of 1-butene to the sample until the amount of butane formed corresponded to less than 1% of the 1-butene introduced. The catalyst was then used in the STO reaction sequence [15]. The sample was first treated with a pulse of H_2 so that every platinum atom available could become saturated. Afterwards, a 15 min sweep-off by He was effected in order to remove excess H_2. A pulse of 1-butene was next introduced and the products were analyzed. The products obtained at this point were butane formed on the hydrogenation sites, cis- and trans-2-butene formed on the isomerization centres and unreacted 1-butene. Some hydrocarbon tends to remain on the catalyst surface and may be removed by a second pulse of H_2. The formation of this second butane is attributed to the two-step saturation sites. According to the terminology suggested by Siegel [19], the direct hydrogenation centres are ^{3}M sites (corner or kink atoms). The two-step hydrogenation sites are ^{3}MH sites and the isomerization sites are ^{2}M sites (edge or step atoms). Other sites which adsorb H_2 but do not take part in any reaction of 1-butene are ^{1}M sites (face or terrace atoms) [15]. As the reaction is stoichiometric, supposing that H_2 migration does not occur on the surface of the catalyst [20], we may presume that each surface site reacts only once in the STO reaction sequence.

3. Results and discussion

Experimental data given as mol product per mol platinum are listed in table 1.

The above data reveal no significant difference between the ^{3}M and ^{3}MH site densities of Cab-O-Sil- and graphite-supported samples. However, for pristine Pt-graphimet, there was a complete lack of ^{2}M and ^{3}MH centres and the concentration of ^{3}M sites was somewhat lower than those of supported platinum catalysts. Elevation of the reduction temperature by 50 K made no difference as concerns the distribution of the active sites in Pt-graphimet, nor did it affect the supported samples.

Augustine et al. recently made a further difference between the ^{3}M and ^{3}MH hydrogenation sites. They proposed that ^{3}M sites might be surface adatoms on top of the crystal faces and ^{3}MH sites might be corner atoms included in an extended

Table 1
STO reaction site densities determined at 298 K for Pt-graphimet and supported platinum catalysts

Sample	^{3}M × 10^{3} (mol butane/ mol Pt)	^{2}M × 10^{5} (mol butene/ mol Pt)	^{3}MH × 10^{3} (mol butane/ mol Pt)	^{3}M/(^{3}M + ^{3}MH)
Pt-graphimet	1.190	–	–	1.0
Pt-graphimet, MTR	12.59	0.997	2.142	0.855
Pt/graphite	2.56	–	1.76	0.592
Pt/Cab-O-Sil	2.78	6.69	2.11	0.569

facial arrangement [21]. We found this theory worth considering in terms of our experimental results.

For supported platinum catalysts, the number of surface adatoms referred to the total number of hydrogenation sites was found to be ~ 0.6. The corresponding ratio for Pt-graphimet was 1.0, suggesting that the latter may be envisaged as an adatom-type catalyst. The reason may be related to the migration of interlayer metal on the surface. Apparently, surface crystal growth takes place by an atomic mechanism.

Although migration may occur when Pt-graphimet is subjected to a H_2 atmosphere at room temperature, the effect of thermal treatment was found to be much more pronounced. By increasing the amount of surface metal, MTR produced an enhanced number of hydrogenation centres. As seen from table 1, both ^3M and ^3MH sites are concerned. As a result, an important change in site distribution can be pointed out.

Transmission electron microscopy measurements earlier revealed the appearance of large surface aggregates following MTR, ranging in size from 2 to 270 nm. Nevertheless, the average particle size merely increased from 4.67 to 5.39 nm [14]. For supported catalysts, no sintering effects were reported below 573 K [22]. On further elevation of the temperature, the particle shape was affected (rounding), rather than the crystallite size [23]. For Pt-graphimet, however, the appearance of surface aggregates after MTR is attributed to crystal growth proceeding via atomic migration [24].

The experimental evidence shows that the thermal treatment of Pt-graphimet resulted in the appearance of corner atoms, isomerization sites and an enhanced number of adatoms. Table 2 contains the active site densities calculated on the basis of platinum dispersions determined by H_2 titration [14]. Besides surface Pt crystallites, the actual dispersions include interlayer active sites inaccessible for 1-butene molecules. Therefore, calculations should be made using dispersions (D_e) which correspond to the number of exposed Pt atoms situated on the catalyst surface [9]. The values of D_e displayed in table 2 were obtained after a short oxidation time of 10 min.

Table 2 suggests that the distribution of the active sites in Pt-graphimet was finally similar to that of the graphite-supported platinum catalyst. The change is attributed to recrystallization of the surface metal particles. It is concluded that

Table 2
STO active site densities based on exposed platinum dispersions

Sample	D_e	$^3M \times 10^2$ (mol butane/mol Pt)	$^2M \times 10^5$ (mol butene/mol Pt)	$^3MH \times 10^2$ (mol butane/mol Pt)
Pt-graphimet	0.105	1.133	–	–
Pt-graphimet, MTR	0.132	9.53	7.55	1.622
Pt/graphite	0.068	0.256	–	0.176

MTR led to the formation of a "regular" surface crystalline structure characteristic of supported samples. Thus the experimental results can be regarded as a confirmation of Augustine's theory of corners and adatoms.

The catalytic activity of Pt-graphimet was studied earlier in the reaction of cyclohexene hydrogenation. It was pointed out that, following MTR, the reaction rate per unit mass of catalyst decreased by nearly one order of magnitude [14]. Thus, the specific activity of the purely adatom-type structure of the original sample was much higher than that of the "regular" crystalline structure observed after MTR. As the number of ^{3}M sites determined from 1-butene titration increased substantially after MTR, and the temperature of 573 K is still fairly low, poisoning of the metal surface by carbon deposition is unlikely to affect the hydrogenation rate.

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