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The Effect of Hydrogen, some Hydrocarbons, Carbon monoxide and Sulphur Treatments on the Structure of Platinum Supported Catalysts

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تأثير المعالجة بالهيدروجين وبعض الهيدروكربونات وأول أكسيد الكربون والكبريت على حفازات البلاتين المدعم

عز الدين أحمد عرفة

تم استخدام تقنيات الإختزال الحراري المبرمج والتقفي بالأثر الأشعاعي والمجهر الألكتروني في دراسة تأثير معالجة عدد من حفازات البلاتين المدعم على السيليكا (Pt/SiO_2) والألومينا (Pt/Al_2O_3) بالمواد: الهيدروجين (H_2) والايثين (C_2H_2) وأول أكسيد الكربون (CO) والكبريت (S).

نتائج الاختزال الحراري المبرمج بينت أن معالجة هذه الحفازات بالهيدروجين عند درجات حرارة تصل إلى ±4K 773 ليس لها أي تأثير على الشكل الخارجي لهذه الحفازات وكذلك على انتقائيتها في هدرجنة الإيثين والبيوتاديين.

إمتزاز المواد المستخدمة في المعالجة يتم على مرحلتين متتاليتين، أولية على ذرات البلاتين وثانوية على مواقع تم تشكيلها على اسطح الحفازات كنتيجة للامتزاز الأولي وهذه المسؤولة على تفاعلات هدرجنة الإيثين والبيوتاديين.

سبب امتزاز الكبريت وهدرجنة الإيثين تغييراً طفيفاً للشكل الخارجي للحفازات المدعمة على السيليكا بينما لم يؤثر في إنتقائية نواتج الهدرجنة.

المواقع الحامضية المتواجدة على سطح الألومينا استقطبت تكون خيوط كربونية على الحفازات المدعمة على الألومينا.

بصفة عامة، جميع الحفازات التي تم دراستها بينت نفس الخواص من حيث امتزاز المواد المستخدمة في المعالجة وثباتها وانتقائيتها في تفاعلات هدرجنة الايثين والبيوتاديين لتؤكد بأن هذه التفاعلات غير حساسة لشكل الحفازات.

Abstract: *The effect of various treatments such as, hydrogen, hydrocarbon, carbon monoxide and sulphur adsorption on the structure of supported platinum catalysts and upon the selectivities of ethyne and buta-1,3-diene hydrogenations were studied, using temperature programmed reduction (TPR), radiotracer and electron microscopy techniques. The TPR results show that hydrogen treatment at temperatures up to 773 K ±4K have no effect upon the selectivity and morphology of the studied Pt-catalysts. The adsorption of these materials on the studied catalysts surfaces occur in two stages, as primary and secondary processes. Catalytic hydrogenation is associated with the sites of the secondary process. Ethyne*

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hydrogenation and sulphur adsorption resulted in some morphological changes to the Pt-particles of the silica-supported catalyst (Europt-1), though such changes have no influence on the selectivity. The acidic sites of the alumina-support induced carbon filament formation on Europt-3 catalyst. Generally, the examined catalysts displayed similar behaviour and low selectivities towards ethyne and buta-1,3-diene hydrogenations demonstrating that such reactions are insensitive to catalysts morphology.

INTRODUCTION

Supported catalysts are frequently found to exhibit activities and selectivities which depend on catalyst preparation and pretreatment conditions. This behavior could have many causes including variation of particle size[1], metal interaction with the support[2] and the existence of poisoning molecules such as carbon and sulphur[3].

This work is undertaken with the aim to look at the effects of hydrogen activation, adsorbed hydrocarbons, hydrogenation reactions and sulphur poisoning on the reactivity and morphology of platinum catalysts supported on various materials using different preparation methods.

EXPERIMENTAL

Apparatus

The apparatus which was used for the deactivation of the catalysts with adsorbed hydrocarbons, reaction mixtures or sulphur adsorption, consisted of a conventional vacuum system, maintained at a pressure of ~ 0.01 pa by means of a mercury diffusion pump backed by an oil rotary pump. The system incorporated a number of glass bulbs for the storage of the required gases and a reaction vessel similar to that described previously[8,12,13].

Materials and Catalysts

All chemicals used were of analytical purity grade and were used without any further treatment.

Three catalysts of platinum supported on silica (Cab-O-Sil), μ-alumina (Dequsa Ltd.) and molybdenum trioxide (Koch-Light Ltd.) of 99.9% purity, were prepared by the impregnation method by adding the aqueous solution of the metal chloride (H_2PtCl_{16}) containing the required weight of the metal, to an aqueous suspension of the support. The excess water was evaporated using a rotary evaporator and the materials were then dried in an air oven at 423 K. These catalysts were characterized as (w/w), 0.8% Pt/SiO_2, 0.8% Pt/Al_2O_3 and 0.5% Pt/MoO_3. Another two supported catalysts designed by the Council of Europe Catalysis group as standard reference catalysts namely, Europt-1 (6% (w/w) Pt/SiO_2) prepared by Johnson Matthey Chemicals, plc., by an ion exchange method of $Pt(NH_3)_4Cl_2$ solution on Sorbosil grade AQ U30 silica gel. The mixture was filtered and the silica material was washed with demineralised water and dried in circulating-air oven at 378 K[4]. Europt-3 (0.3% (w/w) Pt/Al_2O_3-0.82% Cl) which is prepared by alumina (Al_2O_3 CK 300, from Cyanamid Ketjen, Amsterdam) impregnation with an aqueous solution of H_2PtCl_6-HCl. This catalyst is currently being employed as a commercial industrial catalyst under the code KETJEN-CK303[5].

Experimental Procedures

For catalysts reduction typically 0.1g catalyst was placed in the boat of the reaction vessel which was controlled via a 4 mm three-way stopcock to the vacuum system. The vessel was evacuated for ~ 30 minutes, isolated from the vacuum system via the 4 mm tap and the catalyst boat was moved by the aid of a magnet to furnace part of the vessel. H_2 gas stream (flow rate = 30 ml min-1) was introduced on the catalyst and gradually heated to 523 K. After 2 hours the catalyst was evacuated for 30 minutes at 523 K and then cooled in vacuo to room temperature (293±2K).

Deactivation of the catalysts by reaction mixtures was performed by carrying a number of reactions in a static system at room temerature using 6.67 Kpa either of the reaction mixture (3:1, H_2:ethyne) or (3:1, H_2:1,3-butadiene). Deactivation by hydrocarbons or sulphur was carried out by pulsing the catalysts with ~ 2 Kpa of the respected hydrocarbon or hydrogen sulphide. These treatments were followed by evacuation of the reaction vessel for 30 minutes to remove gas phase materials.

In the temperature programmed reduction (TPR) experiments, using a set-up similar to that developed by McNicol *et al.*[7], the catalyst was contained in a Pyrex glass cell and then flushed with a stream of helium gas at a flow rate of 30 ml min^{-1} to remove the physically adsorbed impurities. The gas stream over the sample was then changed to 6% H_2N_2 (flow rate, 30 ml min^{-1}) and the sample temperature ramped at a linear rate of 10 K min^{-1} up to 773 K, with the hydrogen concentration in the effluent gas stream being recorded as a function of sample temperature.

Samples of catalysts pre-deactivated by hydrocarbon adsorption, hydrogenation reactions or sulphur adsorption, were examined by Transmission and Scanning Electron Microscopy (TEM) and (SEM) respectively, to investigate the effects of these processes on the catalyst's morphology. The TEM employed was a JEOL 1200 EX, operated at accelerating voltage of 120 kV and ground catalyst samples were added to H_2O and mounted onto standard 3 mm copper grids, covered with carbon films and then fired. When the catalysts were investigated by SEM (Philips EM420), they were embedded in methylmethacrylate-butyl methacrylate mixture, followed by an ultra thin sectioning using a diamond knife.

RESULTS AND DISCUSSION

Adsorption of Hydrocarbons, Carbon Monoxide and Hydrogen Sulphide

Using the ^{14}C-radiotracer technique the adsorption of ^{14}C-ethyne on these catalysts was studied on freshly reduced catalysts. As shown in figure 1, with the exception of the 0.5%Pt/MoO_3 catalyst, the adsorption of ethyne on Europt-catalysts, Pt/SiO_2 and Pt/Al_2O_3 catalysts occurred in two stages, a non-linear "primary" process followed by a linear "secondary" process. This is in agreement with the results reported on supported Rh, Pd, Ir and Ni catalysts[8], in which the primary adsorption process was suggested for ethyne adsorption on metal sites, whereas the secondary adsorption process was ascribed to ethyne adsorption on the adlayer formed as a

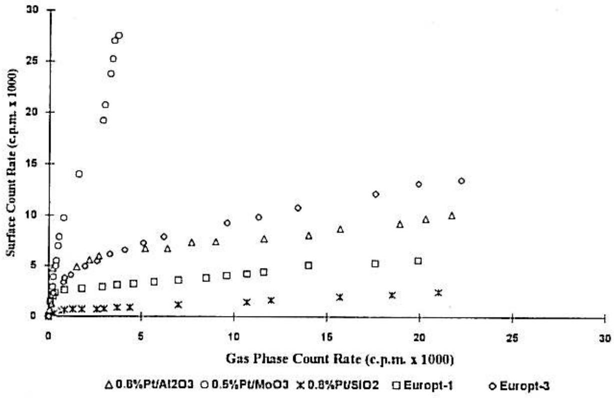

Fig. 1. Adsorption of ^{14}C-ethyne on Pt-catalysts at 293±2K.

result of surface restructuring. The extent of ethyne adsorption on 0.5%Pt/MoO_3 catalyst showed distinctly different behavior: a steep primary region followed by a non-linear secondary region with a sharp slope rising rapidly as the pressure of ^{14}C-ethyne was increased. Even though no specific studies using MoO_3 supported-Pt catalysts have been reported, it is worthwhile considering the possibilities involved in ethyne adsorption on this catalyst. Yashu *et al.*[9] studied the difference in surface properties between Pt/MoO_3/SiO_2 catalysts prepared by different

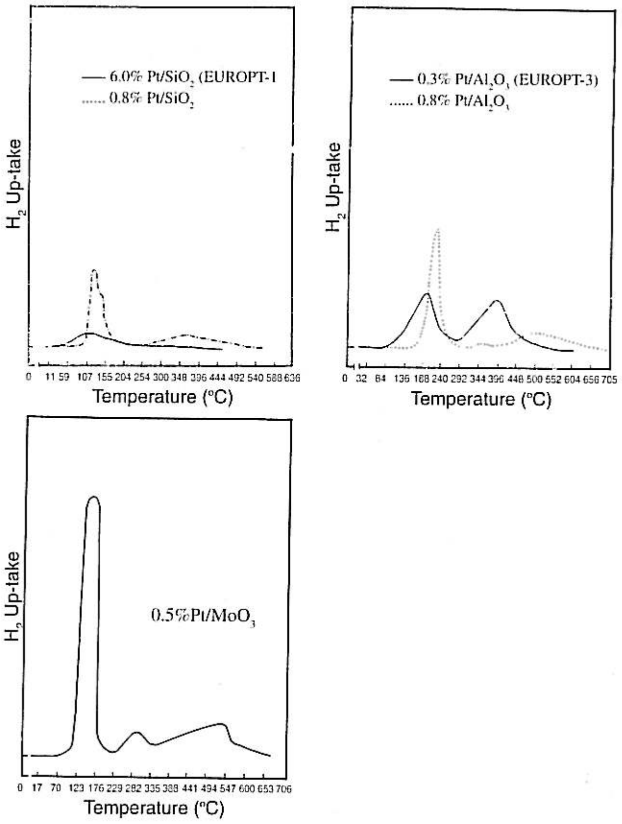

Fig. 2. TPR profiles of Pt-catalysts.

methods. Their results using TPR, electron spin resonance, ESR, and TEM techniques showed that the impregnated catalysts consisted of mixed oxygenated Pt-particles, various molybdenum oxides and a Pt-Mo alloy. The TPR measurements conducted in this work (Fig. 2) showed that, on this catalyst, a large peak appeared at ~ 417 K, accompanied by two broad peaks at 576 and 820 K. It is likely that the low temperature peak corresponds to the reduction of the precursor $H_2(PtCl_6)$ as reported by McNicol *et al.*[7] and the high temperature peak may be assigned to the reduction of the molybdenum oxide species [10]. Thus, it is plausible that the primary adsorption process corresponds to the adsorption of ethyne on the Pt-component and that, the secondary adsorption process is attributable to adsorption on the molybdenum oxide support. No plateau region was observed on these catalysts although gas pressures in excess of 0.67 Kpa were used.

Table 1 shows the effects of evacuation and molecular exchange on ^{14}C-ethyne adsorbed species. Approximately 21-46% of the adsorbed ethyne was removed by evacuation for 30 minutes, with further *ca.* 18% on Europt-1, 3.6% on Europt-3, 5.6% on Pt/MoO_3, 4.0% on Pt/SiO_2 and 3.9% on Pt/Al_2O_3 being displaced by ^{12}C-C_2H_2 with about 2.0-10.0% of the adsorbed hydrocarbon species being removed by treatment with hydrogen. It is interesting to note that a large fraction, ca. 54.5% on Europt-1, 39.7% on Europt-3, 63.6% on Pt/MoO_3, 54.4% on Pt/SiO_2 and 56.5% on Pt/Al_2O_3 of the adsorbed ethyne was retained by the catalysts as strongly bound species. These observations suggest that the adsorbed species in the secondary adsorption region are reactive, which is in accordance with the conclusions of Webb and co-workers[8,11] made on ethyne adsorption on various Group IIIV supported catalysts, that these species are associatively adsorbed on the surface and represent the catalyticaly active species in the hydrogenation reactions.

Adsorption of ^{14}CO on freshly reduced 0.8% Pt/SiO_2 and 0.8% Pt/Al_2O_3 showed isotherms similar to those reported on Europt-1 and Europt-3[12,13]. They showed a primary adsorption region followed by a secondary region which displayed a progressively increasing ^{14}CO uptake as the gas pressure was increased. No plateau region was observed up to a pressure of 0.67 Kpa. ^{14}CO adsorption on 0.5% Pt/MoO_3 showed a Langmuir-type isotherm, i.e. the surface count rate increased slowly as the pressure of ^{14}CO was increased until a saturation plateau was reached. Evacuation of these catalysts for 30 minutes resulted in the removal of ca. 47.4% (Pt/SiO_2), 26.4% (Pt/Al_2O_3) and 68% (Pt/MoO_3) of the adsorbed CO species compared with the removable 2.5% (Europt-1)[12] and 23.1% (Europt-3)[13]. Subsequent treatments of these catalysts with 0.67 Kpa 12CO for 15 hours displaced approximately 1% (Pt/MoO_3), 90% (Pt/SiO_2) and 84% (Pt/Al_2O_3) of the species which could not be removed by evacuation. Collectively, these results provide an evidence that on these catalysts, adsorbed CO exists in two states. One is weakly bound and can be removed by evacuation or molecular exchange with ^{12}CO. The other form of CO (~15-30%) is more strongly bound to the surface and could not be removed with such treatments from either catalyst.

Table 1. The effects of evacuation and molecular exchange on ^{14}C-ethyne adsorption species at 293±2K

Catalyst / treatment	Catalyst / treatment (counts min-1)	Total change (%)
Europt-1 = 0.080 g	5560*	-
(A)	4381	-21.2
(B)	3336	-40.0
(A')	3280	-41.0
(C)	3030	-45.5
Europt-3 = 0.268 g	9950*	-
(A)	5293	-46.8
(B)	4935	-50.4
(A')	4900	-50.7
(C)	3950	-60.3
Pt/MoO_3 = 3.710 g	28157*	-
(A)	19907	-29.3
(B)	18330	-34.9
(A')	18290	-35.0
(C)	17920	-36.4
Pt/SiO_2 = 2.050 g	2513*	-
(A)	1633	-35.0
(B)	1532	-39.0
(A')	1480	-41.1
(C)	1368	-45.6
Pt/Al_2O_3 = 3.710 g	10300*	-
(A)	6488	-37.0
(B)	6084	-40.9
(A')	6010	-41.6
(C)	5815	43.5

*Count rates on freshly reduced catalysts; (A) evacuation of adsorbed ^{14}C-ethyne (0.67 Kpa) on freshly reduced catalyst for 30 minutes; (B) treatment of (A) with 0.67 Kpa ^{12}C-ethyne for 15 hours; (A') evacuation for 30 minutes; (C) treatment of (A') with 13.3 Kpa H_2 for 15 hours.

Table 2, compares the number of adsorbed CO, C_2H_2 and C_2H_4 molecules and the effect of adsorbed hydrogen sulphide on the studied catalysts under identical conditions. Although the radiotracer technique does not permit an absolute comparision of the amounts of CO adsorbed on the different catalysts used, nevertheless, it is possible to draw some comparisions regarding the relative number of adsorbed CO molecules and the CO:Pt ratios. From the results of Table 2, the ratio of the number of CO molecules adsorbed on the freshly reduced catalysts to the total number of Pt atoms present, CO:Pt, was *ca.* 1.9 (Europt-1), 4.0 (Europt-3), 0.60 (0.8% Pt/SiO_2), 1.3 (0.8% Pt/$A1_2O_3$) and 0.3 (0.5% Pt/MoO_3). These values are higher than the reported ratios of 0.60 with Europt-1[4] and of 0.20 for Pt/$A1_2O_3$ and 0.07 for Pt/SiO_2 reported by Bain *et al.*[6]. From these values, it is clear there is an overall excess uptake of CO compared with that expected for a Pt:CO ratio of unity. Three possible reasons for this can be considered: (i) spillover or adsorption of carbon monoxide on the support; (ii) an enhanced adsorption of CO in the presence of hydrogen or other species, such as, oxygen, and (iii) a surface reconstruction as the CO adsorption reaches a semi-saturation.

The effect of spillover or adsorption of CO molecules on to the support is unlikely, as has been reported by Kinnaird *et al.*[14] and as claimed by Levy and Boudart[15], such a phenomenon requires suitable sites on the support.

In studies of co-adsorption of H_2 and CO on Pd and Pt[16,17] a considerable interaction between the two molecules has been observed to occur, resulting in a shift of the C-O stretching frequencies to higher regions. It has also been reported[18] that Pt-supported catalysts retain considerable quantities of hydrogen which can act as a promotor for carbon monoxide decomposition. However, with regard to Europt-1, it has been shown[4] that this catalyst exists in a hydrogen-deficient state under the experimental conditions used in this work and hence such a possibilty can be eliminated. Even though Europt-1 is of a Pt-O character, rather than as a metallic Pt, the possibility of interaction of CO with oxygen has been investigated[4] and found to have no effect on the Infrared (IR) spectra of adsorbed CO.

The other explanation of the high uptake of CO could be as a result of perturbation of the metal atoms leading to surface reconstruction, probably through migration of the metal atoms in the CO-adlayer. This, indeed, could be the case, since, as observed in this work, (Table 2) pre-adsorption of sulphur appears to reduce the amount of CO adsorption to give Pt:CO of ~ 1.0. This may be due to the fact that the presence of sulphur stabilises the metal surface to any restructuring similar to that suggested above under the influence of CO alone.

Table 2. The number of adsorbed CO,C_2H_2 and C_2H_4 molecules on clean and sulphur poisoned Pt-catalysts at 293±2K

Catalyst	H_2S	CO molecules x10^{20}g-1	C_2H_2 molecules x 10^{20}g-1	C_2H_4 molecules x 10^{20}g-1	Condition
Uropt-1	0.00	3.50	3.98	0.49	F
	0.00	0.70	0.40	0.07	S
	0.10	–	1.64	–	P
	0.13	–	0.66	–	P
	0.20	–	–	080	P
	0.28	4.45	–	–	P
	0.32	–	–	0.49	P
	0.40	3.20	–	–	P
	0.46	–	–	0.37	P
	0.54	2.10	–	0.71	P
	0.60	–	1.11	0.98	P
Europt-3	0.00	0.36	0.25	0.05	F
	0.00	0.06	0.04	0.01	S
	0.25	0.00	0.00	0.00	P
0.8%Pt/SiO_2	0.00	0.15	0.01	–	F
0.8%Pt/$A1_2O_3$	0.00	0.33	0.07	–	F
0.5%Pt/MoO_3	0.00	0.05	0.09	–	F

F=freshly reduced; S=steady state (C_2H_2/H_2-deactivated), P=sulphur poisoned; – =not derermined.

The results of Table 2, also shows that the relative amounts of adsorbed CO and those of C_2H_2 and C_2H_4 are in the approximate ratios, CO:C_2H_2, 1.0:1.0 (Europt-1), 1.5:1.0 (Europt-3), 15:1.0 (0.8% Pt/SiO_2), 4.7:1.0 (0.8% Pt/$A1_2O_3$) and 0.6:1.0 (0.5% Pt/MoO^3) with the CO:C_2H_4 ratio being 1.8:1.0 (Europt-1) and 7.1 (Europt-3). These ratios suggest that the primary adsorption region of these hydrocarbons (Fig. 1) occur directly on the metal surfaces and the turning point observed in the adsorption isotherms corresponds to monolayer coverage.

The effect of sulphur poisoning on the adsorption of hydrocarbons and carbon monoxide and on the selectivity of mono-olefin formation from ethyne and buta-1,3-diene hydrogenation has been investigated[19,22] and the results were interpreted in terms of a site blocking mechanism.

Hydrogenation Reactions

The reaction of ethyne with hydrogen has been used as a test reaction to compare the activities and selectivity of these catalysts. The selectivity of Europt-1 and Europt-3 to yield ethene as opposed to ethane has been found to be equal to 0.3 and 0.6 respectively[12,13]. The observed initial selectivity on 0.8%Pt/SiO_2 and 0.8%Pt/Al_2O_3 were found to be 0.85 and 0.40 respectively. No appreciable reaction between ethyne and hydrogen was observed to occur on the 0.5% Pt/MoO_3 catalyst, only traces of unmeasurable amounts of ethene and ethane were detected.

It was decided to perform a series of buta-1,3-diene hydrogenation reaction on Europt-1 and Europt-3 with the aim to compare their reactivity and selectivity behaviur with those observed in ethyne hydrogenation. The kinetic and product distribution results are reported elsewhere[19] and the initial selectivity for both catalysts was found to be 0.6. The kinetics and product distribution results of ethyne and buta-1,3-diene hydrogenations on 0.8% Pt/SiO_2 and 0.8% Pt/Al_2O_3 catalysts showed similar characteristics to those of Europt-1 and Europt-3[12,13,19] which indicated that the major route to paraffin formation is via a route involving the direct hydrogenation of di-unsaturated hydrocarbons rather than via mono-olefin as an intermediate. The results of TPR indicate that sintering of the Pt-particles is likely to be the cause of the inertness of the (0.5% Pt/MoO_3) catalyst for ethyne hydrogenation.

Temperature Programmed Reduction

Samples from the catalysts used in the present work were subjected to TPR investigation to look at the extent of their reduction. The TPR spectra of these catalysts are shown in figure 2. H_2-consumption by Europt-1 was observed to start at room temperature 293±2K with the TPR spectra showing a broad band with its maximal at 383 K. This is in accordance with the findings of Bond and Gelsthorpe[20] who reported a reduction temperature between 200 and 423 K for this catalyst. Similar H_2 uptake behavior was observed with Europt-3, it displayed two large peaks with their maximal at 465 and 668 K. The TPR profiles of the impregnated catalysts, (0.5% Pt/MoO_3), (0.8% Pt/SiO_2) and (0.8% Pt/Al_2O_3) showed intense single peaks in the low temperature region, with their maximal at 417, 458 and 487 K respectively, together with broad bands at the high temperature region 573-823 K. The 417 K peak of the (Pt/MoO_3) catalyst is an indication that this catalyst is likely to exist in the form of the bulk $H_2(PtC_{16})$[7]. The high temperature bands at $<$ 573 K are characteristic of the reduction of support materials[1,2,7]. The consumption of H_2 over Europt-1 at ambient temperature and the appearance of a reduction peak at 383 K is characteristic of PtO_2[20]. This is consistent with the results of extended X-ray absorption fine structure (EXAFS), which indicated that Europt-1 contains a disordered platinum oxide phase[4]. The other catalysts (Europt-3, 0.8% Pt/SiO_2 and Pt/Al_2O_3) showed main reduction peaks at ~ 473 K representative of an interaction between the Pt-particle and the supports.

Electron Microscopy Profiles

Samples of Europt-1 and Europt-3 have been chosen as model catalysts and were investigated by TEM and SEM to examine the platinum particle size and distribution and the effect of hydrocarbon and sulphur adsorptions and hydrogenation reactions on the catalysts morphology. The Pt-containing particles were imaged on the micrographs as small dark spherical or semi-spherical spots. Ten measurements of ten counts each were used to estimate the average Pt-particle size.

Figure 3 (a-d) shows the TEM micrographs of Europt-1. Plate a is a typical micrograph of the catalyst after it had been reduced in H_2 at 523 K for 2 h. From this it can be seen that the Pt-particles

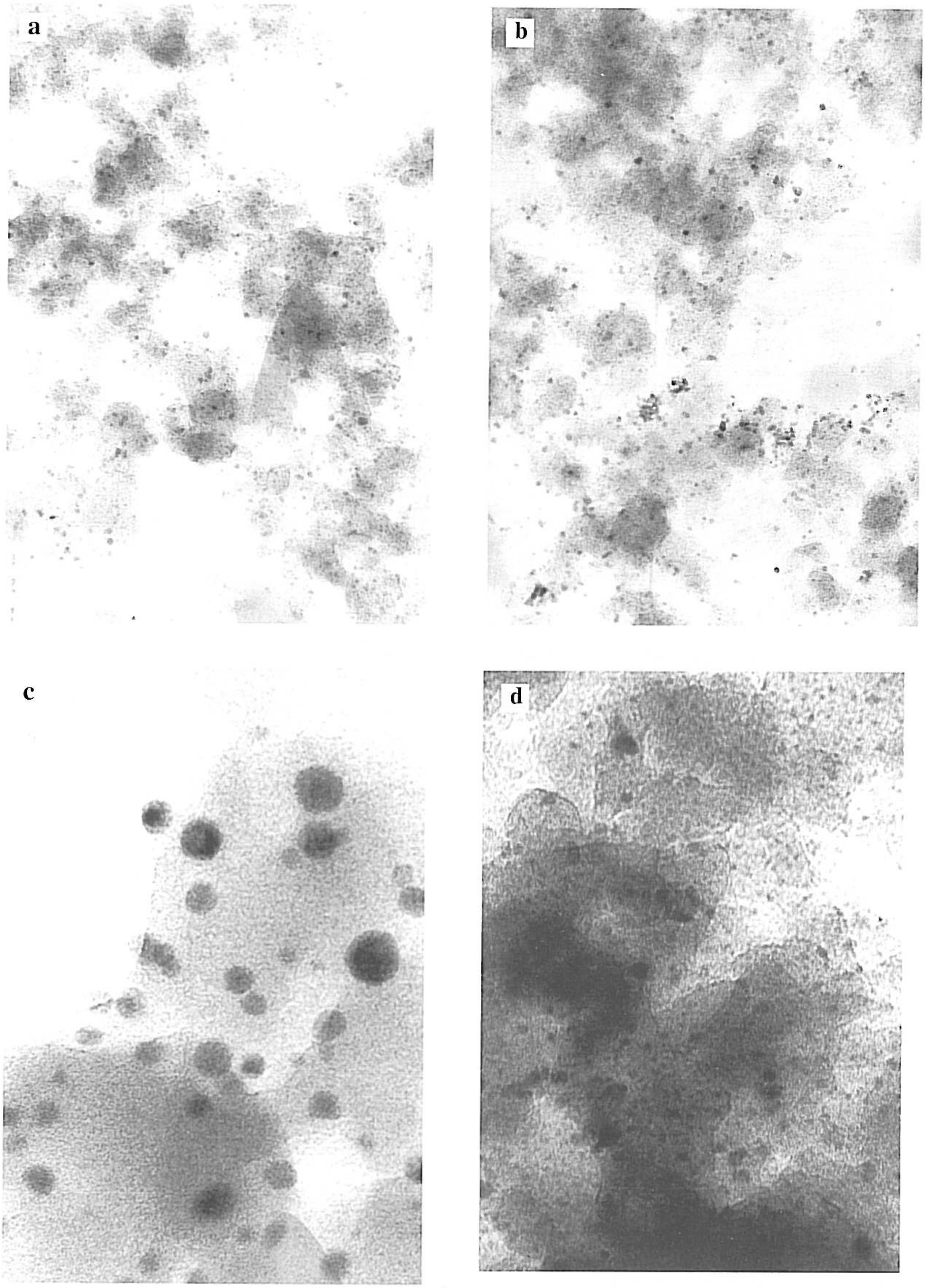

Fig. 3: (a) TEM micrograph of Europt-1 reduced at 523±3K/H_2/2h(x100K);
(b) TEM micrograph of Europt-1 deactivated with C_2H_2/H2 at 293±2K (x100K);
(c) TEM micrograph of Europt-1 deactivated with C_4H_6/H2 at 293±2K (x200K);
(d) TEM micrograph of europt-1 deactivated with H_2S at 293±2K (x200K).

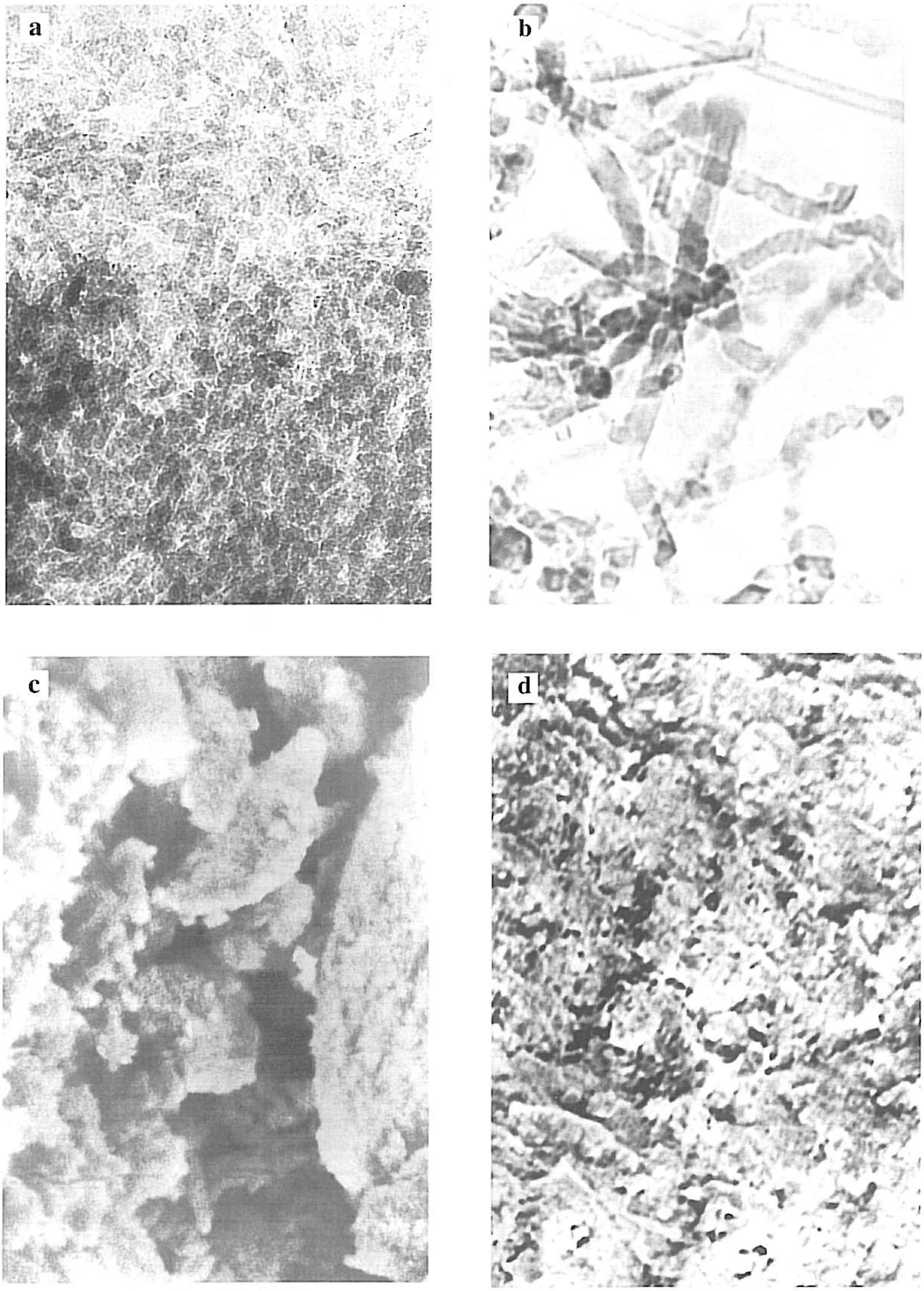

Fig. 4. (a) TEM micrograph of Europt-3 reduced at 523±3K/H_2/2h (x320K);
(b) TEM micrograph of Europt-3 deactivated with C_2H_2/H_2 at 293±2K (x120K);
(c) SEM micrograph of Europt-1 (x320K);
(d) SEM micrograph of Europt-3 (x640).

are homogeneously dispersed, though, in some micrographs, fractions of the Pt-particles are clustered together in the form of aggregates. The particles sizes were calculated as 2.00 ± 0.06 nm, which is consistent with the size range 0.9-3.5 nm, reported by the Council of Europe Catalysis Group[4]. Plate b is the TEM of the catalyst after being employed for ethyne hydrogenation. It showed a similar particle size distribution to that of freshly reduced catalyst (~2 nm), indicating that the catalyst is resistant to sintering under the experimental conditions used in this study. However, when Europt-1 was used for buta-1,3-diene hydrogenation a growth to the particle size ranging between 2 and 10 nm was induced. Furthermore, these particles displayed different shapes, vis, spheres, hemi-spheres, squares and hexagons (plate c). It is possible that buta-1,3-diene and/or the products, butanes, in the presence of hydrogen created a carbon induced faceting to the Pt-particles, similar to that reported to occur with $Pt/A1_2O_3$ catalysts in the presence of various hydrocarbons at elevated temperatures[3,21]. The samples of Europt-1, which were poisoned with H_2S, showed a slight growth in the average particle size from 2.0 to 2.5 nm (plate d). This demonstrates the remarkable stability of Europt-1, even under treatment with sulphur, which is known to severely disturb the morphology of the metal particles[3].

The SEM micrographs of the catalyst (Fig. 4, plate c) show the granular morphology of the silica support. No carbon filaments were observed in these or other micrographs of the catalyst in its working condition.

Europt-3 also showed an even distribution of Pt-particles after the catalyst had been reduced in H_2 at 523 K for 2 h as determined by the TEM. Its particle size was between 3 and 6 nm (Fig. 4, plate a). Interestingly, catalyst samples which had been deactivated by a series of ethyne hydrogenation, displayed carbon filaments in the micrograph (Fig. 4, plate b). Although the mechanism of carbon-filament formation is not well documented in the literature, it is possible that the chlorinated sites located on the alumina of Europt-3 acted as a promoter for carbon deposition on the support, which in turn diffused progressively to the Pt-particles, forming such carbon tubes.

The SEM micrograph of Europt-3 catalyst, which had been deactivated to the steady state activity by C_2H_2/H_2 mixtures, is shown in (Fig.4, plate d). From this it can be seen that the morphological texture of the alumina of Europt-3 is much softer and more amorphous than the silica of Europt-1.

CONCLUSIONS

The results obtained showed that the adsorption of hydrocarbons, carbon monoxide and sulphur takes place primarily on the exposed metal atoms and secondarily on the metal adlayer to the primary adsorbed species formed as a result of a surface restructuring. The adlayer contains the catalytical centers for hydrogenation reactions. Platinum catalysts supported on silica or alumina and prepared by different methods showed almost similar and low selectivity for ethyne and buta-1.3-diene hydrogenations.

The TPR profiles indicate that treatment of the studied catalysts with hydrogen and heat (up to 773K) has no effect on the catalyst morphology and the observed metal support interaction under such treatment has no role on the selectivity of these catalysts for di-unsaturated hydrocarbon hydrogenation.

Hydrocarbon and sulphur adsorption induced morphological changes to the particles of silica-supported Pt-catalyst (Europt-1). The acidic sites of the alumina support on Europt-3 have enhanced carbon filament formation. However, these structural changes have no effect on the selectivity of ethyne and buta-1,3-diene hydrogenation which are known as structure-insensitive reactions[23].

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