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# MONODISPERSED COLLOIDAL METAL PARTICLES FROM NONAQUEOUS SOLUTIONS: CATALYTIC BEHAVIOUR IN HYDROGENOLYSIS AND ISOMERIZATION OF HYDROCARBONS OF SUPPORTED PLATINUM PARTICLES

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Platinum catalysts have been prepared by depositing on alumina monodispersed particles of platinum prepared in reversed micellar solution. After deposition, the particles are well dispersed on the support and the size distribution has a sharp maximum around 2 nm. The isomerization and hydrogenolysis of hexanes were studied in order to get more information about the particle size effects on the selectivities of Pt catalysts in these reactions.

It was found that this catalyst exhibits the same selectivities as a low dispersed ordinary platinum catalyst. These selectivity values are quite different from the ones given by a highly dispersed classical catalyst in spite of the fact that the catalysts have fairly similar average particle size. Such results confirm the conclusions previously proposed that isomerisation via cyclic mechanism and non selective hydrogenolysis of hexanes take place only on platinum particles smaller than 1 nm.

**Keywords:** Catalysis, platinum, microemulsion, isomerisation, hydrogenolysis, hexanes

## 1. Introduction

The preparation method of metallic particles of platinum, rhodium, palladium and iridium in oil-continuous microemulsions has been previously described [1]. From the catalytic point of view, this preparation method is interesting since it gives particles of a very narrow size distribution. It was found to be ±0.5 nm in the 3.0 nm range.

After preparation, the particles originally suspended in microemulsion could be transferred onto the supports, without agglomeration. On the other hand, as it was shown, these particles are also catalytically active in suspension. The hydrogenation of but-1-ene on platinum particles suspended in microemulsion has been

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studied [2]. The activity, however, was about ten times lower as compared to the same particles deposited on a support and used for catalysis in gas phase.

The hydrogenation of but-1-ene on Pt, Pd and Rh particles from microemulsions, deposited on pumice, has showed that they are as active as the classical ones [3]. In addition, on platinum, we observed an unexpected high selectivity for isomerization as compared to hydrogenation.

The very narrow size distribution of these particles makes them an attractive catalyst for structure sensitive reactions such as hydrogenolysis and skeletal isomerization of hexanes. In this paper, preparation of platinum particles in microemulsion and deposition on alumina is briefly reported together with their characterization done by electron microscopy. The catalytic behaviour of such a catalyst, in isomerization of 2-methylpentane and hydrogenolysis of methylcyclopentane is discussed with regard to reaction mechanisms. Furthermore comparison was made with platinum catalysts prepared in classical way that is by impregnation Ipatieff's method [4].

## 2. Experimental

### PREPARATION AND CHARACTERIZATION OF THE CATALYSTS

The microemulsions used for preparation of the metallic particles have been based upon nonionic surfactant (pentaethyleneglycoldodecylether, $C_{12}E_5$). n-hexadecane and water. Within certain concentration limits, these three constituents formed thermodynamically stable solutions containing aggregates (reversed micelles). Knowing that the size of such micellar aggregates is directly proportional to the water concentration [5], a minimum amount of water was used in order to reduce the size of metallic particles to a minimum. Since the chloroplatinic acid itself contains enough water and besides is soluble in $C_{12}E_5$ it was directly solubilised in the surfactant-hydrocarbon mixture without dissolving it in water.

The microemulsions were prepared as follows: $H_2PtCl_6,6H_2O$ was dissolved in the surfactant ($3 \cdot 10^{-2}$ Pt gram/gram solution). Then the surfactant and Pt ions were added to solvent (n-hexadecane) under vigorous stirring. In order to obtain a stable suspension the pH was adjusted to 7 by adding small quantities of 0.1 N NaOH solution prior to reduction. The final composition of the microemulsion was 10% surfactant and 90% hexadecane. The reduction of the platinum ions was accomplished, at ambient temperature by adding hydrazine hydrate. About 100 $\mu$l per gram solution was enough to achieve complete reduction. The metal particles formed a stable suspension.

The transfer of the metal particles onto the support was performed as follows: the support, $Al_2O_3$ (Woelm, surface area: 154 $m^2/g$, mean porous radii: 3.4 nm), was added to the suspension. The destabilisation of the suspension was caused by adding under vigorous stirring excess of tetrahydrofuran in order to remove the surfactant from the surface of the particles.

The catalysts were separated from the microemulsion by centrifugation and washed several times with ethylalcohol and finally dried at 393 K for several hours.

The catalyst was heated for 12 hours at 493 K in the $H_2$ flow before the first catalytic run.

The particle size measurements were performed on a transmission electron microscope (Philips EM 300, yielding 0.5 nm resolution). From the electron micrographs, a histogram $D_1 = N_i/\Sigma N_i$ was obtained (fig. 1a and 1b). The histogram reveals an extremely narrow size distribution with a maximum around 2 nm. The electron diffraction pattern showed that the particles had a crystal structure the same as the metal (fig. 1c).

### APPARATUS AND PROCEDURE OF THE CATALYTIC EXPERIMENTS

The catalytic experiments were carried out in all glass apparatus (free of grease). The total pressure in the system was 1 atm. The catalytic bed was operated isothermally under differential conditions. The used reactants were labelled by $^{13}C$ isotopes.

The reaction products were collected at the boiling temperature of liquid nitrogen. The different species in the reaction mixture have been isolated by a semi-quantitative Gas Liquid Chromatography technique. The positions of $^{13}C$ atoms in the labelled molecules were identified by mass spectrometry. Details of the experimental procedure and assessment of mass spectra can be found elsewhere [6].

The used hydrocarbons, 2-methylpentane (2-MP) and methylcyclopentane (MPC), were delivered by Fluka (puriss grade). These compounds were used without further purification.

The preparation of the labelled species has been earlier reported [7].

## 3. Results and discussion

The experimental results for the isomerization reaction of 2-MP and for the hydrogenolysis of MCP (on a 2 wt% $Pt/Al_2O_3$ catalyst from microemulsion) are presented in tables 1 and 2. For comparison results from refs. [8] and [14] are also shown in the tables. The "classical" catalysts from the references differ only in the loading of the platinum metal, other parameters were the same in the course of the preparation. Different loadings resulted in various degree of dispersion of the metal phase that is particles of different size were produced.

Activities of these catalysts were expressed as a number of moles of the hydrocarbon converted on the Pt atom per second.

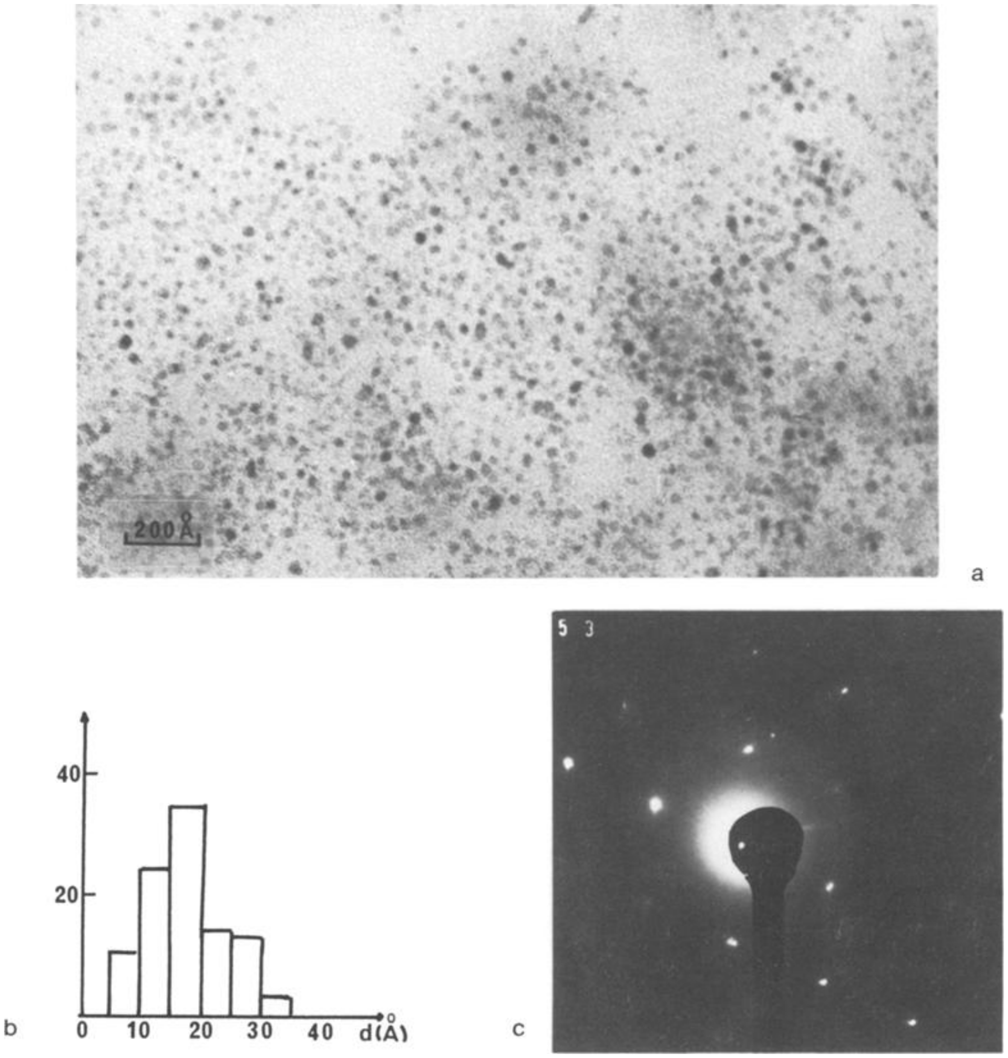
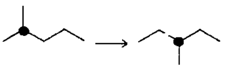
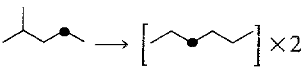


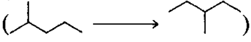
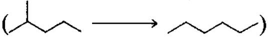
Fig. 1. a) TEM picture of 2% Pt/Al$_2$O$_3$ prepared from microemulsion; b) histogram, $D_1 = N_i/\Sigma N_i$; c) electron diffraction pattern of the platinum particles from the same catalyst.

Conveniently the contribution of the cyclic mechanism in the isomerization reaction of 2-MP to 3-MP or to n-Hexane and the selectivity factor of the hydrogenolysis of MCP are expressed as a ratio of 3-MP to n-Hexane. In this manner it is also expressed in the tables.

The reaction mechanism involved in the skeletal rearrangement of aliphatic hydrocarbons have been extensively investigated. Independently of each other, Anderson and Gault [8,9] suggested specific mechanisms to be operating in the reaction of isomerization of saturated hydrocarbons on metals. Thus according to Anderson a bond shift mechanism is involved in such reactions [8] while Gault

Table 1
Isomerisation of 2-methylpentane

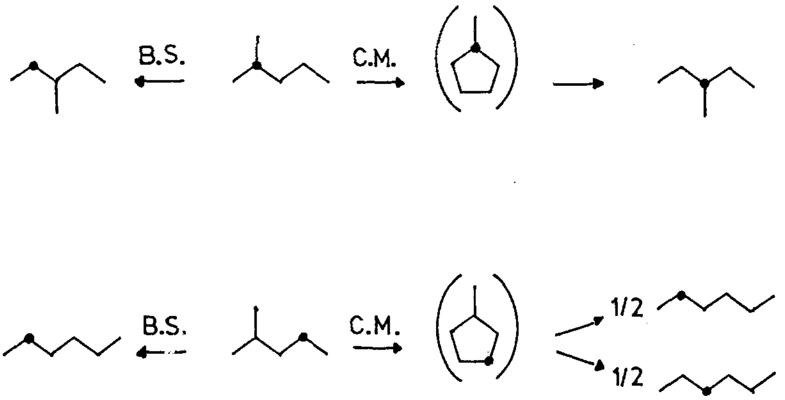
| catalyst | reaction temperature (K) | rate $10^4$ mol./Pt atom/s | % CM 2-MP-2-$^{13}$C → 3-MP-3-$^{13}$C  | % CM 2-MP-4-$^{13}$C → 2-n-H-3-$^{13}$C  |
|---|---|---|---|---|
| 2% Pt/$Al_2O_3$ microemulsion $D_s = 2.2$ nm | 573<br>527 [a] | 2 | 39.0<br>16.8 [a] | 88.8<br>82.2 [a] |
| 0.2% Pt/$Al_2O_3$ "classical" $D_s = 2.0$ nm (ref. [7]) | 527 | 13 | 83 | 100 |
| 8.5% Pt/$Al_2O_3$ "classical" large aggregates (ref. [7]) | 527 | 0.02 | 16 | 72 |
| 10% Pt/$Al_2O_3$ "classical" large aggregates (ref. [13]) | 573 | 3 | 42.5 | 86.2 |

[a] calculated value taking into account of the difference of activation energy between C.M. and B.S. mechanisms: 15 kcal (  ), 7 kcal (  ) [12].

asserted the existence of a cyclic mechanism especially in isomerization of hexanes [9]. Application of $^{13}$C labelled molecules appeared very useful in identifying these mechanisms.

Table 2
Hydrogenolysis of methylcyclopentane

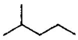
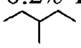
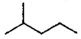
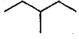
| catalyst | reaction temperature (K) | rate $10^4$ mol./Pt atom/s | 3-MP/n-H |
|---|---|---|---|
| 2% Pt/$Al_2O_3$ microemulsion $D_s = 2.2$ nm | 523 | 1.2 | 2.0 |
| 0.2% Pt/$Al_2O_3$ "classical" $D_s = 2.0$ nm (ref. [7]) | 493 | 3.6 | 0.4 |
| 10% Pt/$Al_2O_3$ "classical" large aggregates (ref. [13]) | 493 | 1.1 | 2.3 |

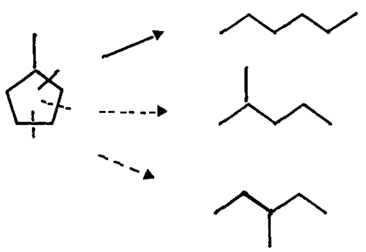


Scheme 1.

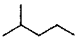
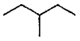
Scheme 1 illustrates application of the 2-MP-$2^{13}$C and 2-MP-$4^{13}$C molecules in identification of the reaction mechanisms.

The already mentioned selectivity factor of the hydrogenolysis of MCP on any catalyst is estimated according to scheme 2. Thus as it is seen if all bonds in the MCP molecule are ruptured indiscriminately that is in a non-selective manner, the ratio 3MP/n-H will be equal to 1/2. On the other hand if only bonds between secondary carbon atoms are ruptured this ratio will strive towards infinity indicating selective behaviour of the catalyst for this reaction. Nevertheless the selectivity factor may also assume intermediate values implying various rates at which the bonds in the MCP molecule are ruptured.

Pathways for isomerisation of 2-MP and selectivity in the hydrogenolysis of MCP are known to be strongly dependent on the platinum particle size [8]. Hence the cyclic mechanism in the isomerization reaction and non-selective hydrogenolysis are favoured by a highly dispersed platinum metal phase, that is on extremely small platinum metal particles. It is seen from the tables that on a 0.2% Pt/$Al_2O_3$ catalyst ($D_s$ = 2 nm) the cyclic mechanism is high (83%  to ) and the selectivity factor of the hydrogenolysis is low (0.4) while on 8.5 or 10% Pt/$Al_2O_3$ catalysts with large aggregates, the contribution of cyclic mechanism is lower (16 or 42.5% in  to ) and the hydrogenolysis selectivity factor is as high as 2.3.



Scheme 2.

Although the particles from microemulsion and the particles of a 0.2% Pt/$Al_2O_3$ catalyst have a fairly similar average particle size ($D_s = 2.0$ nm and $D_s = 2.2$ nm respectively) their catalytic behaviour is rather different. The experimental results on the catalyst from microemulsion showed a low contribution of the cyclic mechanism (39% in  to ) and the selectivity factor of hydrogenolysis is equal to 2. Moreover, it is known that the cyclic mechanism requires higher activation energy than the bond shift mechanism. Accordingly the contribution from the cyclic mechanism at 527 K should be lower than at 573 K. The values of the cyclic mechanism contributions corrected for the temperature differences are shown in the tables. As a matter of fact the results obtained on the catalyst prepared from microemulsion are identical with the ones obtained on the catalysts with large metal particles at different reaction temperatures.

It is supposed that reasons for different behaviour of the catalyst from microemulsion and the "classical" one in spite of the same average particle size, is that the particle size distribution of the catalysts differ. Actually as mentioned already the particles from microemulsion have a very narrow size distribution; consequently only a very little fraction of the particles will have size lower than 1 nm. On the other hand according to reference [10] more than 40% of the particles of a 0.2% Pt/$Al_2O_3$ catalyst have a size that is lower than 1 nm.

Garin et al. [11] on basis of numerous experimental studies of these reactions on various types of catalysts arrived at the conclusion that only metal aggregates in 0.5 to 1 nm size range are able to promote the cyclic mechanism. As it can be seen from the tables, our experimental findings support these conclusions.

As for the hydrogenolysis of MCP the selectivity factor for this reaction on the catalyst from microemulsion was equal to 2. The result indicates that both selective and non-selective hydrogenolysis take place on this catalyst. However as remarked above, the catalyst from microemulsion can contain a little fraction of particles smaller than 1 nm. The presence of these very small particles might give reason for the occurrence of both mechanisms on this catalyst. On the other hand, taking into account experimental findings of Maire and Garin [12], an intervention of a direct but only partially selective mechanism cannot be ruled out.

No systematic studies on the activities of the catalysts were made. However the activity of the catalyst prepared from microemulsion is lower than the activity of the corresponding "classical" catalyst. The possible reason is that some of the surfactant molecules are left on the catalyst in the course of the preparation and poison it. However in similar studies, it was observed that poisoning of a catalyst by hydrocarbon residue led to an increase in the contribution of the cyclic mechanism [13]. Nevertheless in our study any promotion of the cyclic mechanism was not observed Thus it is supposed that the poisoning by the surfactant is not selective but the lowered activity is a result of a random covering of the surface of the metal phase.

In conclusion it should be emphasized that when metal particles are prepared from microemulsion, monodispersed catalyst could be obtained. When they are well dispersed on the support they present a sharp maximum around 2 nm.

In hydrogenolysis and isomerization reactions of hexanes, this catalyst showed the same selective properties as a low dispersed platinum catalyst. It means that the principal mechanisms which are involved in these reactions are respectively, the bond shift and the partially selective hydrogenolysis mechanisms.

Finally it may be said that reactions, involving the cyclic mechanism in isomerization reaction and the non-selective mechanism in hydrogenolysis reaction, which are known to be promoted on highly dispersed platinum catalysts, occur on particles less than 1 nm in size. Our results confirm this statement. The catalyst prepared from microemulsion has a particle size close to the one required for cyclic mechanism but still behaves like classical catalyst with large particles.

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