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Influence of the Preparation Mode on Metal–Support Interactions in Pt/TiO$_2$ Catalysts

A. DAUSCHER,* R. TOUROUDE,*,[1] G. MAIRE,* J. KIZLING,†
AND M. BOUTONNET-KIZLING†

Laboratoire d'Etudes de la Réactivité Catalytique, des Surfaces et Interfaces (LERCSI) U.A. 1498 du C.N.R.S., ULP-EHICS, 4 Rue Blaise Pascal, 67070 Strasbourg, France; and †Institute for Surface Chemistry, P.O. Box 5607, S-114 86 Stockholm, Sweden

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Pt/TiO$_2$ catalysts in which the support was either a pure TiO$_2$ or a TiO$_2$ containing small amounts of K$_2$O, P$_2$O$_5$, and Nb$_2$O$_5$ were prepared either by the microemulsion method, in which the metal particles are formed before depositing on the support, or by the incipient wetness method, where the particles are formed directly on the support following adsorption of the metal precursor and reduction. The catalysts, independently of the preparation mode, were additionally reduced at low and high temperature, 200 and 390°C, respectively. Reduction at 390°C implies that strong metal–support interactions (SMSI) begin to be noticeable. Isomerisation and cracking reactions of 2-methylpentane and hydrogenolysis reactions of methylcyclopentane have been studied over these catalysts. ^{13}C-labelling experiments allowed the determination of the relative contributions of cyclic and of bond-shift mechanisms towards the isomerisation reactions. In the absence of support additives, whatever the reduction temperature, catalysts prepared from microemulsions were more active and selective in the isomerisation reactions than those prepared by the incipient wetness method. The doped catalysts, reduced at high temperature, presented additive-platinum interactions, as observed by XPS analyses. In addition, they were less active and behaved like catalysts in the SMSI state. The metal–support interactions were not observed for the microemulsion-prepared catalysts and the effect of additives was less important for them than for those prepared by the incipient wetness method.

INTRODUCTION

The preparation of colloidal metal particles in a microemulsion results in monodisperse particles in suspension and stabilized by the surfactant molecules (*1*). The concentration of the constituents, the temperature and the pH of the solution are of extreme importance with regard to the stability of the particle suspension. The metal ions dissolved in reversed micelles are reduced "*in situ*" in the microemulsion and are then deposited onto the support without any agglomeration. In other words, the metal particles are prepared in the absence of contact with the support. By contrast, the classical method of transition metal catalyst preparation is characterized by a direct particle formation on the surface of the support on reduction. Close contact between the metal and support may modify the properties of the catalyst. Particles of Pt, Pd, Rh, and Pt–Pd alloy prepared by the microemulsion method deposited on pumice or alumina have been tested for reactions of both hydrogenation of olefins and isomerisation of hexanes (*2–4*).

We thought it would be of interest to study whether the preparation mode has any influence on the catalytic properties of TiO$_2$-supported Pt catalysts, since it is well known that Pt supported on TiO$_2$ after reduction at high temperature is distinguished by strong metal–support interaction (SMSI) (*5*).

The mechanism involved in the interaction between support and metal is a matter

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[1] To whom correspondence should be addressed.

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which is still open to discussion. We have compared Pt/TiO_2 catalysts prepared by the microemulsion method, where the particles prepared separately have their size and structure characterized before deposition on the support, with catalysts whose particles were formed on the support after adsorption of the metal precursor. The effect of the contact of the particles with the support may be different in these two cases; presumably it is weaker for catalysts prepared from a microemulsion.

The isomerisation and hydrogenolysis reactions, which are very sensitive to the effects of SMSI (*6–8*), have been studied on Pt/TiO_2 catalysts prepared by the abovementioned methods. As the heat treatment is a very important factor and often necessary to bring about the SMSI effects, treatments at 200°C, denoted as a low reduction temperature (LRT), and at 390°C, denoted as a high reduction temperature (HRT), were carried out. Moreover, one of the catalysts was even reduced at 600°C in order to examine the effect of an extremely high temperature on its behaviour.

The probe molecules employed in our studies were 2-methylpentane (2MP), methylcyclopentane (MCP), and 2-(2-^{13}C) methylpentane. Two TiO_2 supports, one of them containing a certain amount of impurities, were used. The results are also compared with those obtained on Pt/Al_2O_3 catalysts.

EXPERIMENTAL

Two different titanium oxides were used as supports: TiO_2 P25 from Degussa (80% anatase, 20% rutile) and TiO_2 AT1 from Rhône-Poulenc (100% anatase) containing additionally 0.4% P_2O_5, 0.3% Nb_2O_5, and 0.33% K_2O.

The Pt/TiO_2 (2 wt% Pt) catalysts prepared by the microemulsion method are denoted BK, and those prepared by the incipient wetness method are denoted IW.

The microemulsions used for the preparation of the metal particles consisted of water, hexadecane, and pentaethyleneglycol dodecylether ($C_{12}E_5$). The metal compound ($H_2PtCl_6 \cdot 6H_2O$) was dissolved in the aqueous microemulsion droplets. The metal ions were reduced at room temperature by adding hydrazine hydrate. After reduction the particles formed a stable suspension. They were transferred onto the support by destabilization of the suspension induced by dropwise addition of tetrahydrofuran in the presence of the support. Separated from the microemulsion by centrifugation, the catalyst was washed several times with tetrahydrofuran and ethanol and finally dried at 120°C overnight. Details of the particle preparation and reagents are given in Ref. (*3*). BK1 and BK2 catalysts prepared by this method were supported on titanium oxides P25 and AT1, respectively.

Two other catalysts, 2 wt% Pt/P25 and 8 wt% Pt/AT1, were prepared by the IW method from hexachloroplatinic acid solutions. They were dried overnight at 120°C and stored in air before use.

Prior to the catalytic experiments all catalysts were additionally reduced *in situ*, that is, in the reactor in a hydrogen stream of 60 $cm^3 \, min^{-1}$ either at 200°C (LRT) or at 390°C (HRT) for 16 h.

The catalytic experiments were performed in a flow system equipped with a differential reactor working at atmospheric pressure. The experimental procedure has already been described in Ref. (*9*). The hydrocarbons used, 2-methylpentane (2MP) and methylcyclopentane (MCP), were Fluka puriss grade and were not further purified.

^{13}C-labelling experiments were performed with 2-(2-^{13}C) methylpentane as described in Ref. (*10*).

X-ray photoelectron spectroscopy (XPS) analyses were performed on a VG ESCA III apparatus equipped with an Al $K\alpha$ X-ray source. The base pressure during analysis was 1×10^{-9} Torr. The samples, pressed into pellets, were mounted on a sample holder; then they were subjected to reduction in a preparation chamber connected to the analysis chamber of the spectrometer. The binding energies were referred to the

TABLE 1

Reactions of 2-Methylpentane on Pt/TiO$_2$ Catalysts (BK, Microemulsion-Prepared Catalysts; IW, Incipient-Wetness-Prepared Catalysts)

Catalyst	Reduction temp. (°C)	Reaction temp. (°C)	$v \times 10^3$[a]	% S	3MP/nHx
BK1-2%Pt/P25	200	290	3.3	60	2.6
	200	390	140	72	1.2
	390	390	150	91	1.4
	200–600	290	0.4	57	0
	200–600 Air(500)–200	290	6.8	82	0.6
BK2-2%Pt/AT1	200	290	2.5	90	4.2
	200	390	170	89	1.4
	390	390	8.5	89	1.1
IW-2%Pt/P25	200	300	0.3	97	31
	200	390	6.6	83	4.9
	390	390	7.8	84	2.7
IW-8%Pt/AT1	200	290	8.3	79	1.8
	200	390	120	71	1.1
	390	390	0.2	85	1.9
BK-2%Pt/Al$_2$O$_3$[b]	200	300	1.6	73	1.4

[a] Activity expressed in μl of 2MP having reacted per g of catalyst per s.

[b] Ref. (*3*).

Ti $2p_{3/2}$ peak at 458.9 eV. Relative surface compositions were calculated from photoelectron peak areas after correction for the photo-ionization cross-section and difference in the electron escape depth.

Extended X-ray absorption fine structure (EXAFS) experiments were carried out using the DCI synchrotron facility of LURE (Laboratoire d'Utilisation du Rayonnement Electromagnétique) at Orsay (France), working at 1.72 GeV and 200 mA. Spectra were recorded on the L_{III} edge of Pt at 25°C. The data processing was done at Strasbourg using the GSK Scientific, Inc., EXAFS software.

RESULTS

The catalytic experiments were carried out at 290 and 390°C (240°C in the case of MCP) for samples reduced at 200°C and only at 390°C for the ones reduced at 390°C. Data concerning the reaction of 2MP are compiled in Table 1 and data referring to the reaction of MCP are given in Table 2. The catalytic activity, v, is expressed as μl of reacted hydrocarbon per gram of catalyst per second. We consider that these values are more significant for the comparison of the activities of Pt/TiO$_2$ catalysts than turnover numbers, especially for catalysts reduced at high temperature for which the chemisorption values become very low. In MCP reactions, cracking reactions are very limited; hydrogenolysis leads to the formation of 2-methylpentane (2MP), 3-methylpentane (3MP), and *n*-hexane (nHx) with different ratios 2MP/3MP and 3MP/nHx. In 2MP reactions, cracking products (C_n hydrocarbons, $n = 1$ to 5) are formed together with isomer products (3MP, nHx) and MCP. The selectivity S in isomerisation is expressed as percentage of isomer molecules (including MCP) with respect to overall conversion.

Catalytic Activities

Regarding the reaction of 2MP:

—the catalytic activity of BK1 does not vary with the reduction temperature (200 or 390°C), while for BK2 a severe decrease (a

TABLE 2

Reactions of Methylcyclopentane on Pt/TiO_2 Catalysts (BK, Microemulsion-Prepared Catalysts; IW, Incipient-Wetness-Prepared Catalysts)

Catalyst	Reduction temp. (°C)	Reaction temp. (°C)	$v \times 10^3$[a]	2MP/3MP	3MP/nHx
Bk1-2%Pt/P25	200	240	1.1	3.2	2.6
	200	290	21	2.8	2.1
	390	390	120	2.7	1.3
	200–600	240	0.6	∞	0
	200–600 Air(500)–200	240	3.1	3.0	0.6
BK2-2%Pt/AT1	200	240	3.9	3.9	11.5
	390	390	5.2	2.1	0.7
IW-2%Pt/P25	200	240	0.4	2.8	7.4
	390	390	25	2.3	0.9
IW-8%Pt/AT1	200	240	2.9	3.6	5.7
	390	390	1.0	3.1	1.8
BK-2%Pt/Al_2O_3[b]	—	250	1.0	3.5	2.0

[a] Activity expressed in µl of 2MP having reacted per g of catalyst per s.

[b] Ref. (*3*).

factor of 20) after reduction at 390°C (Table 1) is observed;

—for BK catalysts reduced at 200°C, the nature of the support has no influence on the catalytic activity;

—the Pt/P25 catalyst, prepared by the IW method is 10 to 20 times less active than its homologue BK1, whatever the reduction or reaction temperatures;

—for Pt/AT1 catalysts reduced at 200°C, the way of preparation has only little influence on the catalytic activity but after reduction at 390°C, the IW-prepared catalyst is more affected than the BK catalysts.

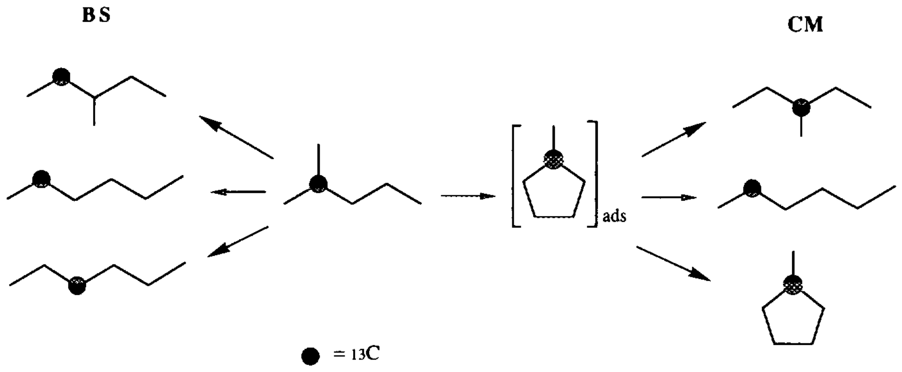
BK1 was additionally tested; after the catalytic experiments performed on BK1 reduced at 200°C, the sample was reduced at 600°C for 1 h. Afterwards it was treated with air at 500°C during one hour followed by a reduction treatment at 200°C. The reduction at 600°C caused a drop of one order of magnitude in the catalytic activity. However, the activity was restored and even enhanced after the treatment with air.

With regard to the reaction of MCP (Table 2), the BK catalysts are also more active than the IW-prepared catalysts, but the differences are less pronounced. Comparing the reaction rates of MCP and 2MP on different catalysts, we can conclude that on catalysts reduced at 200°C, the MCP molecule is more reactive than 2MP (when taking into account the difference in the reaction temperature), while the reverse is observed after reduction at 390°C.

Catalytic Selectivities

The selectivities S in isomerisation of 2MP, whatever the method of preparation, are generally high (>60%) (Table 1), and close to those of Pt/Al_2O_3 catalysts (*3*, *11*). They are still enhanced for BK1 when both the reduction and reaction temperatures are increased, whereas they remain unchanged for BK2. Nevertheless, BK1 presents higher selectivities than the IW-Pt/AT1 catalyst but lower than IW-Pt/P25 catalysts. The most pronounced differences are observed at 290°C. Finally, the selectivity remains unchanged after reduction at 600°C, but the further treatment with air enhances it.

The isomer ratios (3MP–nHx) obtained from 2MP (Table 1) are insensitive to the



SCHEME 1

reduction temperatures between 200 and 390°C, whereas an increase in the reaction temperature leads to a decrease of this ratio, whatever the catalyst, mainly due to a relative decrease in the formation of 3MP. This effect is still more evident after reduction at 600°C, even though the reaction temperature was low. Treatment with air does not restore the initial behaviour.

The isomer ratios (3MP/nHx) obtained from hydrogenolysis of MCP (Table 2) are similar to the corresponding ratios for 2MP. Here also, after reduction of the catalyst at 600°C, the formation of 3MP is inhibited and not totally restored after air treatment.

^{13}C-*Labelling Experiments*

The isomerisation reaction of 2-(2-^{13}C) methylpentane was performed at 290 and 390°C on the BK catalysts reduced at 200°C and 390°C, respectively. The amounts of 3-(2-^{13}C) and 3-(3-^{13}C)MP obtained from the isomerisation of 2-(2-^{13}C)MP allow the determination of the relative percentages of bond-shift mechanism (BS) or cyclic mechanism (CM) in the reaction 2MP → 3MP as described by Scheme 1. The relative percentage of cyclic mechanism (Table 3) does not vary with the reduction or reaction temperature for BK1 (%CM = 44 ± 2) but it is enhanced for BK2 at low temperature (%CM = 73). The IW-prepared catalysts present lower contributions of CM (28 ± 3%) towards the isomerisation under similar experimental conditions.

The overall contributions of CM (ΣCM) and BS (ΣBS) towards the isomerisation, calculated by taking into account the amounts of 3MP, nHx, and MCP (Scheme 1) obtained via these two different mechanisms are listed in Table 3 as well as the amounts of cracking products (Σcrack, with $\Sigma CM + \Sigma BS + \Sigma crack = 100$). We have assumed that contributions of CM to the 2MP → nHx reaction are similar to that obtained in the 2MP → 3MP reaction because experimental values cannot be obtained from only 2-(2-^{13}C)MP reactions (*10*). This assumption, however, provides the total CM at a somewhat underestimated value because the CM contribution to the chain lengthening (2MP → nHx) is always higher than in the 2MP → 3MP reaction (*11*).

The overall contribution of CM at 290°C is lowest for BK1 whereas the cracking reactions are important. Nevertheless, at 390°C, BK1 presents a higher contribution to CM than its IW prepared homologue. For BK2 the total amounts of CM are quite similar at 200 and 390°C while the relative contributions (CM in 2MP → 3MP) were markedly different. This is due to the high contribution of MCP in the product distribution at 390°C. It is, however, plausible to assume that at 390°C the desorption rate of MCP becomes higher than the hydrogenolysis rate. This is

TABLE 3

Isomerisation Reaction of 2-(2^{13}C) Methylpentane over Pt/TiO_2 Catalysts. Distribution of the Different Mechanisms as a Function of Catalyst Preparation

Catalyst	Reduction temp. (°C)	Reaction temp. (°C)	Rel. %CM[a]	Rel. %BS[a]	Σ crack	Σ CM	Σ BS
BK1-2%Pt/P25	200	290	43	57	40	37	23
BK1-2%Pt/P25	390	390	46	54	9	66	25
BK2-2%Pt/AT1	200	290	73	27	10	75	15
BK2-2%Pt/AT1	390	390	41	59	11	72	17
IW-2%Pt/P25	390	390	25	75	16	54	30
IW-8%Pt/AT1	390	390	31	69	15	61	24
BK-2%Pt/Al_2O_3[b]	220	300	39	61	27	37	37
8%Pt/Al_2O_3[c]	390	390	98	2	24	71	5

[a] Relative % of CM determined by 2^{13}C-2MP → 3^{13}C-3MP in 2MP → 3MP; relative % of BS determined by 2^{13}C-2MP → 2^{13}C-3MP in 2MP → 3MP (rel. %CM + rel. %BS = 100).

[b] Ref. (*3*).

[c] Ref. (*7*).

in agreement with the fact that the reactivity of this hydrocarbon is lower than that of 2MP at the same temperature. Here again, the BK catalysts present higher contributions to CM.

EXAFS Analyses

EXAFS analyses were performed on BK1 and BK2 catalysts. They had been reduced at 200°C and were used for catalytic experiments up to 390°C. The radial distributions obtained by Fourier transform of $[k^3\chi(k)]$ weighted primary EXAFS data for k values varying between 4 and 14 Å^{-1} are reported in Fig. 1, together with the corresponding EXAFS fits obtained by inverse Fourier transform of the main peak of the radial distribution sized between 2.3 and 3.1 Å. A mean free path for electrons equal to 5.5 Å has been used to fit the EXAFS curves. Both catalysts show a surrounding of 12 Pt atoms at a distance of 2.75 ± 0.01 Å. The Debye–Waller factors used to fit with 12 Pt atoms are extended between 0.077 and 0.086 Å. None of the neighbours in the first shell is a Ti atom.

XPS Analyses

In order to elucidate the particular catalytic behaviour of the BK2 catalyst with regard to its activity (large activity decrease when increasing reduction temperature), caused perhaps by the presence of numerous impurities, this catalyst was studied by XPS after the following treatments:

—reduction at 200°C and catalytic experiments up to 390°C (sample BK2-200);

—reduction at 390°C and catalytic experiments up to 390°C (sample BK2-390).

The samples, which had been stored in air before the XPS analyses, were again treated with hydrogen under a pressure of 1 atm in the preparation chamber of the spectrometer. Sample BK2-200 was reduced again for 2 h at 290°C (sample BK2-200-290) and further for 3 h at 390°C (sample BK2-200-390). Sample BK2-390 was only re-reduced for 3 h at 390°C (sample BK2-390-390).

From the binding energies (Table 4), we can see that samples BK2-200 and BK2-390 exhibit features of reduced platinum, even though they were stored in air before the XPS analyses. An additional reduction does not modify their binding energies (Pt $4f_{7/2}$ = 70.7 ± 0.1 eV). On the other hand, in sample BK2-200, which was catalytically active, the Nb $3d_{5/2}$ peak is shifted by 1.8 eV towards higher binding energies as compared with the samples re-reduced at 290 or

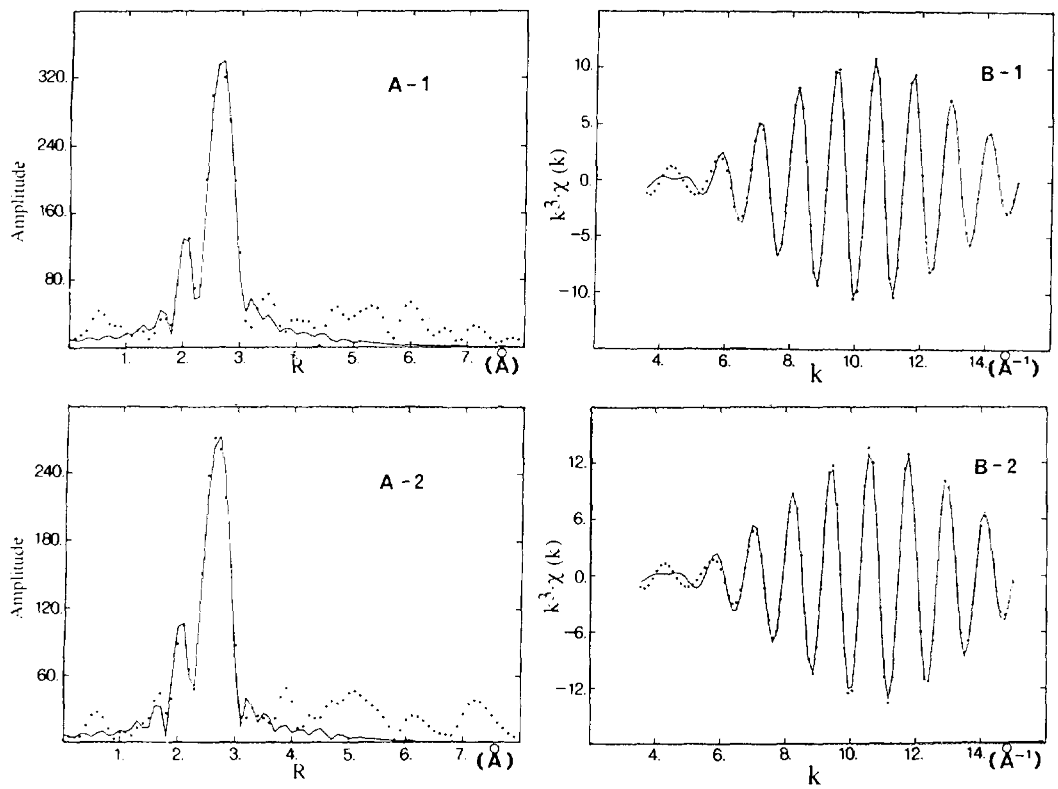


FIG. 1. Radial distributions (A) and EXAFS fits (B) for catalysts BK1 (1) and BK2 (2) reduced at 200°C and after catalytic tests at 390°C (dotted lines, experimental results; full lines, calculated data). Amplitudes for (A-1) and (A-2) are in arbitrary units.

390°C. This is not the case for sample BK2-390, which is catalytically quasi-inactive. Similar features appear for the K $2p_{3/2}$ core level peaks, but not for the P $2p_{3/2}$ peaks. The binding energies of the TiO$_2$ additives (K, Nb, and P) are on the average lower by 0.4 eV in sample BK2-390-390 than in sample BK2-200-390, whereas no changes were observed for the other elements (Pt, O, C).

The relative intensities of platinum as compared with the support (Table 5) are

TABLE 4

XPS Determination of Binding Energies (eV) of the Constituents of BK2 Catalysts, Referred to Ti $2p_{3/2}$ at 458.9 eV

Element	BK2-200	BK2-200-290	BK2-200-390	BK2-390	BK2-390-390
Pt $4f_{7/2}$	70.8	70.8	70.8	70.6	70.8
O $1s$	530.2	530.2	530.2	530.1	530.2
C $1s$	285.1	284.9	284.8	284.9	284.8
K $2p_{3/2}$	294.2	293.4	293.5	292.7	293.1
Nb $3d_{5/2}$	209.4	207.6	207.5	206.9	207.1
P $2p_{3/2}$	133.8	133.8	133.7	132.9	133.4

TABLE 5

Relative Intensities (Ti = 100) of the Constituents of BK2 Catalysts, as Determined by XPS

Element	BK2-200	BK2-200-290	BK2-200-390	BK2-390	BK2-390-390
Pt	1.6	1.6	1.5	2.4	1.9
K	1.6	1.4	1.6	2.1	1.9
Nb	1.0	1.0	1.1	1.5	1.2
P	5.9	5.5	5.6	7.3	6.1

somewhat more important for the initially highly reduced samples; this is also true for the other elements present at the surface. A re-reduction treatment has little effect on the relative intensities.

DISCUSSION

It appears from this study that the nature of the TiO_2 support influences the catalytic behaviour of Pt/TiO_2 catalysts. Such interactions have already been observed (*12*). However, the genesis of metal particles on the support is an important factor in this connection, especially after high reduction temperatures. Another important factor in this context are additives to the support. This discussion will therefore be split up into two parts: first we discuss catalysts supported on TiO_2 P25 and then catalysts supported on AT1 which contain the three additives (K_2O, Nb_2O_5 and P_2O_5).

Catalysts Supported on P25

After reduction at 200°C the activities and selectivities concerning the overall cyclic mechanism are similar for BK1-TiO_2 and BK-Al_2O_3 catalysts, implying that, for the BK-prepared catalysts reduced at low temperature, the support does not exert any influence on Pt behaviour. On the other hand, Boutonnet *et al.* have shown (*3*) that Pt/Al_2O_3 catalysts from microemulsions are less active than classically prepared ones of the same mean particle size (2 nm) due to a partial covering of the active sites by surfactant molecules. However, if TiO_2 is used as a support the BK catalysts are more active than the catalysts prepared by the classical method. This cannot be due to a higher surface area of BK catalysts compared to IW catalysts; a dispersion measurement given by hydrogen chemisorption equal to 0.7 was found for IW catalysts (*7*) and, even though this value is higher for BK catalysts, the difference in activity is too large to be explained by a simple particle size effect. Otherwise, metal–support interactions, of which the nature is certainly different from the ones created by high reduction temperature, could be evoked to explain the decrease in activity observed with IW catalysts for both hydrogenolysis and isomerisation reactions, without any loss of chemisorption.

After reduction at 390°C, the differences in activity between the catalysts prepared by the two modes are still more pronounced, whatever the reacting hydrocarbon. These results confirm the fact that a particle size effect is not the only one responsible for the observed differences in activity. Moreover, a surrounding of 12 atoms (EXAFS results) signifies the presence of large particles for both IW (*12*) and BK catalysts. It seems, therefore, that the formation and/or the migration of TiO_x species, created at high reduction temperature, onto the metal particles where their interactions lead to diminution of a certain number of accessible sites for isomerisation and hydrogenolysis reactions is more hindered on BK catalysts than on IW catalysts.

If we look now at the selectivities in mechanisms, and especially at the contribution of the cyclic mechanism, which is very sensitive to the presence of metal–support interactions (*7*), we can infer that the CM contribution follows the sequence: IW-TiO_2 < BK-TiO_2 < Pt/Al_2O_3. Here again, just as for the activities, the BK catalysts present intermediate situations between IW-TiO_2 catalysts and Pt/Al_2O_3 catalysts.

From these results we can conclude that by way of the preparation procedure it is possible to control the creation of metal–support interactions. Furthermore, it seems that for IW catalysts, an influence of the support occurs already at as low a reduction temperature as 200°C and increases further after reduction at 390°C, while it is less obvious for BK-prepared catalysts. In other words, metal–support interactions are more easily created when the particles are firmly anchored onto reducible supports like TiO_2 than when they are only in loose contact with such a support as is the case with deposition of ready-made particles.

An additional reduction of BK1 catalyst at a temperature of 600°C, at which SMSI is well noticeable, rendered interesting results: first, the catalyst became inactive for neither 2MP nor MCP rearrangements; second, complete absence of 3MP formation was observed. Anderson *et al.* (*8*), on the other hand, have observed on Pt/TiO_2 catalysts reduced at 300°C (LRT) and at 500°C (HRT), a complete inactivity for MCP and a loss of activity by a factor of 5 for nHx after HRT. Similarly, a factor of 40 has been observed with neohexane (*13*). In our case, MCP is less affected than 2MP by HRT (390 or 600°C). Disagreement between our results and those of Anderson *et al.* (*8*) may be due to the fact that their catalysts, prior to the reduction, were treated with oxygen, hence causing the formation of very small particles, particularly sensitive to HRT; on such particles, the size of the catalytic sites is no more suitable for hydrogenolysis reaction. It can be pointed out that calcination in air, prior to reduction, of Pt/TiO_2 catalyst hardly influences the catalytic activities (increase) and selectivities (decrease) for hydrogenolysis and isomerisation reactions by comparison with only reduced catalysts (*14*). Our work shows that neither isomerisation nor hydrogenolysis reactions on BK1 are completely inhibited by HRT. Actually, in spite of the fact that hydrogenolysis of MCP producing nHx, 3MP, and 2MP requires two hydrogen atoms ($C_6H_{12} + H_2 \rightarrow C_6H_{14}$), unlike the isomerisation reaction of 2MP ($C_6H_{14} \rightarrow \text{i-}C_6H_{14}$), the hydrogenolysis reaction is less affected by HRT than the isomerisation. Thus, hydrogen seems to be available at the surface and only the nature of the sites must be different. Lack of the formation of 3MP is, however, observed for both 2MP and MCP, implying that very specific sites are required for 3MP formation. Such sites no longer exist after HRT.

Catalysts Supported on AT1

The BK2 catalyst reduced at 200°C shows similar activities to the BK1 catalyst, whatever the reaction temperature. Nevertheless, the selectivities in isomerisation are higher. The presence of impurities, therefore, must either modify the distribution of the sites for isomerisation and hydrogenolysis, or act specifically only on hydrogenolysis.

After reduction at 390°C, a considerable decrease in activity is observed, though less important for BK2 than for IW-prepared catalysts. It is noteworthy that such an activity decrease when increasing the reduction temperature did not occur with catalysts (BK or IW) supported on P25 TiO_2. This may be due to the interaction between electron-donor elements (K_2O is decomposed at 350°C) and platinum and/or site-blocking on Pt by the impurities. A similar decrease in activity has been observed for doped (potassium and phosphorus) V_2O_5/TiO_2 catalysts used for selective oxidation of methanol and *o*-xylene (*15*). So far, the specific role of these additives has not been well established. On the other hand, Chen and White (*16*) have reported that the addition of potassium to Pt/TiO_2

catalysts, reduced at 200°C, produces catalysts whose behaviour is similar to that observed for catalysts in the SMSI state. They have concluded that metal–support interactions are observed as soon as Pt acquires an excess of electrons, for instance, in the presence of electron-donor elements such as phosphorus or potassium.

At this stage, it is difficult to distinguish between the geometric and electronic effects. Hydrogenolysis of MCP shows a 3MP/nHx ratio near 0.5. Such a value is obtained if the C–C bond ruptures in the C_5 ring occur statistically (which is called nonselective hydrogenolysis mechanism) and is characteristic for small metal particles in Pt/Al_2O_3 catalysts (*11*). Impurities would migrate onto the platinum particles and there create isolated sites on which the nonselective hydrogenolysis reactions would be favoured. This is not in contradiction with the EXAFS results showing the presence of large particles. EXAFS determines the platinum surrounding in the bulk and this is not affected by the presence of impurities located at the surface of the particles.

Impurities, mainly potassium, migrate due to the initial reduction treatments close to the surface as would be seen from XPS results (samples BK200, BK390). These impurities are in lower oxidation states after reduction at 390°C than after reduction at 200°C. Therefore, the support additives (K_2O, Nb_2O_5, P_2O_5) although in a lower state of oxidation, when the catalysts have been reduced at 390°C, might, on account of their electron-donating abilities, modify the electronic structure of the platinum metal. Additive–platinum interactions can prompt an effect at 390°C but not at 290°C; thus, HTR can impair the catalytic activity of platinum. Moreover, it is seen that, depending on the reduction temperature, Nb after storage in air may be in an oxidized or reduced state. This implies that the element Nb which is easily oxidizable is not oxidized after high reduction temperature when it is in contact with Pt. Hence, XPS experiments allow us to conclude that, for Pt/TiO_2 catalysts reduced at high temperature, in the presence of electron-donor additives, the electronic effects dominate over the geometric ones.

The IW-prepared catalysts are affected to a higher degree by high reduction temperature, which suggests that additive–platinum interactions are more important. This can be due either to the possibility that both geometric (migration of TiO_x species on Pt particles) and electronic effects are operative or to the fact that any migration (support or additive) is more favoured with IW catalysts than with BK catalysts.

From a mechanistic point of view, the catalysts supported on AT1 present, whatever the method of preparation, high contributions of cyclic mechanism to 2MP reactions contrary to what can be expected for catalysts presenting metal–support interactions. It is also different from the results obtained by Zahraa (*17*) on Pt/Al_2O_3 catalysts doped with KOH, for which cyclic mechanism decreased. This is because methylcyclopentane formed as a reaction product is not further hydrogenolysed. Independently of the reduction temperature, the presence of impurities at the surface would promote the desorption of MCP rather than its hydrogenolysis. We have already seen that the presence of isolated atoms inhibits hydrogenolysis reactions. Moreover, it is known that the cyclic mechanism is enhanced on small Pt particles (*11*). These results show that particle size effects predominate over electronic effects, both effects being induced by the presence of additives, leading to an enhancement of the cyclic mechanism.

CONCLUSION

The study of the isomerisation and hydrogenolysis reactions of the hexanes used in this work on Pt/TiO_2 catalysts shows a pronounced influence of the method of preparation on the catalytic properties (activity, selectivity and reaction mechanisms) of the catalysts. The microemulsion-prepared catalysts, where the particles are deposited onto the support after their genesis, present behaviours similar to Pt/Al$_2$O$_3$ catalyst. Furthermore, the microemulsion-prepared catalysts required a higher temperature to induce metal–support interaction as compared with the catalysts prepared by the incipient wetness method, for which the effects are already observed after reduction at 200°C.

XPS measurements show that the effects of electron-donor additives, which lead to inhibition of the activity after reduction at high temperature, are also more important for the catalysts prepared by the incipient wetness method than for those prepared from a microemulsion.

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