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CATALYTIC BEHAVIOUR OF POLYCRYSTALLINE Pt_3Ti IN RELATION TO STRONG METAL-SUPPORT INTERACTION PHENOMENON

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Skeletal isomerization reactions of hexanes (2-methylpentane and methylcyclopentane) have been carried out in a flow reactor on a polycrystalline intermetallic Pt_3Ti compound which has been powdered and treated under several oxidative and reductive conditions. The results are compared to those obtained with (i) TiO_2 supported Pt catalysts in or not in the Strong Metal-Support Interaction (SMSI) state, (ii) a bulk Pt_3Ti sample studied under static catalytic conditions in an U.H.V. apparatus, and (iii) bulk Pt surfaces. The powdered Pt_3Ti compound shows a very unstable behaviour under hydrogen. Differences in behaviour between the bulk and the decomposed powdered Pt_3Ti samples are observed, showing the important part played by Pt_3Ti in SMSI phenomena. A model is then proposed.

The strong interaction of noble metals (group VIII) with reducible oxides such as TiO_2 has been widely studied. Numerous explanations of Strong Metal-Support Interaction (SMSI) phenomenon have been proposed and are still nowadays matter of controversy. The most common interpretation is the so-called "decorating model" which assumes migration of reduced support entities TiO_x $(x < 2)$ onto the metallic particles [1–6]. However, the formation of direct metal-Ti bonds is not excluded and more and more studies follow this way [7–10].

The aim of this work was to study, in a flow reactor, the catalytic behaviour, in isomerization and hydrogenolysis reactions of hexanes, of a polycrystalline intermetallic Pt_3Ti compound in order to look if Pt_3Ti could be involved in the SMSI phenomenon. Results obtained with 0.2 wt% Pt/TiO_2 and 10 wt% Pt/TiO_2 supported catalysts which do and do not present respectively the features of SMSI for isomerization and hydrogenolysis reactions (low catalytic activity, low contribution of cyclic mechanism) [11] although they are treated under the same conditions are used as comparison as well as experiments carried out on a bulk Pt_3Ti slice under static hydrogen conditions in an UHV apparatus where the surface can be checked before and after catalytic reactions by Auger Electron Spectroscopy (AES) [12].

The preparation of the intermetallic polycrystalline Pt_3Ti compound is described elsewhere [13]. A slice cut from the bulk sphere of Pt_3Ti obtained by this preparation has been ground and sieved such as to obtain metallic grains $< 10^{-4}$ m. This sample will be called as powdered Pt_3Ti.

The hydrocarbons used are 2-methylpentane (2MP) and methylcyclopentane (MCP) and are Fluka puriss grade. They were purified if necessary by gas-liquid chromatography.

The catalytic experiments with powdered Pt_3Ti were performed in a differential reactor at atmospheric hydrogen pressure already described [14]. The sample was submitted to various oxidoreductive treatments and four different phases of activation were observed, where the activities and selectivities in products are somewhat different. These phases are obtained (i) after reduction under H_2 at 300 °C for 16 h (initial phase), (ii) after 170 h under H_2 at 300 °C, (iii) after oxidation under air at 400 °C for 4 h followed by a H_2 reduction at 300 °C for 16 h, and (iv) after several oxidative-reductive treatments where the activity and the products distributions do not vary (stationary phase).

Turn Over Numbers (TON) have been calculated taking into account the following number of accessible Pt atoms:
- $1.15 \cdot 10^{15}$ atoms $\cdot$ cm^{-2} for bulk Pt surfaces
- $1.15 \cdot 10^{15} \cdot y$ atoms $\cdot$ cm^{-2} for bulk Pt_3Ti where y represents the percentage of Pt in Pt_3Ti and which is determined from the AES Ti/Pt ratios observed before the catalytic test
- $1.15 \cdot 10^{15} \cdot 50$ atoms for powdered Pt_3Ti. The factor 50 is obtained by a rough calculation taking into account the powdering of the sample and an equal % of Pt in powdered Pt_3Ti than in bulk Pt_3Ti for quasi same experimental conditions.
- wt% Pt $\cdot$ wt of catalyst $\cdot\, a \cdot \mathcal{N}/M_{Pt}$ for supported catalysts where $a = H/Pt$ is the accessibility obtained by chemisorption measurements and M_{Pt} the molecular weight of Pt.

The most striking results of this comparative study are reported in tables 1 and 2 for the reactions of 2-methylpentane (2MP) and methylcyclopentane (MCP), respectively. TON show that whatever the phase, the catalytic activity is lower for bulk Pt_3Ti than for powdered Pt_3Ti. Oxidative treatments lead to opposite activities behaviours: increase and decrease for powdered and bulk samples, respectively (compare experiments (2) and (3) for 2MP, and (4) and (5) for MCP for the bulk sample). Calcination conditions nevertheless differ: O_2 10 min 400 °C for bulk Pt_3Ti and air 4 h 400 °C for powdered Pt_3Ti. The decrease of catalytic activity for bulk Pt_3Ti is explained by an enhancement of Ti atoms at the surface leading to a dilution of the Pt atoms [12], (see AES Ti(384 eV)/Pt(223 eV) ratios, tables 1 and 2). On the other hand, the increase of activity for powdered Pt_3Ti can be explained by an enhancement of specific surface area. In fact, an X-ray photoemission study has shown that after a calcination treatment

Table 1
Reactions of 2-methylpentane on various Pt based catalysts

catalyst	treatment	temperature	TON·10^3 (s^{-1})	%S	%C_1	%Bz + cHx	$\frac{3MP}{nHx}$	$\frac{iso}{C_2}$
Pt_3Ti(B)	(1) clean surface [a]	350	0.46	67	0		1.0	2.0
Pt_3Ti(B)	(2) clean surface [a]	390	2.0	68	4.0	20	1.8	1.6
Pt_3Ti(B)	(3) O_2 10 min 400 °C [a]	390	0.15	57	5.0	33	1.8	1.4
Pt_3Ti(P)	H_2 16 h 300 °C	350	1.7	31	37	0	0	1.5
Pt_3Ti(P)	H_2 170 h 300 °C	350	18	45	13	1.0	2.2	0.7
Pt_3Ti(P)	air 4 h 400 °C H_2 16 h 300 °C	300	17	32	10	0	1.9	0.5
Pt_3Ti(P)	stationary phase	350	21	34	23	1.1	1.4	0.6
Pt polyX [b]	clean surface	350	7.2	70	0.7		1.4	1.0
Pt (111) [b]	clean surface	350	0.45	54	–	1.5	1.3	–
0.2% Pt/TiO_2 [c]	H_2 16 h 400 °C	390	1.3	79	0	0.2	8.9	1.7
10% Pt/TiO_2 [c]	H_2 16 h 400 °C	390	50	78	0.5	2.3	1.0	1.1

(B): bulk sample; (P): powdered sample; a: exps. (1) and (2): Ti (384 eV)/Pt (233 eV) = 1.3, exp (3): Ti/Pt = 2.2 (ref. [12]); b: ref. [16]; c: ref. [11] 0.2% Pt/TiO_2: SMSI state, 10% Pt/TiO_2: normal state; %S: % of isomerized products upon the overall conversion; %C_1 %C_1 (Bz + cHx): % of methane (benzene + cyclohexane) in the products distribution; M3P/nHx: 3-methylpentane over n-hexane ratio; iso/C_2: iso mode of hydrogenolysis over C_2 mode of hydrogenolysis

Table 2
Reactions of methylcyclopentane on various Pt based catalysts

catalyst	treatment	temperature	TON·10^3 (s^{-1})	%S	%C_1	% Bz+cHx	$\frac{2MP}{3MP}$	$\frac{3MP}{nHx}$
$Pt_3Ti(B)$	(4) clean surface [a]	350	2.1	23	38	10	2.2	0.7
$Pt_3Ti(B)$	(5) O_2 10 min 400 °C [a]	350	0.16	55	16	49	1.5	1.1
$Pt_3Ti(P)$	H_2 16 h 300 °C	350	5.3	14	71	0	3.3	1.3
$Pt_3Ti(P)$	H_2 170 h 300 °C	350	8.3	57	30	3	2.6	1.9
$Pt_3Ti(P)$	air 4 h 400 °C H_2 16 h 300 °C	300	12	40	38	1	2.6	1.6
$Pt_3Ti(P)$	stationary phase	350	32	25	49	2	2.1	1.7
Pt polyX [b]	clean surface	350	14	93	–	0.4	2.2	1.3
Pt (111) [b]	clean surface	350	0.41	56	–	1.6	2.0	3.0
0.2% Pt/TiO_2 [c]	H_2 16 h 400 °C	390	1.1	93	–	9.1	2.2	0.9
10% Pt/TiO_2 [c]	H_2 16 h 400 °C	390	45	91	–	1.7	2.3	0.9

(same legends as table 1)

of 4 h at 400 °C, not only titanium, but also platinum is slightly oxidized [13]. Reduction under H_2 of such an oxidized surface leads to platinum metallic ensembles surrounded by islands of titanium oxides which have been attributed to Ti_2O_3 and TiO_2 and which are supported on Pt_3Ti. These small metallic Pt ensembles are then very reactive compared to a bulk Pt_3Ti surface.

The selectivity in isomers S, expressed as the percentage of isomerized products upon the overall conversion is the lowest for powdered Pt_3Ti with 2MP as starting hydrocarbon, whereas bulk Pt_3Ti behaves like either bulk Pt surfaces or Pt/TiO_2 catalysts (in or not the SMSI state). For methylcyclopentane reactions, the % S is lower than for 2-methylpentane reactions with bulk Pt_3Ti and with powdered Pt_3Ti in the initial and stationary phases. The enhancement of hydrogenolysis reactions for both 2MP and MCP is due to a very large formation of methane wich can only be obtained by multiple hydrogenolysis reactions. The proportion of C_1 species obtained with MCP is higher than with 2MP showing that MCP is very strongly adsorbed on both bulk and powdered Pt_3Ti surfaces, whatever the surface composition.

Two other interesting differences between bulk and powdered Pt_3Ti are (i) the great formation of benzene and cyclohexane for both 2MP and MCP and (ii) the observation of C_7 hydrocarbons in the products distribution, for bulk Pt_3Ti. These effects are altogether particular to this sample and have been attributed to the existence of bimetallic Pt-Ti sites [12] where H_2 chemisorption is inhibited. Such sites do not exist anymore with the decomposed powdered sample. Nevertheless, the contributions of benzene + cyclohexane obtained with the 0.2 wt% Pt/TiO_2 catalyst in the SMSI state is higher than that obtained with the 10 wt% Pt/TiO_2 catalyst not in the SMSI state [11]. This could be a hint as well as the inhibition of H_2 chemisorption of the involvement of Pt_3Ti in SMSI phenomena.

Few differences are observed on the various catalysts for the 2MP/3MP and 3MP/nHx ratios obtained with MCP and 2MP (tables 1 and 2), the reaction temperatures being a little too high.

Another great difference between the two Pt_3Ti samples is obtained in the hydrogenolysis products distribution. The ratio between the iso-mode of hydrogenolysis involving $C_I - C_{III}$ and C_{II}–C_{III} bond ruptures and the C_2-unit mode involving C_I–C_{II} and C_{II}–C_{II} bond ruptures (table 1), as defined by Anderson et al. [15], is higher for bulk Pt_3Ti than for powdered Pt_3Ti. The values obtained for bulk and powdered Pt_3Ti look like those observed with the supported Pt/TiO_2 catalysts which do and do not present the SMSI state, respectively. This result confirms again the possible involvement of Pt_3Ti in the SMSI phenomenon. Moreover, ^{13}C labelling experiments done with powdered Pt_3Ti in the stationary phase show that the isomerization mechanisms of hexanes are the same as those obtained with Pt/TiO_2 catalysts in the SMSI state [13].

This comparative study allows us to propose the following model for SMSI phenomenon occurring on Pt/TiO_2 supported catalysts, model a little different from the one proposed by Beard and Ross [8] (fig. 1):

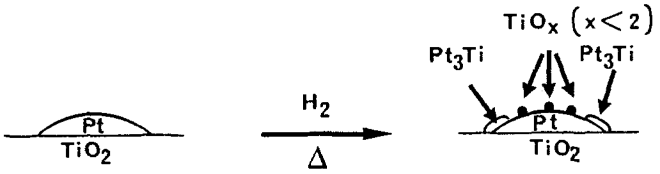

Fig. 1.

Under high temperature and reductive atmosphere, Pt/TiO_2 catalysts undergo morphological changes all the more as catalysts are well dispersed. The migration of TiO_x species onto the Pt particles can explain the similarities of isomerization behaviour between the treated powdered Pt_3Ti sample which can be considered as decomposed at the surface in Pt particles surrounded by TiO_2 and Ti_2O_3 species as observed by XPS analysis [13] and supported Pt/TiO_2 catalysts, while the formation of Pt_3Ti at the Pt-TiO_2 interface can explain the low H_2 chemisorption, the hydrogenolysis reactions and the greater benzene formation, due to specific bimetallic Pt-Ti sites.

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