

Skeletal Rearrangement Reactions of Hexanes on Pt₃Ti Polycrystalline Catalysts

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Reactions of hexanes have been performed on a Pt₃Ti intermetallic polycrystalline sample placed in a cell housed within an ultrahigh-vacuum apparatus where the surface can be monitored before and after the reactions by Auger electron spectroscopy (AES). The catalytic results show that Pt₃Ti is very sensitive to experimental pretreatments, due to changes in surface composition. The main results obtained with the Pt₃Ti compound are (i) low catalytic activities, (ii) formation of highly dehydrogenated products (benzene), and (iii) formation of homologation products, whereas no carbonaceous deposits are observed. These results can be explained by considering that there is no or little hydrogen chemisorption. The homologation reactions require the presence of bimetallic Pt–Ti sites where titanium can be slightly oxidized. These bimetallic sites are also responsible for the large amounts of benzene obtained with Pt₃Ti (or “Pt₃TiO_x”). The fact that Pt₃Ti (or “Pt₃TiO_x”) has low hydrogen chemisorption ability suggests the participation of such a compound in strong metal–support interaction (SMSI) phenomena. Nevertheless, the catalytic behavior observed on a clean surface is different from that obtained on a supported Pt/TiO₂ catalyst in the SMSI state. © 1990 Academic Press, Inc.

INTRODUCTION

Pt₃Ti is an Engel–Brewer intermetallic-type compound characterized by a highly negative enthalpy of formation (1, 2). The chemisorptive properties of this compound have been studied by Bardi *et al.* (3, 4) and Cameron *et al.* (5, 6) to determine if they could be modified by either ensemble (dilution of the active atoms) or ligand (modification of the electronic properties) effects and if Pt₃Ti could be involved in the strong metal–support interaction (SMSI) phenomena occurring for group VIII metals supported on TiO₂ (7). After reduction at 500°C, the catalysts in the SMSI state lose their H₂ and CO chemisorptive properties and the methanation activity becomes higher as compared to alumina- or silica-supported catalysts. The catalysts recover their initial properties after calcination at

400°C. One of the mechanisms suggested for the SMSI effects is the formation of a Pt–Ti alloy in the case of Pt/TiO₂ catalysts. Bardi *et al.* (4) found that carbon monoxide is adsorbed on Pt₃Ti and this result is in opposition with the involvement of Pt₃Ti in SMSI phenomena. Nevertheless, they observed no hydrogen adsorption at room temperature but they could not exclude the fact that the hydrogen adsorbed at room temperature is not desorbed by flash-heating the surface up to 630°C. Beard and Ross (8) propose a mechanism for the SMSI state also involving in part the formation of a Pt₃Ti compound, while Baker *et al.* (9) suggest the formation of a highly mobile phase, i.e., a mixed surface oxide PtTiO_x. Formation of Rh–Ti bonds is also found for highly dispersed Rh/TiO₂ catalysts (10, 11).

The most common model proposed for SMSI phenomena, however, is the “decoration” of the metallic particles by reduced TiO_x support species. Model catalyst

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studies performed either by evaporating titanium on the polycrystalline metal (12–18) or by evaporating the metal on a single-crystal titanium (oxide) surface (12, 19–21) seem to confirm this mechanism.

The aim of our work was to study the catalytic properties of a polycrystalline Pt₃Ti compound for the test reactions of hexanes to check the modifications induced by the environment of titanium atoms around platinum atoms as compared to the intrinsic properties of Pt (polycrystalline and well-characterized crystallographic surfaces) (22) and as compared to Pt/TiO₂-supported catalysts in the SMSI state (23). The sample studied in this work was catalytically tested in a static system lodged in an ultrahigh-vacuum (UHV) apparatus where the chemical state of the surface can be checked before and after the catalytic reactions by Auger electron spectroscopy (AES).

EXPERIMENTAL

Materials

The intermetallic Pt₃Ti polycrystalline compound was prepared at the European Institute for Transuranium Elements, Karlsruhe (FRG), by levitation melting in a Hugin crucible, using the appropriate mixture of polycrystalline platinum (Materials Research Corporation, 5N purity) and titanium (Ventron, 3N). Slices of 1.5×10^{-3} -m thickness were cut by spark erosion from the bulk Pt₃Ti sphere obtained by this preparation method. A slice of 10^{-2} -m diameter was mounted as such on tantalum rods and was catalytically tested under static catalytic conditions in an isolation cell housed within a UHV chamber. The hydrocarbons used were 2-methylpentane (2MP), 3-methylpentane (3MP), *n*-hexane (*n*Hx), and methylcyclopentane (MCP) (Fluka puriss grade). They were purified if necessary before each use by GLC.

Apparatus and Procedure

The catalytic experiments were performed in a Varian LEED chamber with

four-grid optics. A retarding field analyzer (RFA) is used to monitor the surface composition before and after the catalytic reactions. An isolation cell housed within the main UHV chamber allows catalytic reactions up to atmospheric pressure to be conducted while the rest of the chamber remains under ultrahigh vacuum. In each run, 5 Torr of hydrocarbon is introduced with 755 Torr of pure hydrogen when the desired temperature is achieved. The sample is heated slowly at 6°C min^{-1} up to 350 or 390°C. After 1 h reaction, the products are hydrogenated on Adams platinum and are then condensed in a trap at liquid nitrogen temperature. A fraction of the reaction products is analyzed by GLC. More details on the apparatus are given in Ref. (22), in which are also reported the test reactions of hexanes with the Pt surfaces used as comparison in this paper.

The sample was first cleaned by heating to 500°C for 1 week. Several ratios of the peak-to-peak heights given by AES were used to determine the degree of contamination of the surface. These were $a = [h(\text{Pt}+\text{S})148 \text{ eV}]/[h(\text{Pt})167 \text{ eV}]$, $c = [h(\text{C})269 \text{ eV}]/[h(\text{Pt})233 \text{ eV}]$, $n = [h(\text{Ti})384 \text{ eV}]/[h(\text{Pt})233 \text{ eV}]$, and $m = [h(\text{O})508 \text{ eV}]/[h(\text{Ti})384 \text{ eV}]$. The main impurities present were sulfur, carbon, calcium, and oxygen. Then the two faces were cleaned by several sputtering (Ar⁺, 25°C, 290 eV, 40 μA, 15 min) and annealing (500°C, 20 min) cycles before the catalytic experiments. Chemical oxygen treatments were then performed at a pressure of 2×10^{-8} Torr during 10 min at 400°C which led to a decrease of the presence of carbon. Catalytic experiments were then performed on such surfaces.

RESULTS

Reaction of 2MP, 3MP, and nHx

The turnover frequencies obtained with Pt₃Ti, a Pt polycrystalline foil (22), and a Pt(111) single crystal (22) are reported in Table 1. The number of accessible Pt atoms is equal to 1.15×10^{15} atoms cm^{-2} for the Pt

TABLE 1

Isomerization of 2- and 3-Methylpentanes and *n*-hexane: Distribution of the Isomerized Products

Catalyst	HC	<i>T</i> (°C)	TOF × 10 ³ (s ⁻¹)	%S	2MP ^a	3MP	nHx	MCP	Bz + cHx	<i>r</i>
Pt ₃ Ti (1) ^b	2MP	350	0.46	67	—	12	12	75	ε	1.0
Pt ₃ Ti (1)	2MP	390	2.0	68	—	9 (13)	6 (8)	56 (79)	29 (—)	1.5
Pt ₃ Ti (1)	3MP	390	2.0	72	19 (21)	—	23 (24)	50 (55)	8 (—)	0.8
Pt ₃ Ti (1)	nHx	390	14.3	68	15 (22)	13 (19)	—	41 (59)	31 (—)	1.2
Pt ₃ Ti (3)	2MP	390	0.15	57	—	8 (19)	4 (10)	30 (71)	57 (—)	2.0
Pt polyX ^c	2MP	350	7.2	70	—	22	16	62	ε	1.4
Pt polyX ^c	3MP	350	7.6	56	24	—	13	60	3	1.8
Pt polyX ^d	nHx	350	4.4	66	23 (27)	13 (15)	—	51 (58)	13 (—)	1.8
Pt(111) ^e	2MP	350	0.45	54	—	16	12	54	18	1.3

^a 2MP, 2-methylpentane; 3MP, 3-methylpentane; nHx, *n*-hexane; Bz, benzene; cHx, cyclohexane. *r* = 3MP/nHx for 2MP, 2MP/nHx for 3MP, and 2MP/3MP for nHx.

^b (1) Initial phase; (3) after oxygen dosing at 400°C, 10⁻⁸ Torr, 10 min.

^c Reference (22).

^d Reference (25).

foil, and for Pt(111), $1.15 \times 10^{15} \times y$ atoms cm⁻² for Pt₃Ti where *y* represents the percentage of Pt atoms at the surface of Pt₃Ti, determined from the Ti/Pt ratios (Table 2) before the catalytic test by considering that a ratio of 1.9 leads to 70% Pt on the surface (4). Blank experiments undertaken under flow hydrogen conditions on noncleaned polycrystalline titanium samples which were certainly TiO_x at the surface showed

no catalytic activity for skeletal isomerization reactions under the same temperature conditions.

At 350°C, the Pt₃Ti sample presents a very low catalytic activity as compared to the Pt foil but has activity similar to that of the less reactive Pt(111) single crystal (22). It begins to be notably active near 390°C, especially for the reaction of *n*-hexane. After the oxygen treatments, the catalytic

TABLE 2

Auger Electron Spectra Ratios before and after Catalytic Reactions on Pt₃Ti

Catalyst:	Pt ₃ Ti (1)					Pt ₃ Ti (3)		Pt polyX ^a	Pt(111) ^a
	2MP (1)	2MP (2)	3MP	nHx	MCP (1)	2MP (3)	MCP (2)	2MP	2MP
Experiment: <i>T</i> (°C):	350	390	390	390	350	390	350	350	350
a ^b Before	1.1	1.0	1.2	1.3	1.1	1.8	1.4	1.0	1.0
After	4.2	5.1	3.7	3.4	4.7	2.7	1.3	1.0	0.9
c Before	0.6	0.5	0.8	0.9	0.7	0.2	0.1	0	0
After	0.7	0.5	0.7	1.0	0.7	0.2	0.8	2.3	1.2
n Before	1.3	1.3	1.3	1.3	1.2	2.3	3.4	—	—
After	1.3	1.3	1.3	1.3	1.4	2.2	3.7	—	—
m Before	0.2	0.1	0.2	0.5	0.2	0.4	0.5	—	—
After	0.5	0.5	0.6	0.7	0.7	0.6	0.7	—	—



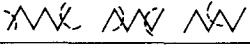
Note. Symbols are explained in Table 1.

^a Reference (22).

^b a = [h(Pt + S) 148 eV]/[h(Pt) 167 eV]; c = [h(C) 269 eV]/[h(Pt) 233 eV]; n = [h(Ti) 384 eV]/[h(Pt) 233 eV]; m = [h(O) 508 eV]/[h(Ti) 384 eV].

TABLE 3

Hydrogenolysis Reactions of 2-Methylpentane, 3-Methylpentane, and *n*-hexane: Distribution of the Hydrogenolyzed Products

Catalyst					$\frac{\text{iso}}{\text{C}_2}$	<i>T</i> (°C)
	iso mode	C ₂ mode	iso	C ₂		
Pt ₃ Ti (1)	17	50	8	25	2.0	350
Pt ₃ Ti (1)	24	38	14	24	1.6	390
Pt ₃ Ti (3)	19	39	8	34	1.4	390
Pt polyX ^a	13	37	8	42	1.0	350
Statistical	40	20	20	20	1.5	—
					$\frac{\text{iso}}{\text{C}_2}$	<i>T</i> (°C)
Catalyst	iso mode	C ₂ mode	iso	C ₂		
Pt ₃ Ti (1)	36	11	53	0.9	390	
Pt polyX ^a	59	13	28	2.6	350	
Statistical	40	20	40	1.5	—	
					$\frac{\text{iso}}{\text{C}_2}$	<i>T</i> (°C)
Catalyst	iso mode	C ₂ mode	iso	C ₂		
Pt ₃ Ti (1)	41	32	27	—	390	
Pt polyX ^b	23	36	41	—	350	
Statistical	40	40	20	—	—	

Note. Experimental conditions and symbols are explained in Table 1.

^a Reference (22).

^b Reference (25).

activity decreases, contrary to what has been observed with a powdered Pt₃Ti sample studied in a flow catalytic system (no UHV conditions) (24).

The selectivity in regard to isomers, *S*, expressed as a percentage of isomerized products upon the overall conversion, does not vary with the structure of the hydrocarbon or with the temperature for Pt₃Ti (Table 1, %*S* = 70 ± 3). It decreases to 57% after the oxygen treatments. These selectivities are not very different from those obtained with the Pt foil.

Isomerization reactions of 2MP, 3MP, and *n*Hx lead essentially to the formation of cyclic molecules, whatever the starting hydrocarbon, mainly to methylcyclopentane (MCP) or to benzene (Bz) and cyclohexane (cHx) before and after the oxidative treatments, respectively (Table 1). Formation of

benzene is observed in spite of the presence of Adams Pt because this molecule is hard to hydrogenate. The cyclohexane obtained comes only from the hydrogenation of Bz. The contributions of 3MP, *n*Hx, and MCP that would be obtained without taking into account those of Bz + cHx, with 2MP as starting hydrocarbon (values in parentheses in Table 1), are the same for the three experiments independently of the treatment or the temperature. The 3MP/*n*Hx ratios can be considered as quasi-similar (1.5 ± 0.5) for the three experiments due to errors induced by a very low overall conversion (0.15 ± 0.09%). Generally, the ratios *r* (one acyclic isomer to the other acyclic isomer) are almost the same for Pt₃Ti, for the Pt foil, and for Pt(111) except when 3MP is the starting hydrocarbon. The main difference for all hydrocarbons consists in the great formation of Bz + cHx with Pt₃Ti.

Another interesting point is the formation of C₇ hydrocarbons only with Pt₃Ti, not with the other Pt samples. The sum of all the heptanes obtained represents about 10% of the overall products.

Hydrogenolysis of 2MP, 3MP, and *n*Hx

Since hydrogenolysis reactions are present (Table 1, %*S*), a distinction between two modes of hydrogenolysis has been made following the proposal of Anderson (26). The iso-unit mode of hydrogenolysis involving the presence of a tertiary carbon atom predominates on Pt₃Ti with 2MP as starting hydrocarbon, before the oxidative treatments (Table 3). The C₂-unit mode involving primary carbon–secondary carbon (C_I–C_{II}) and secondary carbon–secondary carbon (C_{II}–C_{II}) bond breaks slightly increases by enhancement of the C_{II}–C_{II} bond ruptures after oxidative treatments. As compared to the platinum foil, the Pt₃Ti sample presents less C_{II}–C_{II} and more primary carbon–tertiary carbon (C_I–C_{III}) bond ruptures. With 3MP as starting hydrocarbon, the situation is reversed: Pt₃Ti presents a lower iso-unit mode of hydrogenolysis/C₂-unit mode ratio than the

TABLE 4
Hydrogenolysis Reactions of Methylcyclopentane at 350°C: Distribution of Products

Catalyst	TOF $\times 10^3$ (s ⁻¹)	%S	2MP	3MP	nHx	Bz + cHx
Pt ₃ Ti (1)	2.4	23	25 (42)	17 (29)	17 (29)	41 (-)
Pt ₃ Ti (3)	0.16	55	5 (45)	3 (27)	3 (27)	89 (-)
Pt polyX ^a	14	93	55	25	20	ϵ
Pt(111) ^a	0.41	56	58	29	10	3

Note. Experimental conditions and symbols as are explained in Table 1.

^a Reference (22).

Pt foil. The C_I-C_{II} bond ruptures are favored on Pt₃Ti while the secondary carbon-tertiary carbon (C_{II}-C_{III}) ones predominate on Pt foil. With nHx as starting hydrocarbon, the nearly statistical behavior of Pt₃Ti is also different from that obtained on Pt alone, where the formation of propane is most important.

Hydrogenolysis of Methylcyclopentane

The Pt₃Ti sample presents again (i) a low catalytic activity as compared to the Pt foil, the activity being nevertheless more important than for Pt(111), and (ii) a decrease in activity after oxidative treatments (Table 4). The percentage selectivity is very low and methane is the main cracked product. Pt₃Ti leads essentially to ring enlargement reactions (Bz + cHx), as for the reactions with the acyclic hydrocarbons. Again, without taking into account the contributions of Bz + cHx, those of 2MP, 3MP, and nHx would be the same for Pt₃Ti before and after the oxidative treatments. In that case, the contributions are similar to those obtained with the Pt samples.

As for the reactions with the other hydrocarbons, homologation products are observed to the same extent on Pt₃Ti.

Auger Electron Spectroscopy

The surface of the polycrystalline Pt₃Ti sample was checked before and after each

catalytic reaction by AES. The ratio $c = [C(269 \text{ eV})]/[Pt(233 \text{ eV})]$ shows the presence of carbon before the catalytic reactions (Table 2) and represents a carbon coverage of 1 carbon atom for 5 (Pt + Ti) atoms. This coverage is obtained by multiplying c by the factor 0.3, determined from LEED patterns of Pt samples in a C₂H₄ atmosphere (27-29). It was nevertheless lower after the oxidative treatments, before the catalytic reactions [Experiments 2MP(3) and MCP(2)], the carbon coverage being 3 carbon atoms for 50 (Pt + Ti) atoms. This coverage corresponds to carbon impurities which cannot be eliminated and are present at the surface before any reaction and, thus, are independent of the reaction studied (30). A noticeable fact is the lack of increase in the ratio c after the catalytic reactions, contrary to the platinum surfaces. No carbon seems to be retained at the surface during the catalytic reaction except for the experiment MCP(2).

The ratio $n = [Ti(384 \text{ eV})]/[Pt(233 \text{ eV})]$ did not vary before and after the catalytic reactions and showed Pt enrichment at the surface before oxidative treatments ($n = 1.3$) (4). On the contrary, Ti enrichment occurred at the surface after oxidative treatments ($n > 2$). It is noteworthy that the presence of oxygen {ratio $m = [O(508 \text{ eV})]/[Ti(384 \text{ eV})]$ } is always greater after the catalytic reactions, but is not higher for

the sample treated under oxygen than for the untreated compound. Even with the cleanest sample, oxygen is always detected.

DISCUSSION

Catalytic Activity

From the results, it is clear that the oxidative treatments lead to a decrease in the catalytic activity of Pt₃Ti. The only important differences before and after the oxidative treatments concern the Ti/Pt ratios which rise from about 1.3 to 3.0 (Table 2). The O/Ti ratios either do not change or change little. The O/Pt ratios have not been taken into account because platinum cannot be considered as oxidized under 10⁻⁸ Torr of oxygen at 400°C as seen by photoemission studies (31). During the experiments themselves, the Ti/Pt ratios do not vary whereas the O/Ti ratios slightly increase. Since the O/Ti ratios do not vary before and after the oxidative treatments, the decreases in catalytic activity for both 2MP (Table 1) and MCP (Table 4) after oxidative treatments seem to be attributable only to a *geometric effect* by dilution of the platinum atoms by the titanium atoms. The catalytic active ensembles no longer possess enough contiguous platinum atoms. The formation of a TiO_x monolayer would also explain the decrease in the activities but could not explain the constancy of the O/Ti ratios if we consider that TiO grows as a monolayer form (32) and not as rafts or pillar forms. Nevertheless, we cannot discard the fact that titanium can be slightly oxidized at the surface and that the inactivity of Pt₃Ti can be due to this effect. However, a powdered Pt₃Ti sample studied under flow catalytic conditions showed an enhancement of the catalytic activity after air treatments under 1 atm at 400°C for 4 h, explained by the formation of Pt ensembles surrounded by TiO_x islands (24). Moreover, the values found for the AES O/Ti ratios never exceed 0.7 (Table 2). According to Bardi and Ross (32) who studied by LEED

the formation of TiO_x species as a function of various oxidative treatments on Pt₃Ti(111) and Pt₃Ti(100) single-crystal surfaces, a value of 0.7 for the O/Ti ratios corresponds to a value of *x* lower than 1. Thus, it is possible that Pt₃Ti still exists at the surface. Moreover, XPS analysis on the Ti 2p_{3/2} core levels showed that even after an oxygen treatment under 10⁻⁶ Torr at 400°C for 30 min, Ti still exists partly in the Pt₃Ti form (31). Hence we can think that, at the surface, Pt₃Ti is still present even after oxidation together with "Pt₃TiO_x" species. The observed phenomena can therefore be due to the presence of the two compounds.

The reaction rates of 2MP and MCP on the Pt₃Ti or "Pt₃TiO_x" polycrystalline sample are 7 to 15 times slower before the oxidative treatments than on the Pt foil, whereas a similar rate is obtained on the Pt(111) single crystal at the same reaction temperature. Beside geometric effects, *ligand effects* are important due to the nature of the intermetallic bond itself. Pt in electronic interaction with Ti must lose its own reactivity. On the other hand, a decrease in the density of states at the Fermi level has been observed by UPS for both polycrystalline Pt₃Ti and Pt₃Ti(111) single crystal as compared to polycrystalline Pt and Pt(111) single crystal, respectively (4, 31), leading to a decrease in the ability of chemisorbing H₂ or CO. Moreover, Pt(111) is less able to chemisorb H₂ than a stepped or irregular surface, leading to a lower catalytic activity (33). The low catalytic activity as well as the UPS experiments show therefore that hydrogen cannot be or is poorly chemisorbed on a Pt₃Ti or "Pt₃TiO_x" surface.

Nevertheless, the reaction rate of nHx would certainly be the same for Pt₃Ti or "Pt₃TiO_x" and the Pt foil if the reaction temperatures had been identical. This means that the presence of a tertiary carbon inhibits the skeletal isomerization reactions on Pt₃Ti (or "Pt₃TiO_x"), although the need for hydrogen is less important. This is discussed later.

Impurities may also play an important

part in the nonreactivity of Pt_3Ti (or " Pt_3TiO_x "). The presence of carbon after the catalytic reactions is not greater than before, as is the case for the pure platinum surfaces (Table 2). No reversible or irreversible carbonaceous deposit would be formed during the reaction. Oxygen always segregates a little during the catalytic act but does not seem to influence catalytic behavior. After the oxidative treatments where the O/Ti ratios are slightly increased, the extensive hydrogenolysis reactions are not especially exalted as observed by Luck (34) when oxygen is largely present at the surface. In fact, under our conditions, the influence of the impurities at the surface cannot be very important in comparison with the ligand effect induced by the presence of titanium or TiO_x species ($x < 1$) in explaining the very weak catalytic activity observed for the Pt_3Ti (or " Pt_3TiO_x ") compound.

Catalytic Selectivities

The *selectivities in isomers S* are nearly the same for Pt_3Ti (or Pt_3TiO_x) and pure Pt when starting with acyclic hydrocarbons (Table 1), which means that the addition of titanium (or TiO_x) to platinum would not change the relative number of isomerization and hydrogenolysis sites. Nevertheless, for MCP (Table 4), the selectivity is lower for Pt_3Ti than for the Pt foil. The main hydrogenolyzed product obtained is methane, meaning that MCP is more strongly adsorbed at the Pt_3Ti surface than at the Pt surface.

The *distribution of hydrogenolyzed products* (Table 3) shows that the iso-unit mode of hydrogenolysis is favored with 2MP, whereas the C_2 -unit mode is favored with 3MP, contrary to the Pt polycrystalline foil. The hydrogenolysis reaction intermediates are therefore different on the one hand on Pt and Pt_3Ti (or Pt_3TiO_x), and on the other hand as a function of the structure of the hydrocarbon. With 2MP on Pt_3Ti (or Pt_3TiO_x), a model with 1,1,3-adsorbed species could explain the hydrogenolysis of the

C-C bonds. The bond which is broken is located in the β position with regard to the carbon doubly bonded to platinum, as in Anderson's proposal (35). Such species and bond breaks cannot explain the high contribution of isopentane obtained with 3MP. In that case, a chain of 3 carbons contains necessarily the tertiary one whereas this is not the case for 2MP. 1,2- or 1,1,2-adsorbed species (besides 1,1,3-adsorbed species) must also exist although higher activation energies are needed to hydrogenolyze such bonds.

The hydrogenolysis reactions of $n\text{Hx}$ are nearly statistical because this molecule does not possess a tertiary carbon atom which influences the reaction pathway. This hydrocarbon is therefore also more reactive.

The influence of the oxidative treatments on the distribution of the hydrogenolyzed products is not important. A slight decrease in the iso-/ C_2 -unit modes is, however, observed, mainly as an increase in the $\text{C}_{\text{II}}-\text{C}_{\text{II}}$ ruptures. This bond would be more sensitive to the presence of oxygen.

The *distribution of isomer products* obtained with all the hydrocarbons on Pt_3Ti (or Pt_3TiO_x) shows large contributions of Bz and cHx , as compared to the Pt polycrystalline foil (Tables 1 and 4). Again, the Pt(111) single crystal looks more like Pt_3Ti (or Pt_3TiO_x) by its higher contribution of Bz + cHx . The aromatization reactions are not one-step reactions for 2MP and 3MP. MCP cannot be considered an intermediate for this reaction because the increase in the contribution of Bz + cHx goes to the detriment of all isomer products. With $n\text{Hx}$, 1-6 ring closures lead to the direct formation of Bz or cHx . Nevertheless, this hydrocarbon does not lead to more Bz + cHx than the other hydrocarbons. Hence a direct reaction pathway does not increase the formation of Bz. Thus, $n\text{Hx}$ is not a necessary intermediate species for the aromatization reactions of the other hydrocarbons. The contributions of Bz + cHx are greater after the oxidative treatments, where, as seen before, the main difference

consists in an enhancement of the Ti/Pt ratio. When the Ti/Pt ratio is the highest, the Bz + cHx formation is the greatest [experiment MCP(2), Tables 2 and 4]. The presence of metallic titanium or very slightly oxidized titanium must therefore be responsible for this enhancement. *Pt-Ti bimetallic sites are necessary for the formation of Bz + cHx* and the dehydrogenation steps can occur on the Ti or TiO_x ($x < 1$) part of the bimetallic site or perhaps on isolated Pt atoms. The obtaining of products such as Bz + cHx is again consistent with the low ability of the Pt₃Ti (or Pt₃TiO_x) compound to chemisorb hydrogen. In fact, the dehydrogenated species would exist to give, on the surface, the hydrogen necessary to hydrogenate the intermediates of hydrogenolysis and isomerization reactions, hydrogen that could not be obtained by dissociation of the H₂ of the gas phase.

Another important point is the *formation of homologation products* with the Pt₃Ti (or Pt₃TiO_x) compound, the opposite of what was observed with the Pt foil. Again, the obtaining of these products must be linked to the presence of bimetallic Pt-Ti sites, to the same extent as the formation of Bz + cHx. In fact, Ti catalysts in which Ti is in a reduced state are well known Ziegler-Natta catalysts used for the polymerization reactions of ethylene, showing the homologation property of reduced Ti. The homologation products result, like benzene and cyclohexane, from at least two reaction steps. A readsorption of the initial products under static conditions could also explain these abnormal products, but if this assumption were correct, the same phenomenon would be observed for the Pt single crystals or the Pt foil. Luck (34) has observed that a diminution in the partial pressure of hydrogen leads to an enhancement of the contributions of homologation products for Pt-black catalysts. One can suppose that a diminution in the partial pressure leads to a decrease in the quantity of chemisorbed hydrogen.

These results confirm again that the abil-

ity of Pt₃Ti (or Pt₃TiO_x) for hydrogen chemisorption is very low. The C₁ or C₂ species formed, whose migration ability is great, would be recombined with the species strongly adsorbed at the surface. The very low carbon quantities found after the catalytic reactions are also explained by the presence of these homologation reactions. The surface of Pt₃Ti (or Pt₃TiO_x) would be self-cleaned for carbon. Such a phenomenon has already been observed by Aeiyaeh *et al.* (25) for Pt-Ni alloys where the carbon coverage remains very small when the surface concentration of nickel increases, Ni being more a cracking than an isomerizing metal. Nevertheless, in the case of nickel, the desorption rates of the C₁ species are greater than the rates of migration followed by a recombination. For MCP, the extensive cracking reactions are greater because this hydrocarbon must certainly be more strongly adsorbed at the surface than acyclic hexanes. This explains why more carbon is found after the catalytic experiments with MCP, essentially after experiment MCP(2) (Table 4).

A "clean" Pt₃Ti surface does not behave like a supported Pt/TiO₂ catalyst in the SMSI state (no Bz and formation of homologation products, differences in hydrogenolysis and isomerization reactions) (23). Nevertheless, a Pt₃Ti compound which has been hardly oxidized and in which small Pt metallic ensembles surrounded by TiO_x ($x \leq 2$) islands supported on Pt₃Ti are formed shows the same reaction mechanisms as a 0.2 wt% Pt/TiO₂ catalyst in the SMSI state (31). Moreover, it has been shown here that a Pt₃Ti (or Pt₃TiO_x) surface is not able to chemisorb H₂ and that is consistent with SMSI phenomena.

CONCLUSION

Study of the isomerization and hydrogenolysis reactions on a Pt₃Pt polycrystalline sample illustrate that the addition of Ti to Pt induces a decrease in the catalytic activity of platinum, as a consequence of two effects. On the one hand, there is a geometric effect leading to blockage of the

reactive sites [by Ti or TiO_x ($x < 1$) species] and/or to a diminution of the number of contiguous Pt atoms necessary for the catalytic act; on the other hand, there is an electronic or ligand effect leading to a diminution of the ability to chemisorb hydrogen. The low hydrogen chemisorption ability of Pt_3Ti (or Pt_3TiO_x) is confirmed by the formation of homologation products and by the presence of highly dehydrogenated species producing the hydrogen necessary for the other reactions. The contributions of benzene, cyclohexane, and homologation products are obtained by consecutive reactions and require the presence of bimetallic Pt-Ti sites where Ti can be slightly oxidized. Self-cleaning procedures occur on the surface, leading to an absence of carbonaceous deposits.

The Pt_3Ti (or Pt_3TiO_x) compound could be involved in strong metal-support interaction phenomena because it presents (i) a low ability for hydrogen chemisorption, (ii) a low catalytic activity for isomerization and hydrogenolysis reactions, and (iii) similar reaction mechanisms.

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