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Role of tungsten in supported Pt-W reforming catalysts Part II. Influence of the tungsten loading and metal-support interactions effect

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Support Pt-W catalysts are studied for 3-methylhexane reforming. The increase in tungsten loading and the use of SiO_2 support instead of Al_2O_3 in Pt-W catalysts leads to the decrease in total activity and aromatization selectivity. X-ray Photoelectron Spectroscopy (XPS) has been applied to bimetallic Pt-W/Al_2O_3 and SiO_2 catalysts with different Pt/W ratios to try to explain the catalytic results. Observations lead to the conclusion that tungsten species are strongly anchored on the support in Pt-W/Al_2O_3 catalysts at low tungsten concentration. In this case, tungsten species are not reducible (oxidation state +VI) and not accessible catalytically; tungsten is hindered by small Pt particles. At large tungsten loadings, beyond the theoretical monolayer capacity of the support, a fraction of tungsten species migrates to the surface and becomes reducible. This fraction of tungsten-reducible species and large platinum particles are accessible on the surface, but another fraction of tungsten species strongly anchored on the support remains not accessible and not reducible. A model is proposed.

Keywords: XPS; bimetallic catalyst; metal-support interaction; aromatization reaction

1. Introduction

Interactions with a support can dramatically change the properties of transition metals or transition metal oxides. It has been mentioned in the literature that the strength of the interactions between alumina and tungsten oxide inhibits the conversion of γ-Al_2O_3 into α-Al_2O_3 [1] and the reduction of tungsten oxide into tungsten metal [2]. Metal-support interactions also depend on the transition metal oxide loading, i.e. the coverage over the support surface. For example in supported-WO_3 systems, a monolayer coverage occurs at a loading of about 24% WO_3 over alumina (190 m^2/g) and reduction studies

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show, in this case, that the tungsten species, in interaction with alumina are not reducible at 550 ° C under H_2. Above this loading, bulk WO_3 present in excess of a monolayer coverage is reduced into tungsten metal [3,4]. On the other hand, the WO_3-SiO_2 interaction is weaker than WO_3-Al_2O_3, and WO_3 is reduced more easily on SiO_2 than on the Al_2O_3 support under the same conditions [5,6]. Unsupported WO_3 in completely reduced to tungsten metal under these conditions [6]. Supported platinum oxides are easily reduced at 200 ° C in H_2, even in bimetallic catalysts [5,7,8] and the catalytic behaviour of supported or bulk platinum metal is identical if the metallic particle size is large enough $d_s > 25$ Å [9].

In this paper we use X-ray photoelectron, spectroscopy (XPS) to bring some information about the influence of tungsten loading on the maxima activity rates and aromatization selectivity of 3-methylhexane.

2. Experimental

SAMPLE PREPARATION

Catalyst samples are prepared by successive impregnation method, taking into account the isoelectric point of Al_2O_3 (Woelm alumina [10]). WO_3 is dissolved in NH_4OH at 140 ° C (PH = 9) and the support carrier is impregnated with this solution. The pretreatment steps can be summarized as follows:

1–Impregnation of support Al_2O_3 (140 m^2/g, BET N_2) or SiO_2 (410 m^2/g) with ammonium paratungstate ($WO_3 + NH_4OH$).

2–drying at 60 ° C for 12 h;

3–reduction at 550 ° C for 2 h under H_2;

4–reimpregnation with hexachloroplatinic acid, for 1 hour;

5–drying at 120 ° C for 12 h;

6–reduction in-situ at 400 ° C for 2 h under H_2.

The atomic composition of the Pt-W catalysts used in the study and their codes are given in table 1.

Table 1
Atomic composition of the catalyst

Catalyst	Actual atomic percent		Other notation
	%Pt	%W	
5Pt-5W/Al_2O_3	4.42	3.79	
5Pt-5W/SiO_2	4.78	4.13	Pt-low W/support
5Pt+10W/Al_2O_3	4.19	10.67	
5Pt-25W/Al_2O_3	4.11	17.83	Pt-high W/support
5Pt-35W/Al_2O_3	2.76	21.24	

APPARATUS AND PROCEDURE

Have already been described in Part I [11].

X-RAY PHOTOELECTRON SPECTROSCOPY

All ESCA spectra are acquired with a VG ESCA 3 photoelectron spectrometer. The X-ray source is aluminum anode (Al Kα = 1486. 6 eV) operating at 12 kV and 10 to 20 mA without monochromator. The base pressure of the spectrometer is typically $< 10^{-9}$ Torr. All catalyst samples are analysed as pressed pellets and in-situ treatments are performed in a preparation chamber. The Al 2p (74.6 eV) and Si 2p (102.8 eV) photoelectron line for Al_2O_3 and SiO_2 supports respectively are used as references for bimetallic catalyst samples. According to the authors, the reference choice is delicate in the case of catalysts having two metals. This point has been discussed by Katrib et al. [12].

A Doniach-Sunjic [13] line shape is used to analyze the spectra. It describes an XPS peak as resulting from the convolution of a lorentzian curve depending on the core hole life time γ, an assymmetrical Gaussian curve whose asymmetry factor α is proportional to the density of states at the Fermi level and a second Gaussian curve taking into account the experimental resolution and the width of the incident radiation. Estimation of the surface concentrations are made by comparing the areas of the peaks after background subtraction and corrections due to differences in escape depths (a root square approximation is used) and in cross sections (using Scofield's tabulations [14]).

3. Results and discussion

CATALYTIC REACTIONS

We focussed our attention on the catalytic activity of the 3-methylhexane reaction and on the selectivity in aromatization process. The experiments are performed on alumina supported catalysts with a constant loadmg of platinum (5%) and various tungsten loadings from 5 to 35%. One silica supported catalyst is also used. The experiments are performed as a function of the partial hydrogen pressure. We may note, in fig. 1a and 1b, the existence of reactivity maxima for the various catalysts as a function of partial hydrogen pressure. This phenomenon has already been described in part I [11] for total activity, fig. 1a, and we have added the results for aromatization reaction, fig. 1b.

These results show that, when the tungsten loading in Pt-W catalysts increases from 5 to 35%, the maxima of aromatization rate and total activity for 3-methylhexane over Pt-W catalysts have a downwards tendency. On the other hand, when we compare 5Pt-5W/Al_2O_3 and 5Pt-5W/SiO_2 catalysts, we observe that the 5Pt-5W/Al_2O_3 catalyst is more performant for aromatization and total activity than 5Pt-5W/SiO_2 catalyst although the metals concentration is the same in both bimetallic catalysts.

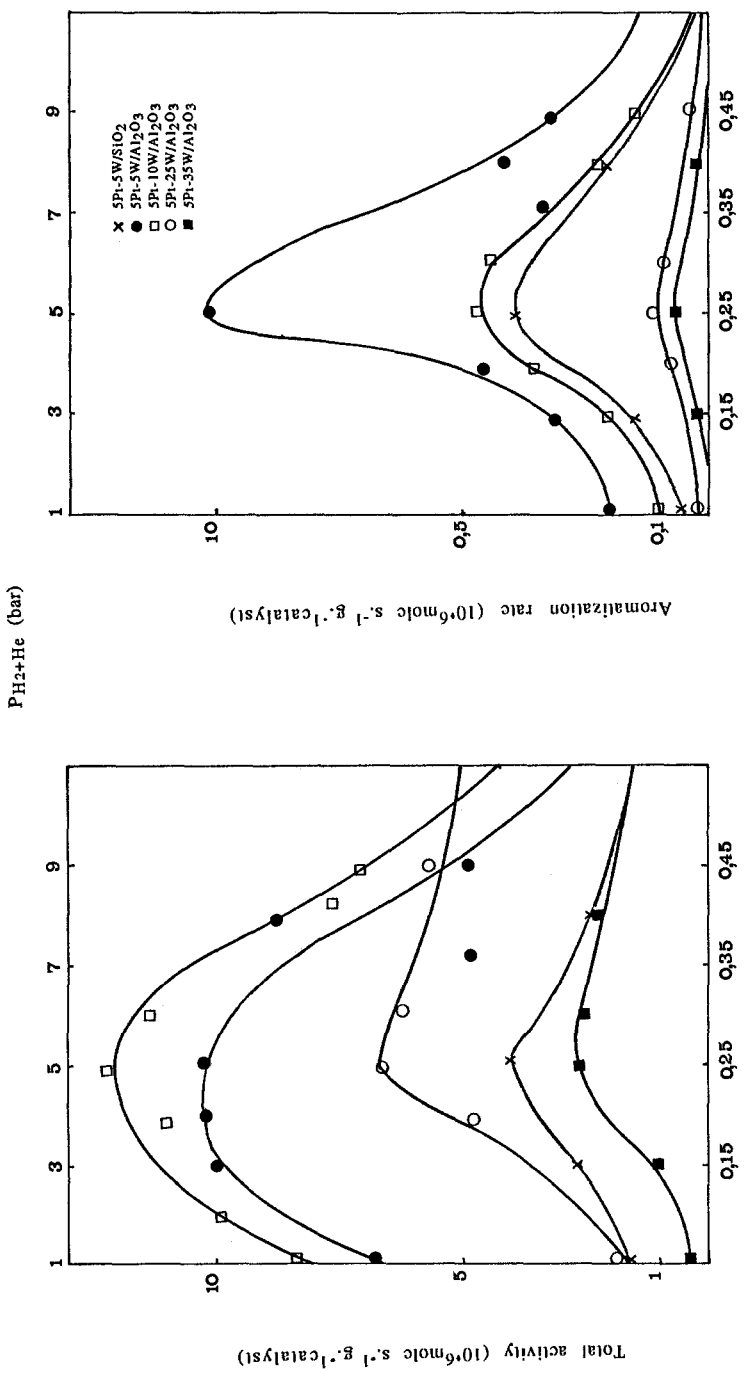


Fig. 1. Total activity (a) and aromatization rate (b) of 3-methylhexane as a function of hydrogen pressure over various catalysts. P_{HC}: 0.5 bar; T: 275 °C.

Table 2
ESCA binding energies (eV) of some tungsten and platinum compounds *

Tungsten compound	$4f_{7/2}$	Platinum compound	$4f_{7/2}$
W (metal)	31.3	Pt (metal)	71.2
WO_2	32.8	PtO	73.7
WO_3	35.5	PtO_2	74.5
$Al_2(WO_4)_3$	36.1	$PtCl_2$	73.4
WS_2	31.9	$PtCl_4$	75.5

* Binding-energy values were reproducible within ±0.15 eV.

From these results we tried to find a correlation between the change in catalytic behaviour, caused by the tungsten loading variation, and the surface state of the catalysts by using XPS facilities for the three typical catalysts: 5Pt-5W on Al_2O_3 and SiO_2 and 5Pt-35W on Al_2O_3.

X-RAY PHOTOELECTRON SPECTROSCOPY

Table 2 lists the binding-energy values determined for a number of standard tungsten and platinum compounds. In general, the values reported here are in good agreement with previously reported data for tungsten [6,15,16] and platinum [17–20].

Platinum binding energy analysis

After the final in-situ reduction (H_2 at 400 °C), the Pt $4f_{7/2}$ binding energy is always at 71.15 eV (see table 3) for 5Pt-5W/Al_2O_3 and 5Pt-35W/Al_2O_3 catalysts. These values are identical to that of Pt metal reported in table 2.

The value of the binding energy measured for the Pt $4f_{7/2}$ peak of the 5Pt-5W/SiO_2 sample (70.75 eV) is lower than the one measured for 5Pt-5(or 35)W/Al_2O_3 sample (71.15 eV). This positive shift may be due to: (a) the reference choice (Al 2p: 74.6 eV and Si 2p: 102.8 eV); or (b) the interactions between Pt and W which are different over Al_2O_3 and SiO_2 supports.

We can see from these results that upon reduction (H_2, 400 °C 2h) in all the Pt-W catalysts, metallic platinum is present whatever the support and the tungsten loading.

Table 3
XPS platinum binding energies analysis

Sample	Pt $4f_{7/2}$BE eV
5Pt-5W/Al_2O_3	71.15
5Pt-35W/Al_2O_3	71.15
5Pt-5W/SiO_2	70.75

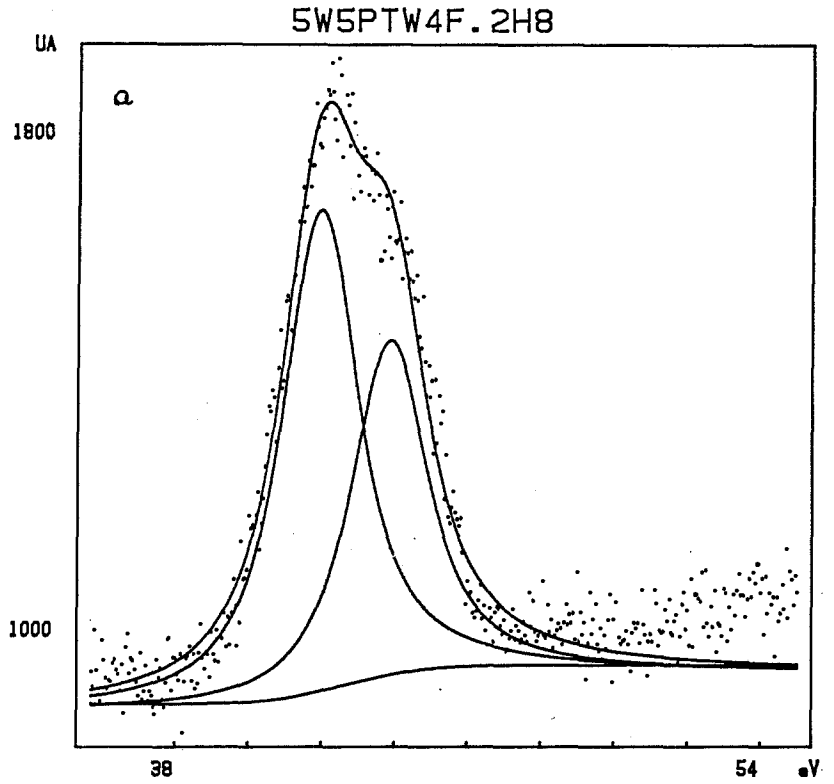


Fig. 2.a, b, c. Tungsten $4f_{5/2,7/2}$ XPS spectra of catalysts: (a) 5Pt-5W/Al_2O_3; (b) 5Pt-35W/Al_2O_3; and (c) 5Pt-5W/SiO_2, after reduction in-situ H_2 at 400° C/2 h. (·····) experimental curves; (———) deconvoluted curves; $0 < x < +VI$.

Tungsten binding energy analysis

5Pt-5W/Al_2O_3 catalyst. Representative XPS spectra of W $4f_{7/2,5/2}$ of this catalyst are reported in fig. 2a. It can be seen from the spectra that the binding-energy position of the W $4f_{7/2}$ remains at 36.2 eV after in-situ reduction. Although the binding-energy measured for the W $4f_{7/2}$ of this catalyst (36.2 eV) is close to the value measured for $Al_2(WO_4)_3$, the occurrence of this species cannot be based unambiguously on binding energy alone. It is evident from the data, however, that the tungsten is present exclusively in the +VI oxidation state. No reduction occurs on this catalyst.

5Pt-35W/Al_2O_3 and 5Pt-5W/SiO_2 catalysts. The W $4f_{7/2,5/2}$ spectra of these catalysts are reported in fig. 2b and 2c respectively. A peak corresponding to W $4f_{7/2}$ (W^{+VI}) is always obtained on the two catalysts at 36.2 eV associated to broadening on the lower binding energy side. This shift towards lower binding energy can be interpreted as partial reduction of W^{+VI}.

This reduction corresponds to a W oxidation state between +VI and 0. Depending on the catalysts, the reduction can be explained differently: For the 5Pt-35W/Al_2O_3 catalyst, the reduction of tungsten is due to an excess of

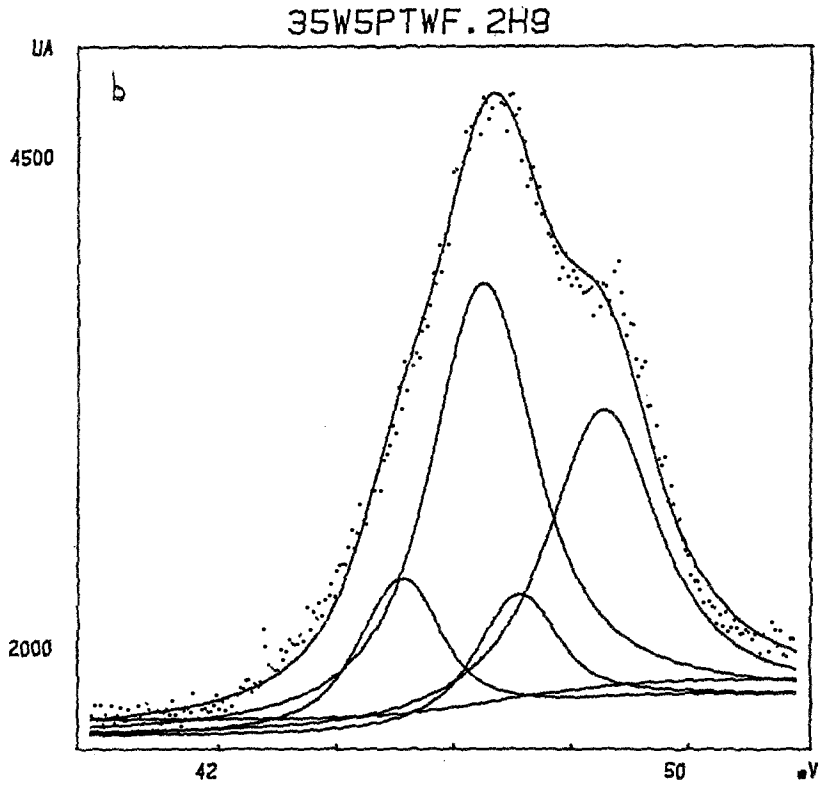


Fig. 2b.

monolayer coverage, the bulk WO_3 present is able to be reduced because of the weak interactions between bulk WO_3 and Al_2O_3 support; for 5Pt-5W/SiO_2 catalyst (no reduction of W occurs in 5Pt-5W/Al_2O_3 catalyst having the same metal loadings), reduction of tungsten is due to the weaker interactions between metal and SiO_2 compared to Al_2O_3 support.

In both catalysts, the reduction of tungsten oxide is likely to be accelerated by the presence of platinum [21]: catalysis by platinum is apparently due to the dissociation of molecular hydrogen on the metal, followed by diffusion of adsorbed hydrogen atoms across the metal-oxide interface.

Pt, W, Al and Si atomic ratios

It has been shown that XPS metal-to-support intensity ratios can provide important information regarding the dispersion and crystallite size of supported metal particles [22–24]. A linear relationship between the XPS intensity and the catalyst loading is expected for catalysts having constant crystallite size. Modification from linearity can be used to detect changes in the nature of catalyst surface species.

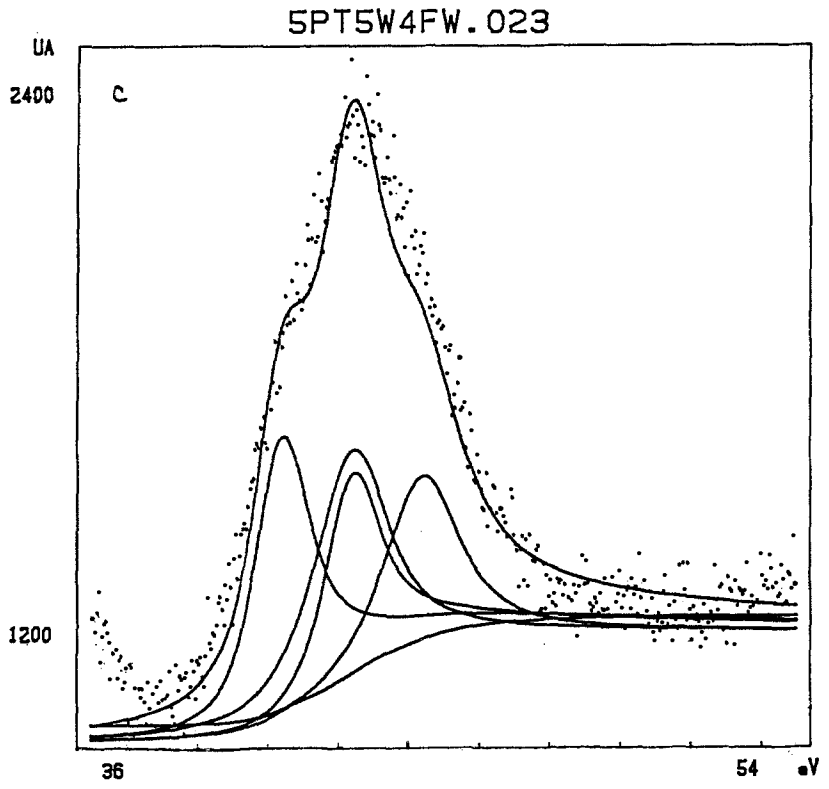


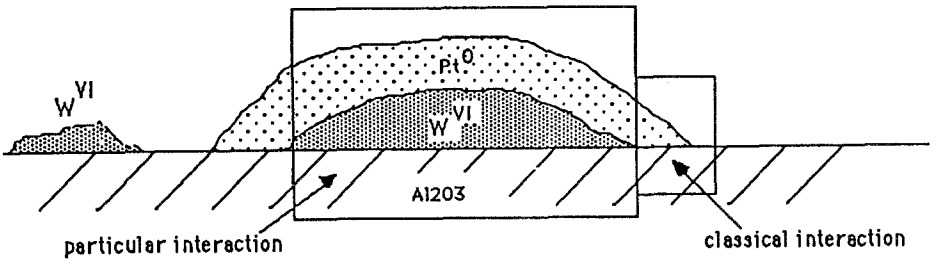
Fig. 2c.

Results are reported in table 4. The "expected" values are calculated from the results of microanalysis given in table 1, taking into account the oxygen of alumina and supposing that all the tungsten is WO_3. The Pt/W, Pt/Al (or Si) and W/Al (or Si) ratios are therefore true metal/metal atomic ratios. So are of course the "observed" values calculated from the XPS spectra. It is worth noting that the probing depths in all cases are very similar since the binding energies lie in the range 30 eV (W4f) to 100 eV (Si2p).

A first result is that the observed Pt/Al (or Si) ratios are not very different from the expected values, within experimental errors. This is not the case when

Table 4
Atomic Pt/Al, Pt/Si and Pt/W ratios obtained from XPS data, of the four reduced catalyst series versus W loading and support

Catalyst	Atomic Pt/W		Atomic Pt/Al (or Si)		Atomic W/Al (or Si)	
	observed	expected	observed	expected	observed	expected
5Pt-5W/Al_2O_3	0.56	1.11	0.009	0.012	0.017	0.010
5Pt-35W/Al_2O_3	0.01	0.12	0.009	0.007	0.916	0.060
5Pt-5W/SiO_2	0.20	1.08	0.008	0.014	0.041	0.013



Model A.

considering W. For Pt-low W support catalysts, W/Al and W/Si are significantly higher, and therefore Pt/W are lower than expected. For Pt-high W/aluminum, the differences are huge. There are at least 10 times more tungsten atom, as compared to Pt and Al, than expected. If one remembers that tungsten was impregnated first our results mean that the activation treatment has resulted in a diffusion of tungsten oxide on top of platinum.

These two groups of catalysts corresponding to two different catalytic behaviors lead us to suggest two kinds of surface structure.

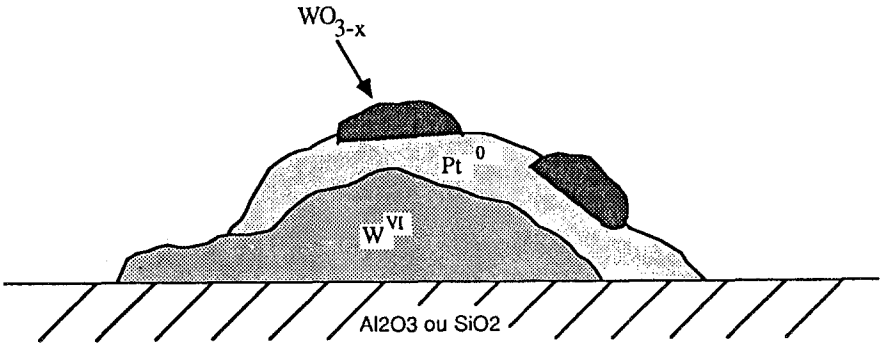
(i) For Pt-low W/Al_2O_3 catalyst (Model A).

The platinum particles are small (Part 1). A synergistic activity and selectivity of the catalyst is found which may be due to a particular interaction between Pt° and WO_3, instead of the classical Pt°-Al_2O_3.

(ii) For Pt-high W/Al_2O_3 catalyst (Model B).

There are on the surface, metallic platinum and tungsten with various oxidation states from +VI to 0. The W^{+VI} may correspond to the tungstate for which is strongly anchored on the support; the lower tungsten oxidation states may be obtained by the reduction of migrating fraction on top of platinum particles.

The model of Pt-low W/SiO_2 catalyst is in between these two models.



Model B.

4. Conclusion

These results pointed out two types of catalysts: (i) Pt-low W/Al_2O_3 catalysts, with no reduced tungsten. (ii) Pt-high W/Al_2O_3 and Pt-low W/SiO_2 catalysts, with a fraction of reduced tungsten attributed to the weak interactions between WO_3 and the support.

"Classical" strong metal-support interactions, as observed in Pt/TiO_2 catalysts, lead to the suppression of the ability of chemisorbing H_2 and CO and to a decrease in activity for some reactions (electronic effect) [25]. The "metal-support-interaction" between the low tungsten concentration and the support in Pt-W catalysts does not affect the activity and selectivity. Contrary to the insertion of high tungsten loading in supported Pt-W catalysts which increases the tungsten moderator interaction effect between Pt and the support leading to Pt migration-agglomeration phenomenon over the surface (sintering). In this case, we observe a decrease in activity and selectivity.

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