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Reactions of Labelled Hexanes on Pt–WO_3/Al_2O_3 Catalysts

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Pt–WO_3/Al_2O_3 (Pt : W = 1 : 1) catalysts were prepared by different methods and characterized by chemisorption, TPD, TPR, and TEM techniques. The various catalysts do not show important differences in the catalytic reactions studied. Pt–WO_3/Al_2O_3 systems catalyse hexane isomerisation with low selectivity. Isotopic tracer measurements show that the reaction proceeds via classical cyclic and bond-shift mechanisms. Inside the general reaction pathways of the isoalkanes, methyl migration is favoured and involves the participation of the tertiary carbon atom both in the carbon–carbon bond rupture and in the carbon–carbon bond reformation. On these catalysts no correlation between the relative contribution of the cyclic mechanism and the nonselective hydrogenolysis of the methylcyclopentane was found. Moreover, 2-methyl-2-pentene follows an exactly similar reaction pathway to 2-methylpentane. The results are explained by the suggestion that the "Pt–WO_x" interface is responsible for the catalytic behavior of these systems. A mechanism for hydrocracking and isomerisation is proposed. © 1993 Academic Press, Inc.

INTRODUCTION

Alloy or bimetallic catalysts show high activity and selectivity in reforming reactions. In general they are composed of platinum associated with a Group VIII metal, such as Pt–Re/Al_2O_3 (*1*) or Pt–Ir/Al_2O_3 (*2*). Besides these catalysts, sometimes Pt is associated with Sn (*3*) or Mo (*4*) but it is seldom done to associate platinum with tungsten, which is rarely in the metallic form but rather an oxide.

The main goal in our case was to modify the catalytic properties of an alumina-supported platinum catalyst by adding WO_3. It is known that this oxide has some specific catalytic properties in metathesis reactions or disproportionation of alkanes (*5*), whereas on the contrary metallic tungsten surfaces are poor catalysts for bond shift rearrangement. However, they are capable of breaking chemical bonds, but the fragments are bound too tightly to the surface to allow for recombination into useful products. On the other hand, at low hydrogen pressure, O'Donohoe *et al.* (*6*) have found that tungsten films are very good catalysts for homologation. Their results revealed how sensitive the yields of homologated products are to hydrogen pressure and they pointed out that the metal surface and carbided surface may thus be envisaged as constituting a dual-functional catalyst. Levy and Boudart (*7*) have shown that tungsten carbides catalyse hydrocarbon conversion reactions at temperatures similar to those of supported noble metals.

In this paper we describe hexane hydrocracking and isomerisation on Pt–WO_3/Al_2O_3 using isotopic tracer studies.

EXPERIMENTAL

Catalyst Preparation

Two series, a and b, of Pt–WO_3/Al_2O_3 catalysts were prepared by successive impregnation of γ-alumina (ex Woelm A.G., specific surface area 164 $m^2\ g^{-1}$, pore volume 0.28 $cm^3\ g^{-1}$) as follows.

For catalysts 1a, 3a, and 4a the carrier was first impregnated (24 h) with a solution of $(NH_4)_{10}H_2W_{12}O_{42} \cdot nH_2O$, which was

0021-9517/93 $5.00

TABLE 1

Atomic and Weight Percentages, and Methods of Preparation of $Pt-WO_3/Al_2O_3$ Catalysts

Cat.	Percentages				Methods of preparation
	Atomic		Weight		
	Pt	W	Pt	W	
1a	51	49	3.8	3.4	"dry" impregn., reduction in H_2
1b	47	53	3.2	3.4	"dry" impregn., calcination in air[a]
2b	52	48	3.8	3.3	"wet" impregn., calcination in air[a]
3a	84	16	4.4	0.8	"wet" impregn., reduction in H_2
4a	52	48	4.4	3.8	"wet" impregn., reduction in H_2

[a] Calcination in air means that the samples were calcined after the two impregnation steps.

slowly evaporated. Then the impregnated support was dried at 390 K (24 h), reduced in a stream of H_2 at 670 K (4 h), and reimpregnated with a solution of H_2PtCl_6. The same procedures were undertaken for the drying and reduction steps.

Catalysts 1b and 2b were prepared under the same conditions, but instead of the reduction step, after each impregnation, the samples were calcined in air at 670 K (4h).

Catalysts 1a and 1b were prepared from aqueous minimum volume solution ("dry" impregnation), and 2b, 3a, and 4a were prepared following a "wet" impregnation technique.

The composition of the samples and the methods of preparation are listed in Table 1.

TPR and TPD Measurements

The catalysts were characterized by using thermoprogrammed techniques and also by hydrogen and oxygen chemisorptions, as described elsewhere (*8*). Temperature-programmed reduction (TPR), oxidation (TPO), and desorption (TPD) have been followed in the apparatus described in Ref. (*9*). A stream of H_2–Ar or of O_2–Ar (10% vol. H_2 or O_2) mixture, purified by passing through Pd/Al_2O_3 and molecular sieves, was used as a reducing or oxidising gas. The gas flow rates were 60 cm^3 min^{-1} and standard heating rates 25 K min^{-1} within the temperature range 290–670 K. The carrier gas (argon) for hydrogen TPD was passed through a system for purification and removal of oxygen traces and water impurities (*10*). The water produced in the TPR process was cooled and trapped using a dry ice–ethanol mixture.

Catalytic Reactions

The supported $Pt-WO_3/Al_2O_3$ catalysts were studied for the hydrocarbon (C_6) - hydrogen reactions in an all-glass, grease-free system already described in Ref. (*11*). Before the reaction, catalysts were reduced under a hydrogen flow at 770 K (4 h). Reactions were performed at atmospheric pressure. The hydrocarbon pressure was around 0.6 kPa and the temperature was kept at 520 or at 550 K. The weight of the catalyst samples was about 0.22 g. Reaction products were analysed by gas chromatography.

Labelled Hydrocarbons

All ^{13}C-labelled hydrocarbons were prepared from the corresponding labelled alcohols. The synthesis of these compounds has been described previously (*12*). The ^{13}C content in reaction products was measured by mass spectrometry after separation in a chromatography column.

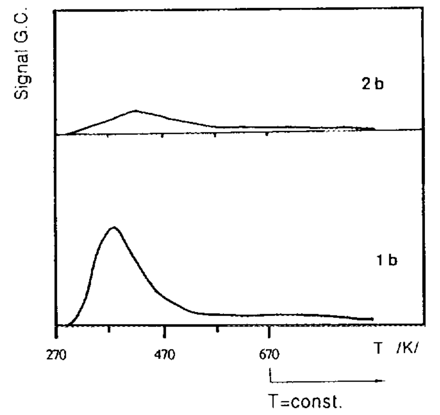


FIG. 1. TPR profiles of Pt-WO_3/Al_2O_3 catalysts prepared by "dry" (1b) and "wet" (2b) impregnation.

RESULTS

CATALYST CHARACTERIZATION

TPR and TPD Measurements

Figure 1 shows the TPR profiles of oxidised 1b and 2b catalysts. The curves are characterized by the presence of two steps of reduction of the oxidised catalysts. The first step has a maximum rate at about 380 K, which corresponds to the maximum rate of reduction of Pt/Al_2O_3 (*13*, *14*). The amounts of hydrogen taken up for the TPR of catalyst 2b are lower than those for 1b. The second step is characterized by nonreturn to the base line. This may be due to the reduction of tungsten oxides and/or to the reduction of the Pt-WO_3 interface. This process is initiated at about 570 K. The alumina-supported tungsten oxide, especially when the WO_3 coverage is around a monolayer or less, is more difficult to reduce than bulk WO_3, which is not reduced below 700 K (*15*). For our catalysts the presence of platinum crystallites is responsible for the observed shifts of the initial reduction towards lower temperatures. The platinum crystallites act as active centres for hydrogen dissociation and thus via hydrogen spillover catalyse the reduction of the interfacial and/or the supported tungsten oxide on alumina. It has been shown that partial reduction of tungsten oxide by Pt occurs at a lower temperature to yield hydrogen tungsten bronzes (HTB_x) (*16–18*).

Hydrogen TPD profiles are presented in Fig. 2, (i) after pulsed adsorption technique (full lines) and (ii) after temperature activated adsorption and cooling in the stream of hydrogen from 670 to 290 K (dashed lines). The TPD spectra are stretched over a relatively wide temperature range (290–670 K) showing three flattened maxima. The amount of hydrogen desorbed at low temperature (up to 570 K), after pulsed adsorption, is greater for catalyst 1b than 2b, as well as after temperature activated adsorption, for TPD above 570 K. Catalyst 1b, prepared by "dry" impregnation, shows greater adsorptive properties compared to catalyst 2b prepared by the "wet" route.

The TPR and TPD results presented above and the chemisorption data described in a previous paper (*8*) show that the "dry" impregnation leads to three times higher platinum surface area (catalyst 1b 140 $m^2\ g_{Pt}^{-1}$; average particle size ~ 2 nm) than "wet" impregnation. No substantial changes

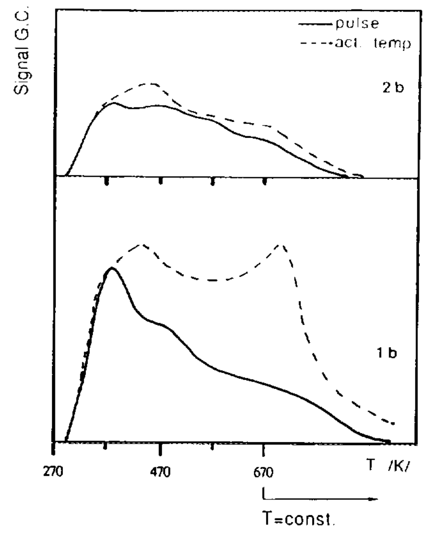


FIG. 2. TPD profiles of Pt-WO_3/Al_xO_3 catalysts (prepared by "dry" (1b) and "wet" (2b) impregnation) after pulsed (——) and temperature activated adsorption (– – –).

take place in the adsorptive–desorptive properties for the catalysts prepared with different techniques via either the calcination in air or reduction in hydrogen at 670 K.

TEM Measurements

Catalysts 3a and 4a, reduced in hydrogen at 670 K, have been examined by transmission electron microscopy. The extractive technique was used for separation of the platinum particles by the destruction of alumina in a diluted HF solution. A Philips TEM 300 G transmission electron microscope was used, with a resolution of about 0.5 nm (*19, 20*). The mean particle size, determined from measurements of more than 2000 particles, is about 1.7 nm for these two catalysts.

Two series of measurements (TPD–TPR and TEM) show that catalysts 1b, 3a, and 4a have approximately the same particle size of 2.0 nm compared to 5.5 nm for catalyst 2b.

CATALYTIC REACTIONS

Unlabelled C_6 Hydrocarbon Reactions

The catalytic reactions were performed on five alumina-supported Pt–WO_3 catalysts (1a, 1b, 2b, 3a, and 4a) prepared following the different methods mentioned above. The results are compared to those obtained on the 4.1% Pt/Al_2O_3 catalyst having a dispersion of H/Pt = 0.55 (*21*). The hydrocarbons used were: 2-methylpentane (2MP), 3-methylpentane (3MP), *n*-hexane (*n*H), 2-methyl-2-pentene (2MP2═), methylcyclopentane (MCP), and 2,3-dimethylbutane (23DMB). All these hydrocarbons were purchased from Fluka and were puriss grade.

Hydrocarbon reactions can be divided into two groups: hydrocracking and isomerisation.

Hydrocracking reactions. In the hydrocracking process one has to distinguish between the different carbon–carbon bonds involving primary, secondary, and tertiary carbon atoms.

The hydrocracking distributions are shown in Table 2. The table contains the following terms: the nature of the catalyst (Cat.), the starting hydrocarbon (HC), the reaction temperature (*T*), the overall conversion (Conv.), the hydrocracking selectivity (S_H), and the various products (expressed in mol %) obtained by only *one* carbon–carbon bond rupture of the starting compound. These reactions are: depropylation ($2C_3$), deethylation ($iC_4 + C_2$ and $nC_4 + C_2$), and demethylation ($iC_5 + C_1$ and $nC_5 + C_1$). This table also includes the reactivity factor ω as defined by Leclercq *et al.* (*22*). It represents the ratio between the experimental and the statistical hydrocracking reaction rates. We may note that extensive cracking does not occur; it represents less than 2% of the overall cracked products.

The total activity measured at 520 K is low and increases about five times at 550 K. For the catalytic reactions performed at 520 or 530 K we observed high hydrocracking selectivity values, namely about 70–80% for 2MP and 3MP and 60% for *n*H. These values suggest that the selectivity depends on the structure of the hydrocarbon molecule but not on the catalyst preparation method. On the other hand, the 2-methyl-2-pentene reacts as the alkane both for the total conversion and for the selectivity and the cracking distribution.

The reactivity factor ω shows that middle fission, depropylation, is favoured for *n*H. When a comparison is made of 2MP and 3MP cracking patterns obtained on Pt–WO_3/Al_2O_3 catalysts and on Pt/Al_2O_3 catalyst we may note some differences in the carbon–carbon bond rupture involving a tertiary carbon atom. This reaction is favoured on Pt-WO_3–Al_2O_3 catalysts for the demethylation reaction giving $nC_5 + C_1$ from 2MP and 3MP; ω has a value higher than 1, whereas its value is lower than 1 on Pt/Al_2O_3 catalyst.

Isomerisation reactions. Table 3 shows the results concerning the same experiments as mentioned in Table 2 but for the isomer distributions obtained on Pt–WO_3/Al_2O_3 catalysts with *n*H, 2MP, 3MP, 23DMB, and

TABLE 2

Hydrocracking Distributions on Pt–WO_3/Al_2O_3 Catalysts

Cat.	HC	T (K)	Conv. (mol %)	S_H (mol %)	Cracking products									
					$2C_3$		$iC_4 + C_2$		$nC_4 + C_2$		$iC_5 + C_1$		$nC_5 + C_1$	
					(mol %)	ω	(mol %)	ω	(mol %)	ω	(mol %)	ω	(mol %)	ω
1a	nH	550	2.2	62	37	1.8	0	—	33	0.8	0	—	30	0.7
	2MP	520	2.5	83	19	1.0	21	1.1	0	—	12	0.6	48	1.2
		550	13.8	76	19	1.0	22	1.1	1	—	14	0.7	44	1.1
	2MP2═	550	8.8	75	19	1.0	18	0.9	1	—	18	0.9	44	1.1
	3MP	520	2.4	83	0	—	0	—	25	0.6	51	1.3	24	1.2
		550	14.3	75	1	—	1	—	26	0.7	52	1.3	20	1.0
	23DMB	550	0.8	84	15	1.8	0	—	0	—	85	1.1	0	—
1b	2MP	520	0.8	89	21	1.1	17	0.9	0	—	13	0.7	49	1.3
		550	5.5	69	20	1.0	20	1.0	0	—	14	0.7	46	1.2
2b	nH	520	2.3	66	49	2.5	0	—	22	0.6	0	—	29	0.7
		550	12.7	70	47	2.4	0	—	24	0.6	1	—	29	0.7
	2MP	520	1.9	85	22	1.1	19	1.0	0	—	12	0.6	47	1.2
		550	15.5	75	20	1.0	20	1.0	1	—	13	0.7	46	1.2
	2MP2═	520	2.0	85	21	1.1	20	1.0	0	—	11	0.6	48	1.2
		550	15.2	76	23	1.2	22	1.1	2	—	15	0.8	38	1.0
	3MP	520	2.0	84	0	—	0	—	22	0.6	55	1.4	23	1.2
		550	16.6	76	3	—	1	—	24	0.6	51	1.3	21	1.1
3a	2MP	530	6.5	67	23	1.1	22	1.1	0	—	15	0.7	40	1.0
4a	2MP	530	25.0	80	22	1.1	24	1.2	3	—	19	0.9	32	0.8
Pt (*21*)	2MP	527	18.0	43	19	1.0	23	1.2	2	—	21	1.1	35	0.9
	3MP	527	12.0	41	2	—	1	—	29	0.7	55	1.4	13	0.7

Note. Cat, nature of the catalyst; HC, reactant hydrocarbon; T, temperature; Conv., overall conversion; S_H, hydrocracking selectivity; ω, reactivity factor (*22*). C_3, propane; iC_4, nC_4, iso and *n*-butane; iC_5, nC_5, iso and *n*-pentane; *n*H, *n*-hexane; 2MP, 2-methylpentane; 2MP2═, 2-methyl-2-pentene; 3MP, 3-methylpentane; 23DMB, 2,3-dimethylbutane.

2MP2═. In Table 3 we present the total reaction rates r_T (10^8 mol s^{-1} g^{-1}) and the various ratios of reaction products: R_1 = 2MP/3MP, R_2 = 3MP/*n*H, and R_3 = 2MP/*n*H. The relative contribution of the methylcyclopentane is high even though the conversion is high. The 2,2-dimethylbutane is formed in a very small amount from *n*H, 2MP, and 3MP. From 2,3-dimethylbutane only 2,2-dimethylbutane is formed. The ratios R_1, R_2, and R_3 do not vary strongly with the catalyst used. We have also compared these results to those obtained on 4.1% Pt/Al_2O_3 (*21*).

Methylcyclopentane hydrogenolysis. The results of the hydrogenolysis of methylcyclopentane are presented in Table 4. The selectivity in hydrogenolysis, S_{HG} (mol %), is between 96 and 100%. Some extensive cracking reactions are observed but their relative contributions are low and methane is the main product. On the other hand the ring enlargement reaction is not observed. Benzene and cyclohexane products are not formed. We can see the presence of cyclopentane (CP) which is obtained by a simple carbon–carbon bond rupture. For this product an exocyclic bond rupture between primary and tertiary carbon atoms is involved. Its contribution is around 8 ± 2% compared to endocyclic bond ruptures which are around 92 ± 2%.

The R_1 = 2MP/3MP and R_2 =3MP/nH ratios are similar for all catalysts. The aver-

TABLE 3

Isomerisation Product Distributions on $Pt-WO_3/Al_2O_3$ Catalysts

HC	Cat.	T (K)	r_T	S_i	Isomerisation products (mol %)					R
					22DMB	2MP	3MP	nH	MCP	
nH	1a	550	1.2	38	0	20	38	—	42	R_1 = 0.5
	2b	520	2.8	34	0	18	49	—	33	0.4
		550	16.1	30	0	49	28	—	23	1.8
2MP	1a	520	2.4	17	3	—	22	23	52	R_2 = 1.0
		550	13.5	24	2	—	29	43	26	0.7
	1b	520	0.5	11	5	—	12	18	65	0.7
		550	3.3	31	2	—	28	31	39	0.9
	2b	520	1.3	15	2	—	15	22	61	0.7
		550	13.4	25	2	—	27	43	28	0.6
	3a	530	4.3	33	0	—	48	52	—	0.9
	4a	530	2.7	20	0	—	48	33	19	1.5
	Pt (*21*)	527	—	56	0	—	42	54	4	0.8
2MP2=	1a	550	6.4	25	2	—	29	43	26	R_2 = 0.7
	2b	520	1.2	15	2	—	17	24	57	0.7
		550	7.8	24	2	—	28	47	23	0.6
3MP	1a	520	1.8	17	4	39	—	14	43	R_3 = 2.8
		550	16.9	25	4	54	—	23	19	2.3
	2b	520	1.9	16	3	39	—	15	43	2.6
		550	11.8	24	3	56	—	25	16	2.2
	Pt (*21*)	527	—	58	0	64	—	30	6	2.1
23DMB	1a	550	0.9	16	75	0	0	0	25	—

Note. S_i, isomer selectivity ($S_i + S_H = 100$ %) (mol %); r_T, total reaction rates (10^8 mol s^{-1} g^{-1}); MCP, methylcyclopentane, plus legend in Table 2; R_1 = 2MP/3MP; R_2 = 3MP/nH; R_3 = 2MP/nH.

TABLE 4

Product Distributions of the Hydrogenolysis of Methylcyclopentane on $Pt-WO_3/Al_2O_3$ Catalysts

Cat.	T (K)	r_T	S_{HG}	Hydrogenolysis products (mol %)				R_1	R_2
				CP + C_1	2MP	3MP	nH		
1a	520	3.6	96	7	48	19	26	2.5	0.7
	550	30.4	97	6	49	17	28	2.9	0.6
1b	520	3.4	96	6	47	20	27	2.4	0.7
	550	18.0	97	3	47	21	29	2.2	0.7
2b	520	7.0	96	11	40	20	29	2.0	0.7
3a	520	47.4	100	3	45	19	33	2.4	0.6
	550	320.0	100	2	45	19	34	2.4	0.6
4a	520	20.0	100	10	36	18	35	2.0	0.5
	550	150.0	100	8	38	20	34	1.9	0.6

Note. S_{HG}, hydrogenolysis selectivity (mol %); CP, cyclopentane; C_1, methane; R_1 = 2MP/3MP; R_2 = 3MP/nH, plus legend in Table 2.

TABLE 5

Isomer Distributions (mol %) in Labelled Hexane Reactions on Pt–WO_3/Al_2O_3 Catalysts at 520 K

Cat.												
			% CM (1)		 [b]	% BS A[a] (2)			% CM (3)			% CM (4)
1a	13	87	13	87	13	13	71	29	58	70	30	70
2b	25	75	25	86	14	14	—	—	—	68	32	68
3a	31	69	31	82	18	18	—	—	—	—	—	—
4a	31	69	31	90	10	10	63	37	74	—	—	—
Pt(21)	30	70	30	99	1	1	57	43	86	90	10	90

[a] % BS A (2) + % CM (3) = 100% − BS B(21).

[b] *n*-Hexane-2-^{13}C includes *n*-hexane-1-^{13}C formation.

age value is 0.6 ± 0.1 for the 3MP/nH ratio, which is near the statistical one of 0.5, characteristic for highly dispersed supported platinum catalysts (*21*). In the R_1 ratio only secondary carbon–carbon bonds are involved; the only difference is the position of the C–C bond from the tertiary carbon atom. The 2MP formation involves a β bond rupture and the 3MP is formed via a γ bond rupture by comparison with the tertiary carbon atom. We may note that R_1 is higher than 2, which is the statistical value, on catalysts 1a, 1b, and 3a. We can observe that on catalyst 4a only statistical carbon–carbon bond ruptures occur.

Labelled C_6 Hydrocarbon Reactions

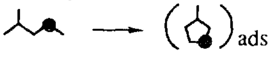
The experiments were carried out on catalysts 1a, 2b, 3a, and 4a using 2-methyl-2-^{13}C-pentane, (),

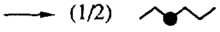
2-methyl-4-^{13}C-pentane, ()

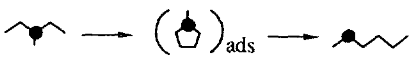
and 3-methyl-3-^{13}C-pentane, ().

The relative distributions of the various mechanisms are presented in Table 5.

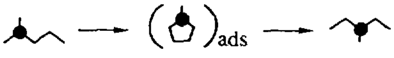
The relative contribution of the cyclic mechanism depends on the studied reactions. In other words, it will depend on the carbon–carbon bond rupture which will occur in the intermediate adsorbed species, i.e., in the adsorbed methylcyclopentane; either the tertiary carbon atom is involved or not. This means we look either to *n*-hexane or to 3-methylpentane formation, respectively.

For the labelled-*n*-hexane formation, the percentage of the cyclic mechanism is about 60–70% for 



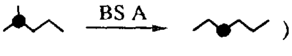
and for 

on these catalysts. For the reaction



the percentage is about 15–30% on the four catalysts. These values are smaller than those obtained on well-dispersed supported platinum catalysts, which are around 90% and higher than 30%, respectively, for *n*H and 3MP formation (*21*, *23*).

Concerning the bond-shift mechanisms we have already seen (*21*) that in the chain-lengthening reaction, two types of mechanism occur: these are bond shift A and B, involving either a methyl migration or a propyl migration, respectively. The bond shift A contribution on Pt–WO_3/Al_2O_3 catalysts

()

is between 10 and 18%. These values are higher than those already obtained on alumina-supported platinum catalysts of low dispersion (6–10%); on the contrary, for catalysts where platinum particles are well dispersed, the bond shift A is not at all present (*21*). It is necessary to mention that WO_3/Al_2O_3 is not active in these reactions below 620 K (*24*). One has also to mention that alkane (2MP) and alkene (2MP2=) react with the same rate and give the same product distributions.

DISCUSSION

The catalysts used are constituted of alumina-supported tungsten oxide and platinum. We may expect that reactive sites could be located either on the metallic or on the oxide surface or even at the interface Pt–WO_x. As all the experiments were performed at low conversions, we do not focus on the activity but on the selectivity of these reforming reactions.

The Cracking Reactions

The Pt–WO_3/Al_2O_3 catalysts have a high cracking power, always higher than 65% compared to 42% on Pt/Al_2O_3 catalysts, within the same temperature range (*21*) (Table 2). The increase in the carbon–carbon bond rupture process may be due to the Pt–WO_3 interaction. It has been observed by Iglesia *et al.* (*25*) and Frennet *et al.* (*26*) that *n*-heptane and *n*-hexane hydrogenolysis is the predominant reaction on Pt–WO_3/Al_2O_3 rather than on Pt/SiO_2 or oxygen-exposed WC, and the cracking reactions strongly favour midmolecule rupture.

The cracking reactions are simple; there is no repetitive process as seen in Table 2. From *n*-hexane, neither isobutane nor isopentane are formed. Propane and *n*-butane are not formed from 3-methylpentane and 2-methylpentane, respectively, and with 2,3-dimethylbutane only propane and isopentane are formed, following the statistical ruptures around 20 and 80%, respectively. When the five hydrocarbons used are compared (Table 2), we may note that the presence of a tertiary carbon atom increases the selectivity in cracked products (with 2MP $S_H \approx 80\%$; with *n*H $S_H \approx 60\%$). This is not the case when two tertiary carbon atoms are present in the molecule; then the selectivity is similar to that obtained for a molecule having only one tertiary carbon atom.

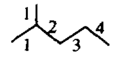
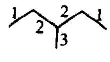
The influence of temperature on hydrocracking selectivity (S_H) follows the same trends as for classical Pt/Al_2O_3 catalysts. S_H decreases when the temperature increases. The apparent activation energy for isomerisation, on platinum catalysts (*11, 28–30*) is higher than for cracking. From 520 to 550 K, S_H decreases from 85 to 75% for all the products, except for *n*H, and on all the catalysts used.

Looking to the cracking mechanisms we have compared our results for Pt–WO_3/Al_2O_3 with those obtained on various platinum catalysts, using the reactivity factor ω as defined by Leclercq *et al.* (*22*), the ratio of the experimental to the statistical rate of cracking, which is presented for different platinum catalysts in Table 6. The catalyst used by Leclercq *et al.* (*22*) was 2 wt% Pt/Al_2O_3 with a platinum dispersion of 60 ± 4%; the four other platinum catalysts, presented in Table 6, have a hydrogen accessibility measured by H_2 chemisorption of 55% for 4.1% Pt/Al_2O_3 (21) and 100, 35, and 2% for 0.2% Pt/Al_2O_3, 10% Pt/Al_2O_3, and platinum black, respectively (*27*). We can see that the reactivity factor ω concerning the rupture C_I–C_{III} is higher on Pt–WO_3/Al_2O_3 compared with those obtained on Pt catalysts, and this is true for 2MP and 3MP. This factor decreases when the dispersion of Pt/Al_2O_3 catalysts also decreases, whereas it stays stable for different Pt–WO_3/Al_2O_3 catalysts.

The cracking distribution is the same with 2-methyl-2-pentene and 2-methylpentane. This point shows that the influence of WO_3 alone does not occur in our case. We can see that on the platinum catalysts the β carbon–carbon bond rupture from the tertiary carbon atom is favoured both for 2MP and for 3MP, whereas on Pt–WO_3/Al_2O_3 cata-

TABLE 6

Reactivity Factor ω for Hexane Hydrocracking on Different Platinum Catalysts

Hydrocarbon bond rupture		Pt–WO_3/Al_2O_3 (550 K) 1a		Pt–WO_3/Al_2O_3 (550 K) 1b	Pt–WO_3/Al_2O_3 (550 K) 2b	0.2% Pt/Al_2O_3 (27) (570 K)	2% Pt/Al_2O_3 (22) (570 K)	4.1% Pt/Al_2O_3 (21) (527 K)	10% Pt/Al_2O_3 (27) (570 K)	Pt black (27) (570 K)
	1	1.1	1.1[a]	1.2	1.2	0.90	0.85	0.9	0.65	0.40
	2	1.0	1.0[a]	1.0	1.0	0.95	0.90	1.0	1.00	1.30
	3	1.1	0.9[a]	1.0	1.0	1.25	1.20	1.2	2.00	1.60
	4	0.7	0.9[a]	0.4	0.7	1.00	1.15	1:1	0.70	1.30
	1	1.3	—	—	1.3	1.35	1.80	1;4	1.35	1.25
	2	0.7	—	—	0.6	0.80	0.40	0.7	0.75	0.80
	3	1.0	—	—	1.1	0.70	0.60	0.7	0.80	0.90
Dispersion (%)		—		55	20	100	60	55	35	2

[a] Results obtained with 2-methyl-2-pentene.

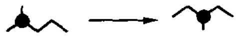
lysts only the α-methyl bond rupture is favoured and not the α-ethyl bond rupture or α-propyl bond rupture. The Pt–WO_3/Al_2O_3 catalysts are very reactive for cracking, which means that this pathway is energetically favoured.

If we look now at the methylcyclopentane hydrogenolysis reaction there are two types of carbon–carbon bond ruptures, one of which is endocyclic and gives hexane isomers (2MP, 3MP, and *n*H) and one which is exocyclic and gives cyclopentane (CP + C_1). The latter one has to be taken into account in the total process of hydrogenolysis because it also involves a simple C–C bond rupture. Moreover, the contribution of this reaction is between 2 and 11% compared with the endocyclic reactions which are between 98 and 89%. This reaction is a minor one but it also involves a C_I–C_{III} carbon–carbon bond rupture. If we look at the endocyclic reactions we obtain 2MP, 3MP, and *n*H in which 2MP and 3MP are obtained via the same carbon–carbon bond ruptures involving only secondary carbon atoms, and we observed (Table 4) that the ratios R_1 = 2MP/3MP are around the statistical value of 2. On the other hand, *n*-hexane is obtained via a C_{II}–C_{III} carbon–carbon bond rupture and the ratio R_2 = 3MP/*n*H reflects a rupture selectivity, as the two bonds ruptured are different to obtain 3MP and *n*H. The value of this ratio was correlated with the metallic particle size for platinum catalysts (*19, 21, 30, 31*). When the R_2 values are low it has been shown that the amount of small metallic particles is high (*21*). With Pt–WO_3/Al_2O_3 catalysts the R_2 values are small, around 0.6 ± 0.1. At this point it is difficult to conclude whether the metallic platinum particles are well dispersed because these catalysts are composed of Pt + WO_3 supported on alumina and we may have to take into account the influence of either the tungsten oxide alone or of the interface Pt–WO_x in the catalytic reaction.

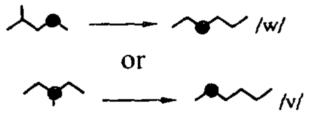
The Isomerisation Reactions

From the previous work on platinum catalysts (*11, 30–35*), we associated the relative contribution of the cyclic mechanism with the amount of small platinum particles, which means that corner or edge atoms, mostly present on small crystallites, may be responsible for this type of mechanism. On the other hand the proportion of selective and nonselective-cyclic mechanism was determined from the selectivity ratio R_2 = 3MP/*n*H obtained in the methylcyclopentane hydrogenolysis. All these results were obtained with platinum catalysts alone, supported on inert refractory oxides, and from these results it was impossible to extrapolate to bimetallic catalysts or to catalysts where the support or other oxidic phases may participate in the catalytic process, i.e., for the Pt–WO_3/Al_2O_3 catalysts.

In the reaction

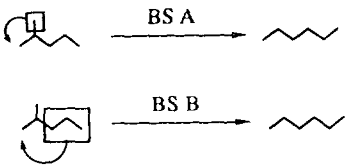


the percentage of cyclic mechanism increases from catalysts 1a to 2b and to 3a, 4a (Table 5). On catalyst 1a the percentage is very low: 13%. This tendency to obtain a low cyclic mechanism contribution is confirmed for the other reactions



giving *n*-hexanes. For the platinum catalyst, 4.1% Pt/Al_2O_3 with the dispersion of 55% (*21*) (Table 5), the relative contributions for reactions /w/ and /v/ are as follows: 86 and 90% compared to 58% (for /w/ reaction) and 70% (for /v/ reaction) for catalyst 1a. Putting together these results with those obtained from methylcyclopentane hydrogenolysis we observe an apparent contradiction. The latter reaction, on catalyst 1a, gives a selectivity ratio R_2 = 0.7 or 0.6, which could have been correlated with the presence of small metallic particles in the catalyst. This hypothesis is not verified by the use of labelled hydrocarbons; the percentage of cyclic mechanism is too low.

Let us examine now the bond shift mechanism. In the chain lengthening (bond shift mechanism) we have two different pathways. The bond shift A (BS A) corresponds to a methyl migration and the bond shift B (BS B) is a propyl migration:



Unfortunately, starting with 2-methyl-2-^{13}C-pentane, the BS B cannot be directly determined because n-hexane-2-^{13}C can also be obtained from the ring opening of the methylcyclopentane intermediate. The BS B is calculated from the equation: %BS B = 100% − (%CM + %BS A), where the %CM is obtained from

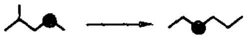


TABLE 7

Results of Chain Lengthening Reactions for the *n*-Hexane Formation

Cat.	% CM	% BS A	% BS B
1a	58	13	29
4a	74	10	16
Pt (*21*)	86	1	13

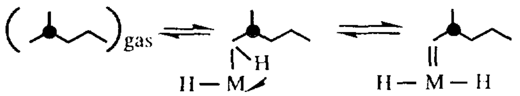
This equation is based on the assumption, always verified, that the 2-methyl-2-^{13}C-pentane and 2-methyl-4-^{13}C-pentane behave in exactly the same way.

The results for chain lengthening reactions on catalysts 1a, 4a, and the reference Pt catalyst (*21*) are shown in Table 7. The BS A (methyl migration) is favoured on Pt–WO_3/Al_2O_3 compared with the Pt/Al_2O_3 catalyst. Bearing this result in mind and recalling the results obtained in the cracking processes, we now make a synthesis and establish a mechanistic proposal to explain the results obtained with the Pt–WO_3/Al_2O_3 catalysts.

Mechanistic Approach

For Pt–WO_3/Al_2O_3 catalysts we have to explain the following points: (i) they are very active in hydrocracking, (ii) they show a particular selectivity in carbon–carbon bond breaking, i.e., the demethylation corresponding to a C_I–C_{III} bond rupture is preferred and (iii) the bond shift A is favoured. The cracking reactions were first interpreted via $\alpha\alpha\gamma$ triadsorbed species as postulated by Anderson and Avery (*36*), but these species do not explain the selectivity. Anderson and Avery (*36*) proposed that the C–C rupture will occur at the β bond to the diadsorbed ($\alpha\alpha$) carbon and Leclercq *et al.* (*22*) proposed that the α bond to the diadsorbed carbon was involved. We suggested that metallacyclobutene species are formed on highly dispersed platinum catalysts where a secondary carbon is σ-bonded to the metal and has an electron deficiency (*28, 29, 37, 38*). Such species were proposed for highly dispersed catalysts where the cracking reactions are important.

To explain (i) the various cracking modes involving or not a tertiary carbon atom in the carbon–carbon bond rupture, i.e., iso and C_2 modes as named by Anderson (*39*), and (ii) the isomerisation reactions, we proposed a common so-called "agostic" intermediate (*40, 41*). Such an agostic species (*42*) will be in equilibrium with a carbene species (A) favoured on tungsten (*43*):



(A)

This intermediate species (A) gives either cracking via a metallacyclobutene species (demethylation from a tertiary carbon atom) or isomerisation via a metallacyclobutane (methyl migration, bond shift A), which is obtained from a hydride migration giving terminal olefins (from 2MP and 3MP)—the more reactive olefins. This proposed mechanism is presented in Fig. 3. On the other hand the mechanism proposed by Rooney and his co-workers (*44*), which is very well able to explain 1-2 methyl bond shift without any side reactions (no cracking (*45*)) has not been taken into account in our case because we have always isomerisation and cracking reactions. The Samman–Rooney mechanism was used by us (*11*) to explain the isopentane to *n*-pentane isomerisation and the reverse reaction where no cracking were involved.

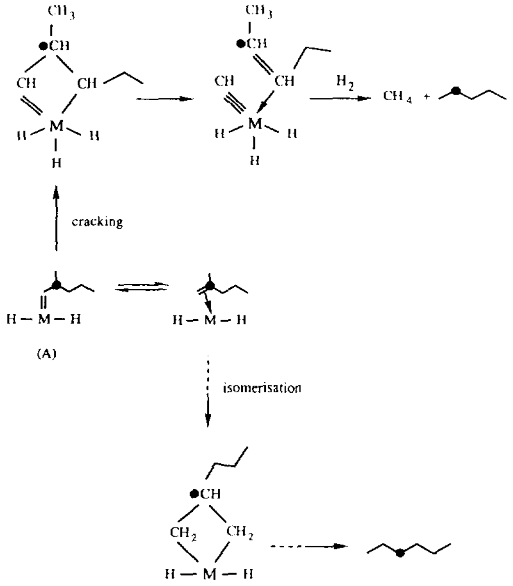


FIG. 3. Hydrocracking and isomerisation mechanisms for hexanes on Pt–WO_3/Al_2O_3 catalysts.

CONCLUSIONS

Our studies on Pt–WO_3/Al_2O_3 catalysts suggest that alkane rearangements proceed via bond-shift and cyclic reactions. In that sense the platinum behaviour is preserved. However, looking more carefully we can observe that within the various bond shift mechanisms, the methyl migration is favoured and, more precisely, it involves the tertiary carbon atom (BS A). The increase in the BS A reaction may be correlated to the tungsten oxide behaviour. As olefin reacts like the corresponding alkane we may rule out the presence of active acidic WO_3 sites in the catalytic reactions under our experimental conditions. Finally, we have observed that the nonselective hydrogenolysis of the methylcyclopentane cannot be correlated with the relative contribution of the cyclic mechanism which is low, in our case. This result suggests that the "Pt–WO_x" interface is responsible for the catalytic behaviour of these catalysts.

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