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Physicochemical Properties and Isomerization Activity of Chlorinated Pt/Al_2O_3 Catalysts

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Alumina-supported platinum catalysts with various metal contents have been prepared and chlorinated by CCl_4 at 473 and 573 K. Their acidity has been measured by pyridine adsorption and catalytic activity in n-butane isomerization. The state of platinum has been followed by infrared spectroscopy, whereas the modifications of the dispersion were measured by electron microscopy and by H_2–O_2 titrations.

The presence of metal in chlorinated alumina produces only small changes in acidity but a great enhancement in isomerization activity for samples chlorinated at 573 K. After chlorination, platinum is oxidized to platinum chloride, which reacts with $AlCl_3$ to produce the $PtCl_2 \cdot 2AlCl_3$ complex. This complex is mobile on the support and agglomerates in large particles. During the isomerization of n-butane, platinum is reduced in the metallic state leading to very low metal dispersion. Very small platinum clusters are also present, they are able to perform the hydrogenation of butenes and to decrease the coke formation. Thus ageing is limited in comparison with pure alumina. The possible role of HCl leading to superacid species is also discussed.

One of the aims of catalytic reforming is to isomerize paraffins in order to get more branched ones that increase the octane number of gasoline. The catalyst usually consists of platinum supported on alumina acidified by halogens. That solid is the classical example of a dual catalyst, where both metallic and acidic properties are present on the surface of the catalyst.[1]

In a previous study we have shown that chlorination of alumina by CCl_4 leads to a very acidic solid because of an enhancement of the strength and the number of strong Lewis sites[2] evidenced by infrared spectroscopy and gravimetric adsorptions of pyridine. At 573 K, the chlorination by CCl_4 goes into the bulk and produces nascent $AlCl_3$ and the catalyst so obtained is very active in n-butane isomerization. Similar activity was also detected when $AlCl_3$ was allowed to react with the surface silanol groups of silica. Thus surface species like (Al or Si)—O—$AlCl_2$ have been postulated on both samples. In contrast, hydrogenolysis of butane is the main reaction in the case of the Pt/Al_2O_3 catalysts, whereas the selectivity in isomerization does not exceed 1%.[3]

The goal of this work is to compare properties of Pt/Al_2O_3 samples chlorinated by CCl_4 at 473 and 573 K with the properties of the same catalysts free of platinum. The acidic properties as well as the state of the metal will be related to the catalytic activity in n-butane isomerization.

Experimental

Samples were prepared according to the following procedure: γ-Al_2O_3 GFS 400 from Rhône-Poulenc was impregnated with an aqueous solution of hexachloroplatinic acid in order to obtain a solid containing the required amount of metal (between 0.1 and

5 wt%). Water was evaporated under reduced pressure and the solid obtained was dried overnight at 400 K. The catalyst was then flushed with argon at 773 K for a few hours, reduced under hydrogen at 773 K for 10 h and finally flushed with argon overnight at the same temperature. Chlorination of the reduced catalyst was performed by treating the sample under a flow of Ar–CCl_4 at either 473 or 573 K. The CCl_4 partial pressure was maintained at 50 Torr (1 Torr ≈ 133.3 Pa). After chlorination, the sample was purged under flowing Ar at 473 K for 2 h.

For infrared measurements, the samples were compressed in order to obtain a disc (diameter = 18 mm, weight 30–40 mg). The disc was introduced into a cell allowing *in situ* reduction and chlorination processes. Carbon monoxide or pyridine adsorptions were performed at room temperature. Spectra were recorded at 300 K using a Perkin-Elmer 580A spectrometer in the 4000–1200 cm^{-1} range.

The catalysts were also examined under an electron microscope (JEOL JEM-100 CX type) with 0.3 nm resolution. The extractive replica technique was used; a carbon film was evaporated on the sample. After immersion in dilute HF, the carbon film was separated from the alumina carrier and the platinum particles remaining on the carbon film were observed by transmission (TEM).

For butane and neopentane isomerizations, microdifferential reactors made of quartz were used. The reactions were performed at atmospheric pressure, the catalyst was submitted to a flow of hydrocarbon and hydrogen and the products were analysed by gas chromatography using a flame ionization detector. Butane isomerization was studied between 473 and 573 K with a hydrogen/hydrocarbon ratio close to 7, the contact time was *ca.* 1 s. Neopentane conversion was investigated at 573 K using a mixture of hydrogen, neopentane and argon with respective partial pressures of 0.02, 0.42 and 0.56 atm;† the contact time was *ca.* 0.1 s.

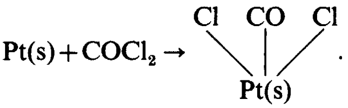
Results

Physicochemical Changes after Chlorination at 473 K

State of Platinum

After chlorination by CCl_4 at 473 K, the i.r. spectrum showed two $\nu(CO)$ bands at 2195 and 2145 cm^{-1}. The first disappeared after evacuation of the sample at 473 K, whereas the latter was eliminated after desorption at 573 K.

Carbon monoxide adsorption on the chlorinated sample subsequently evacuated at 473 K did not change the intensity of the 2145 cm^{-1} band. The $\nu(CO)$ band close to 2078 cm^{-1} observed for the unchlorinated sample[4] did not appear. In contrast, the 2195 cm^{-1} band developed (fig. 1) and its intensity increased with the chlorination time at 473 K. It has been shown previously[5,6] that adsorption of phosgene onto Pt/Al_2O_3 gave rise to a band at *ca.* 2140 cm^{-1}, attributed to a dissociative adsorption on the metallic particles according to the scheme:



$$Pt(s) + COCl_2 \rightarrow \overset{Cl\quad CO\quad Cl}{\underset{Pt(s)}{\diagdown\ |\ \diagup}}\ .$$

In the case of chlorinated Pt/Al_2O_3 solids, the absence of the 2078 cm^{-1} band as well as the presence of the 2145 cm^{-1} band clearly showed that surface platinum atoms are not in the metallic state. Chlorination of the Al_2O_3 support gave $COCl_2$ as intermediate;[7] subsequent adsorption of $COCl_2$ onto platinum led to the $\nu(CO)$ band at 2145 cm^{-1} and suggested that surface platinum atoms are in the form of platinum dichloride. The second band at 2195 cm^{-1} could be assigned to CO adsorbed on the Lewis centres of alumina,[8, 9] but CO is reversibly adsorbed on Al_2O_3 at room temperature. The increase

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† 1 atm = 101325 Pa.

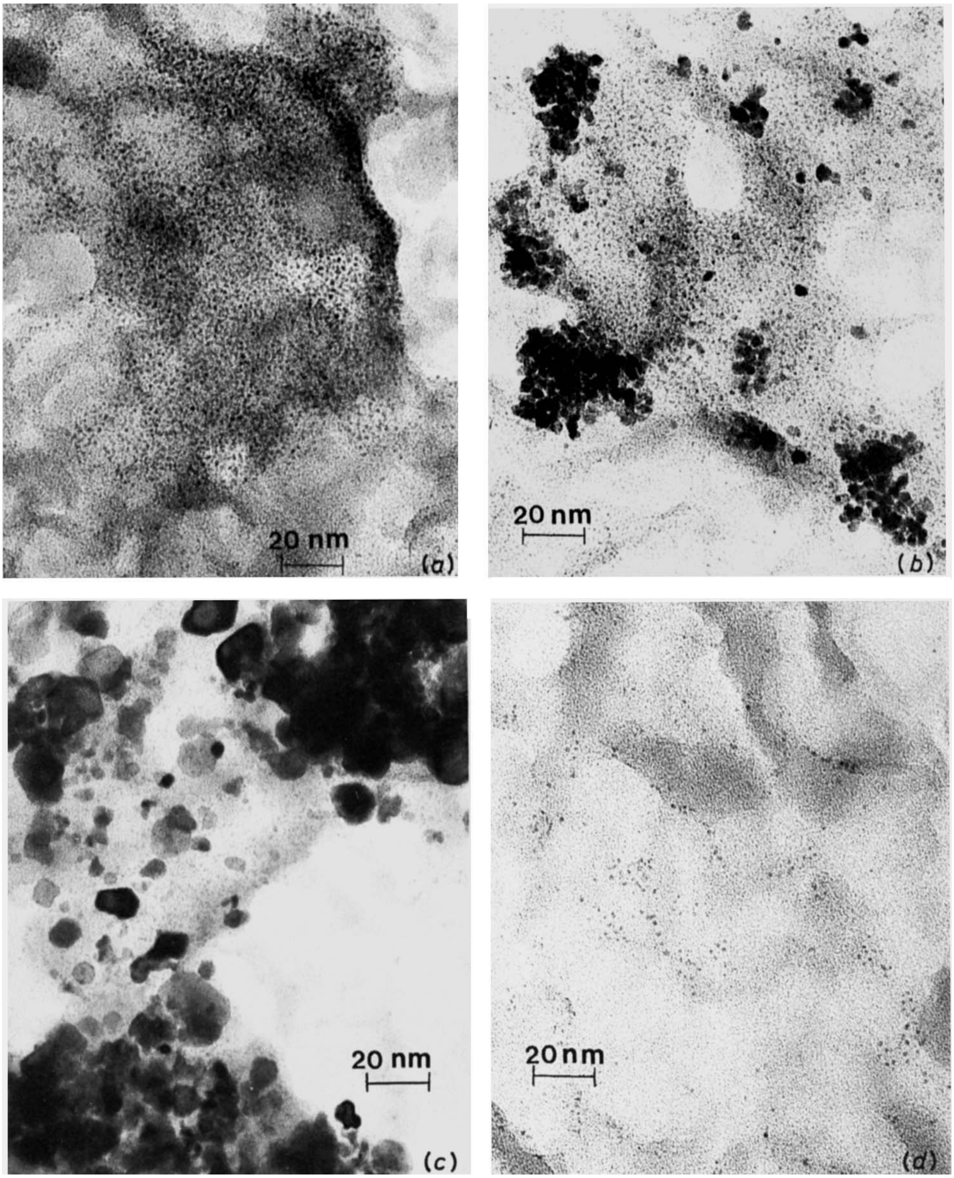


Plate 1. Electron transmission micrographs of Pt/Al_2O_3 catalysts: (*a*) unchlorinated 1 wt% Pt/Al_2O_3 sample, (*b*) 1 wt% Pt/Al_2O_3 sample chlorinated by CCl_4 at 473 K for 6 h, (*c*) 1 wt% Pt/Al_2O_3 sample chlorinated by CCl_4 at 573 K for 0.5 h, (*d*) 0.1 wt% Pt/Al_2O_3 sample chlorinated by CCl_4 at 573 K for 0.5 h then reduced at 573 K.

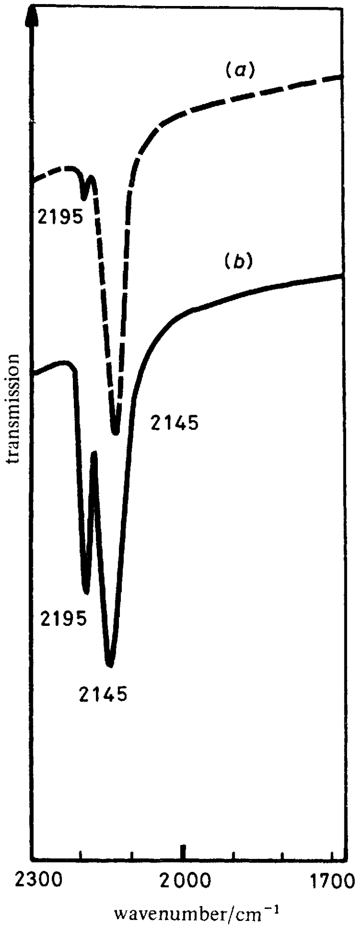


Fig. 1. Infrared spectra of carbon monoxide irreversibly adsorbed at 300 K onto the 5 wt% Pt/Al_2O_3 sample chlorinated at 473 K by CCl_4 (*a*) for 2 h, (*b*) for 6 h.

of the intensity of the 2195 cm^{-1} band with the metal content and the chlorination time at 473 K suggests that platinum is concerned with this absorption. The i.r. spectrum of the *cis*-$PtCl_2(CO)_2$ complex shows two ν(CO) bands at 2200 and 2162 cm^{-1}.[10] If we suppose the progressive extraction of $PtCl_2$ or $PtCl_2(CO)_2$ molecules from the platinum particles as the chlorination time increases at 473 K, the observation of the 2195–2145 cm^{-1} bands can be related to the presence of $PtCl_2(CO)_2$ at the surface of the catalyst.

Dispersion of the Metallic Phase

The Pt/Al_2O_3 samples were examined by TEM before and after chlorination by CCl_4 at 473 K. Before chlorination, the 1 wt% Pt/Al_2O_3 catalyst exhibited a sharp particle size distribution with a mean particle size close to 1.3 nm. Chlorination of this sample by CCl_4 at 473 K for 2 h led to the formation of crystallites with diameters lying between 3 and 7 nm. The sintering of platinum increased with the time of chlorination at 473 K under Ar+CCl_4. For instance, particles of 20 nm diameter could be observed after 6 h of chlorination (plate 1).

Oxygen–hydrogen titrations have been used to follow the changes in the dispersion of the metallic phase. Samples resulting from the chlorination by CCl_4 at 473 K and evacuated at the same temperature did not adsorb oxygen at room temperature; this result confirms that the platinum particles are oxidized at least at the surface as suggested from i.r. measurements. On the contrary, hydrogen is slowly consumed at room temperature. After reduction of the chlorinated sample by hydrogen at 473 K, H_2–O_2 cycles have been performed. In accordance with the TEM observations, a sintering of the metal occurred during the treatment by CCl_4. The dispersion of Pt, initially close to 74%, fell to 20% after chlorination by CCl_4 at 473 K. The sintering occurs during the chlorination step and not during the subsequent hydrogen reduction performed for H_2–O_2 titrations.

Modifications of the Support

Pyridine adsorption was used to measure the changes in surface acidity of the support. After chlorination by CCl_4 at 473 K and evacuation at the same temperature, pyridine was contacted with the Pt/Al_2O_3 samples at room temperature. Weakly adsorbed base was removed by vacuum treatment at 423 K. No protonic acidity has been detected. Lewis centres were detected by frequency changes of the 19*b* and 8*a* modes. As previously shown, the absorbance of the 1455 cm^{-1} band (19*b* mode) allows the determination of the number of Lewis centres per unit area.[2] For chlorinated Pt/Al_2O_3 samples, 1.5 sites per nm^2 have been found, *i.e.* the same value as for chlorinated alumina free of platinum. By contrast with chlorinated alumina, the 8*a* mode was split into two bands: 1613 and 1626 cm^{-1} (fig. 2). The latter was only eliminated by desorbing the sample at 773 K and must be assigned to pyridine linked to strong Lewis acid sites. The first band corresponds to pyridine less firmly bonded, since it disappears by evacuation at moderate temperature (523 K). In addition its intensity increases with the chlorination time and with the platinum content. The intensity of the 1613 cm^{-1} band followed very closely the intensity of the 2195 cm^{-1} band, *i.e.* the intensity of the ν(CO) band at 2195 cm^{-1} increased with the platinum loading and the same trend was observed for the 8*a* mode of pyridine at 1613 cm^{-1}. In addition, the 2195 cm^{-1} band which disppeared upon pyridine adsorption was previously ascribed to the $PtCl_2(CO)_2$ complex. Finally, the 1613 cm^{-1} band was no longer observed if chlorinated Pt/Al_2O_3 samples were reduced by hydrogen prior to pyridine adsorption. As a consequence, the pyridine at the origin of the 1613 cm^{-1} band is probably adsorbed on platinum chloride in interaction or not with platinum particles.

Physicochemical Changes after Chlorination at 573 K

At 573 K, CCl_4 reacts with Al_2O_3 leading to the formation of nascent $AlCl_3$.[7] With platinum dichloride previously formed, $AlCl_3$ gives a volatile complex $PtCl_2 \cdot 2AlCl_3$ already identified by u.v.–visible spectroscopy.[11–12]

In the case of chlorination by CCl_4 at 573 K exceeding 30 min, this complex is no longer adsorbed on the support and a loss of Pt occurs by sublimation of this volatile complex. Thus the duration of chlorination by CCl_4 at 573 K has been restricted to 30 min.

State of Platinum

After chlorination at 573 K and evacuation at 473 K, CO was contacted at 300 K onto the samples. As for chlorinations performed at 473 K, no ν(CO) band characteristic of metallic platinum was observed. Two ν(CO) bands at 2200 and 2160 cm^{-1}, *i.e.* very close to the bands of the *cis*-$Pt(CO)_2Cl_2$ complex, were detected. The intensities of these bands were very weak and did not depend upon the metal loading.

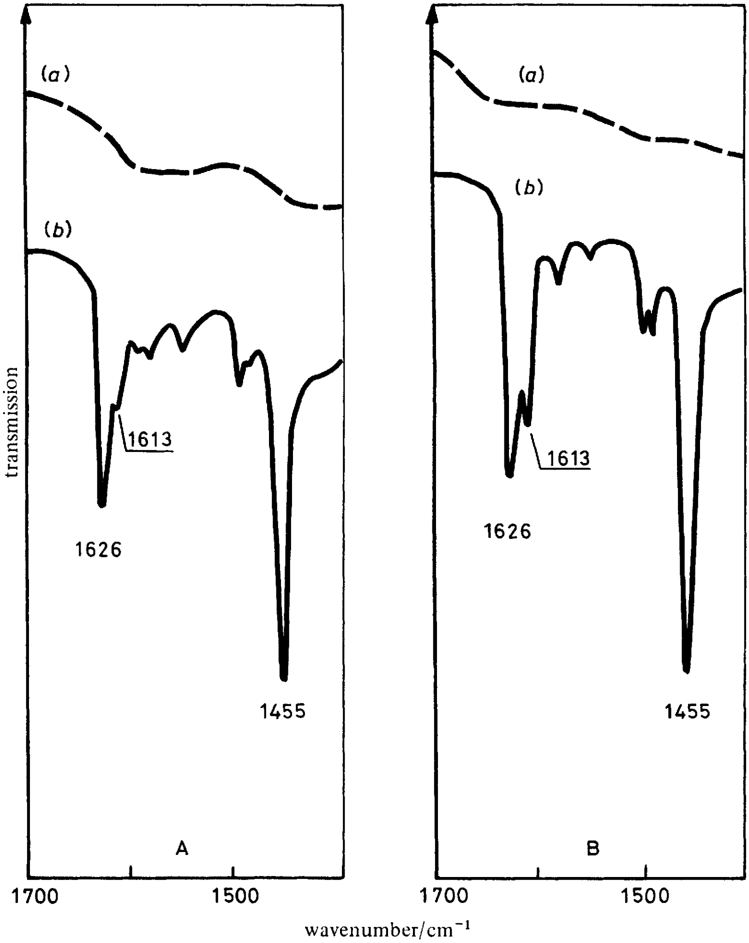


Fig. 2. Infrared spectra of pyridine adsorbed on the 5 wt% Pt/Al_2O_3 sample chlorinated by CCl_4 at 473 K. Chlorination time (A) = 2 h, (B) = 6 h. (*a*) Chlorinated sample, background; (*b*) after pyridine adsorption at 300 K and subsequent evacuation at 423 K for several hours.

Dispersion of the Metallic Phase

TEM measurements showed a sintering of the metallic phase more important than in the case of chlorination at 473 K. The distribution of particle size was very broad; particles of diameter lying between 1.5 and 30 nm were observed for the 1 wt% Pt/Al_2O_3 sample (plate 1). For low platinum contents (0.1 wt%), no sintering was observed (plate 1).

No oxygen absorption can be measured on chlorinated samples. At *ca.* 423 K hydrogen led to the reduction of platinum chloride into metallic platinum. From the amount of consumed hydrogen, it can be deduced that all the platinum atoms were in the +2 oxidation state. Hydrogen reduction occurred according to the following scheme:

$$PtCl_2 + H_2 \rightarrow Pt^0 + 2HCl.$$

Subsequent H_2–O_2 titrations were in accordance with the sintering observed before reduction by TEM; for instance, the dispersion of the 1 wt% Pt/Al_2O_3 sample after chlorination was very low, *i.e.* only 3%.

Table 1. Adsorption of pyridine on Pt/Al_2O_3 samples chlorinated for 0.5 h at 573 K by CCl_4 with various metal contents; pyridine was then evacuated at 423 K for several hours

	8*a* mode		19*b* mode	
Pt (wt%)	absorbance of the 1626 cm^{-1} band[a]	absorbance of the 1613 cm^{-1} band[a]	absorbance of the 1455 cm^{-1} band[a]	sites per nm^2
0.54	13.3	2.0	26.2	1.3
1.05	12.6	3.6	26.0	1.3
2.20	11.4	5.1	26.0	1.3
4.65	9.2	5.2	28.1	1.4

[a] Arbitrary units of absorbance per g catalyst.

CO and NO Adsorptions

After chlorination at 573 K, the 1 wt% Pt/Al_2O_3 sample was reduced under hydrogen at 573 or 773 K. CO adsorption on such a solid gave rise to a ν(CO) band close to 2080 cm^{-1}, characteristic of metallic platinum. The intensity of this band is very low in comparison with that of the same band in the case of the unchlorinated sample (a factor of 25). This result confirms the sintering already observed by TEM and chemisorption measurements.

Previous work[13] has shown that the ν(NO) frequency of NO adsorbed on platinum is sensitive to the metal particle size: the lower particle size, the higher the ν(NO) frequency. A 1 wt% Pt/Al_2O_3 sample was chlorinated by CCl_4 at 573 K, then reduced by hydrogen at 573 K and finally contacted with NO at room temperature. The resulting i.r. spectrum showed a broad band between 1700 and 1800 cm^{-1} which must be attributed to NO adsorbed on large metal particles. Moreover a small but sharp ν(NO) band was observed at 1840 cm^{-1}. For small Pt particles occluded in Y zeolites and having a diameter of 1 nm, the ν(NO) frequency was found at 1828 cm^{-1}.[14] A ν(NO) frequency of 1840 cm^{-1} must correspond to platinum particles having a diameter smaller than 1 nm. Thus, Pt/Al_2O_3 samples chlorinated by CCl_4 at 573 K contain large platinum crystallites as well as very tiny metal clusters not evidenced by TEM.

Support Modification

Pyridine adsorption following treatment by CCl_4 at 573 K led to results similar to those encountered after chlorination at 473 K: the absorbance of the 19*b* mode allows the determination of the number of Lewis sites per unit area (1.5 sites nm^{-2}); and the 8*a* mode is split into two components (1627–1613 cm^{-1}).

The 1627 cm^{-1} band is attributed to pyridine chemisorbed on the Lewis acid centres of the support; its intensity decreases when the metal loading increases. The 1613 cm^{-1} band corresponds to pyridine bonded to platinum chloride; its intensity slightly increases with the metal content up to 2 wt% (table 1).

Catalytic Activity Measurements

Because of the drastic modifications of platinum state by CCl_4 chlorination, it might be predicted that the catalytic activity of chlorinated Pt/Al_2O_3 catalysts would be strongly changed by comparison with unchlorinated Pt/Al_2O_3 and chlorinated Al_2O_3. Two reactions were examined: the conversion of neopentane and the isomerization of n-butane.

Table 2. Catalytic activity[a] in neopentane conversion at 573 K over 1 wt% Pt/Al_2O_3

sample	hydrogenolysis rate	isomerization rate
reduced catalyst	9.9×10^{-2}	0.9×10^{-2}
after chlorination at 473 K	4.3×10^{-2}	3.9×10^{-2}
after chlorination at 573 K	0.4×10^{-2}	0.8×10^{-2}

[a] Rates are expressed in mol h^{-1} (g Pt)$^{-1}$. Chlorination was performed by CCl_4 treatment at 473 K for 2 h and 573 K for 0.5 h.

Neopentane Conversion

This reaction is specific for the metallic state and is also structure sensitive. By comparison with the activity of the unchlorinated 1 wt% Pt/Al_2O_3 sample, the overall activity for neopentane conversion decreased at 573 K when the temperature of chlorination increased (table 2).

The decrease in activity is in accordance with the platinum sintering already shown. Two reactions occur in neopentane conversion on metals: isomerization into isopentane, and hydrogenolysis. The selectivity in isomerization strongly increases with the temperature of chlorination: 8% for an unchlorinated sample, 48% for a sample chlorinated at 473 K and 67% for a sample chlorinated at 573 K. These results are in accordance with the conclusions of Foger and Anderson[15, 16] which showed that the selectivity in isomerization of neopentane increases with the metal particle size. Moreover, it was noted that no ageing occurred within 12 h of reaction either for hydrogenolysis or for isomerization activity.

n-Butane Isomerization

This reaction has been performed either at 473 K or 563 K for samples chlorinated by CCl_4 at 473 or 573 K. Note that on unchlorinated Pt/Al_2O_3, hydrogenolysis is the main reaction, the selectivity towards isomerization does not exceed 1%.

Samples Chlorinated at 473 K. The reaction of n-butane + hydrogen with the chlorinated 1 wt% Pt/Al_2O_3 was performed at 473 K. The sample exhibits an isomerizing activity as well as hydrogenolysis activity (fig. 3). Hydrogenolysis is fully inhibited by pretreating the chlorinated sample by H_2S, whereas the isomerization is unaffected. In the absence of H_2S the selectivity for isomerization is close to 55% at the beginning of the reaction. The rate of isomerization extrapolated to zero time is 0.2×10^{-4} mol h^{-1} (g catalyst)$^{-1}$, whereas similar experiments performed on chlorinated Al_2O_3 free of platinum leads in the same conditions to a value of 0.18×10^{-4} mol h^{-1} (g catalyst)$^{-1}$, *i.e.* very close to the value reported for the chlorinated 1 wt% Pt/Al_2O_3 sample. The deactivation of the isomerization activity is limited in the case of the platinum-containing sample; the activity is reduced by a factor of 2 after 12 h for Pt/Al_2O_3 and after 3 h for Al_2O_3 free of platinum.

Samples Chlorinated at 573 K. The 1 wt% Pt/Al_2O_3 sample was chlorinated for 0.5 h under ($Ar + CCl_4$) at 573 K then flushed under Ar at 473 K. In the case of reaction performed at 473 K (fig. 4), the rate of isomerization extrapolated at zero time equals 0.6×10^{-4} mol h^{-1} (g catalyst)$^{-1}$, *i.e.* three times higher than the rate measured for the same sample chlorinated at 473 K. The selectivity for isomerization is close to 100% since (i) no hydrogenolysis reaction occurs and (ii) no butenes were detected in the reaction products. Nevertheless, the activity in isomerization linearly decreased with time and was reduced by a factor of two after 12 h of reaction at 473 K.

If the reaction is performed at 573 K, the isomerization activity strongly increases

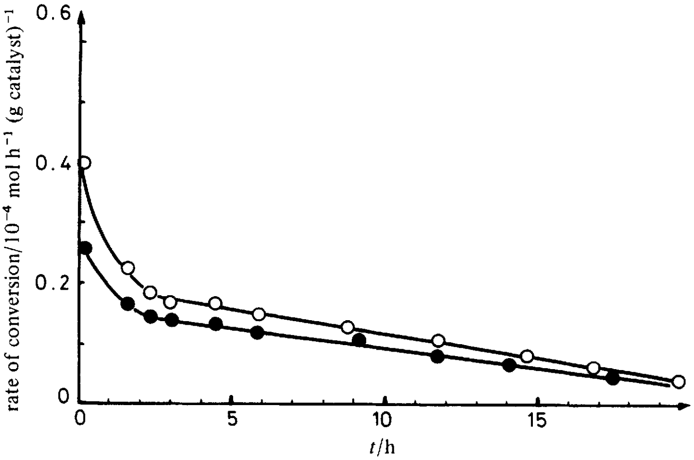


Fig. 3. Catalytic activity of the 1 wt% Pt/Al_2O_3 sample chlorinated by CCl_4 at 473 K for 2 h towards butane conversion: ○, isomerization; ●, Hydrogenolysis. Temperature of reaction = 473 K.

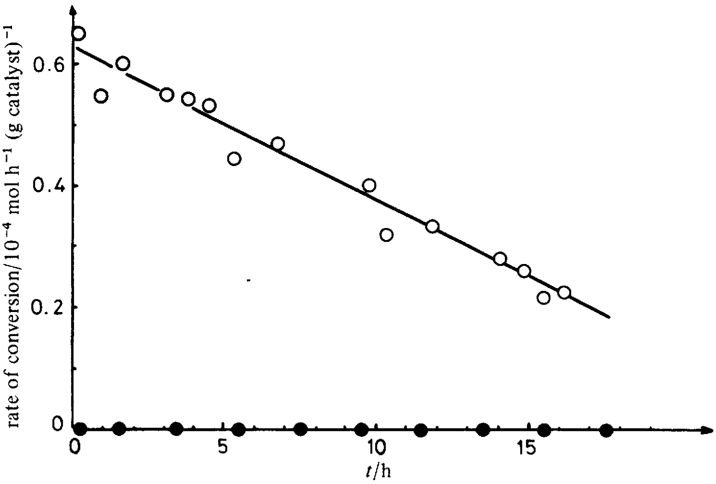


Fig. 4. Catalytic activity in n-butane conversion of the 1 wt% Pt/Al_2O_3 sample chlorinated by CCl_4 at 573 K for 0.5 h: ○, isomerization; ●, hydrogenolysis. Temperature of reaction = 473 K.

since the rate of isomerization extrapolated at zero time reaches 12×10^{-4} mol h^{-1} (g catalyst)$^{-1}$ (fig. 5). The isomerization activity decreases linearly with time and is reduced to half its initial value in 9 h. No butenes were observed in the reaction products. Hydrogenolysis activity did not change with the time of reaction, being 0.4×10^{-4} mol h^{-1} (g catalyst)$^{-1}$. The unchlorinated 1 wt% Pt/Al_2O_3 sample had, in the same conditions, a hydrogenolysis activity close to 20×10^{-4} mol h^{-1} (g catalyst)$^{-1}$. This strongly reduced hydrogenolysis activity is the consequence of the platinum sintering during the chlorination process. Since the hydrogenolysis is not affected by ageing, the selectivity in isomerization continuously decreases with the working time: 92% at $t = 0$, 72% after 15 h and 24% after 19 h of reaction.

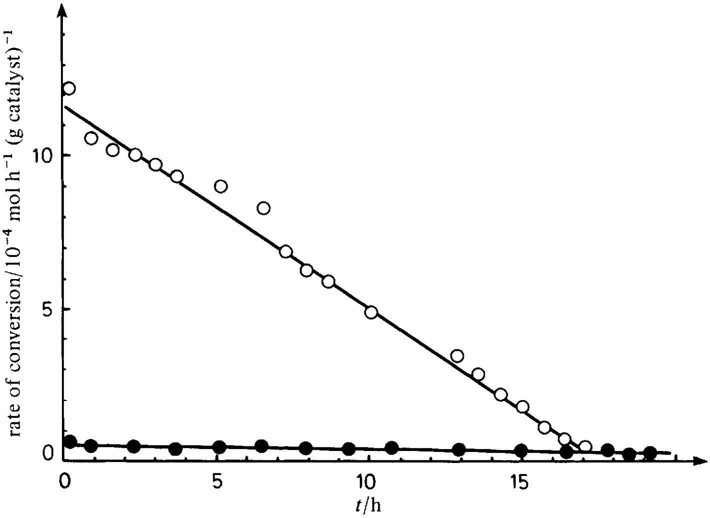


Fig. 5. Catalytic activity in n-butane conversion of the 1 wt% Pt/Al_2O_3 sample chlorinated by CCl_4 at 573 K for 0.5 h: ○, isomerization; ●, hydrogenolysis. Temperature of reaction = 573 K.

Table 3. n-Butane isomerization over Pt/Al_2O_3 catalysts chlorinated by CCl_4 for 0.5 h at 573 K as a function of the metal loading (temperature of reaction = 573 K)

Pt (wt%)	initial rate of hydrogenolysis /mol h^{-1} (g Pt/Al_2O_3)$^{-1}$	initial rate of hydrogenolysis /mol h^{-1} (g Pt)$^{-1}$	initial rate of isomerization /mol h^{-1} (g Pt/Al_2O_3)$^{-1}$	initial isomerization selectivity (%)
0.13	0.1×10^{-4}	0.5×10^{-2}	8.8×10^{-4}	99
0.28	0.1×10^{-4}	0.3×10^{-2}	9.1×10^{-4}	99
0.54	0.5×10^{-4}	0.9×10^{-2}	11.0×10^{-4}	96
1.12	0.4×10^{-4}	0.4×10^{-2}	11.3×10^{-4}	97
2.20	1.0×10^{-4}	0.4×10^{-2}	12.6×10^{-4}	93
5.0	0.9×10^{-4}	0.2×10^{-2}	11.5×10^{-4}	93

The influence of the metal loading of Pt/Al_2O_3 samples has been investigated in the n-butane conversion at 573 K for samples previously chlorinated by CCl_4 at 573 K. The results are summarized in table 3 for platinum contents varying from 0.13 to 5.0 wt%; they show the following features: (i) isomerization rate extrapolated to zero time does not depend on the metal loading; (ii) the hydrogenolysis activity remains very low whatever the platinum concentration; the rate of hydrogenolysis expressed per gram of metal does not follow the platinum content and keeps a value smaller than 10^{-2} mol h^{-1} (g Pt)$^{-1}$ in the range of concentrations investigated; and (iii) as a consequence the initial selectivity in isomerization is very high (close to 100%) and does not depend on the metal loading.

Rates of hydrogenolysis and isomerization in butane conversion for various catalysts are summarized in table 4.

Table 4. Initial isomerization and hydrogenolysis rates of various catalysts in butane conversion

	reaction at 473 K		reaction at 573 K	
sample	isomerization rate /mol h^{-1} (g catalyst)$^{-1}$	hydrogenolysis rate /mol h^{-1} (g catalyst)$^{-1}$	isomerization rate /mol h^{-1} (g catalyst)$^{-1}$	hydrogenolysis rate /mol h^{-1} (g catalyst)$^{-1}$
Al_2O_3 chlorinated by CCl_4 at 473 K	0.18×10^{-4}	—	—	—
Al_2O_3 chlorinated by CCl_4 at 573 K	—	—	0.4×10^{-4}	—
unchlorinated 1 wt% Pt/Al_2O_3	—	—	20×10^{-4}	0.2×10^{-4}
1 wt% Pt/Al_2O_3 chlorinated by CCl_4 at 473 K	0.2×10^{-4}	0.16×10^{-4}	—	—
1 wt% Pt/Al_2O_3 chlorinated by CCl_4 at 573 K	0.6×10^{-4}	0	12×10^{-4}	0.4×10^{-4}

Discussion

Sintering of Platinum under CCl_4

All the above results show that the state and the dispersion of platinum deposited on alumina as well as the catalytic activity in isomerization are strongly affected by the temperature of chlorination under the ($Ar+CCl_4$) mixture.

In the case of chlorination restricted at 473 K, CCl_4 reacts with the Al_2O_3 support with the formation of phosgene as intermediate. $COCl_2$ chemisorbs dissociatively on surface platinum atoms, leading to superficial platinum dichloride. Owing to its low melting point (468 K),[17] platinum dichloride can leave the platinum particles and migrate on the alumina support. The chemical transport of platinum on the support increases with the time of chlorination under CCl_4 at 473 K as evidenced from TEM measurements and H_2–O_2 titrations. However, after 6 h of chlorination at 473 K, the sintering of the 1 wt% Pt/Al_2O_3 sample is not too severe since the dispersion of platinum is close to 20%. Thus, properties of the metallic phase are expected in catalytic reactions involving hydrocarbons.

In the case of chlorination performed at 573 K, the sintering of platinum proceeds in a different way: CCl_4 reacts with alumina to produce nascent aluminium trichloride,[7] the reaction ceases to be superficial and becomes reticular leading to a lattice attack. In addition, $AlCl_3$ is known to form volatile complexes with transition-metal chlorides.[18–20] In the case of $PtCl_2$, the formation of a $PtCl_2$, $2AlCl_3$ complex has been evidenced by u.v.–visible spectroscopy.[11, 12] As a consequence the rate of the chemical transport of platinum is favoured by the formation of the volatile $PtCl_2 \cdot 2AlCl_3$ complex and complete removal of the platinum particles may be achieved. Under our experimental conditions, a loss of platinum is observed for chlorination times exceeding 0.5 h at 573 K, leading to a deposit of the purple $PtCl_2 \cdot 2AlCl_3$ complex on the cold parts of the reactor. For chlorination times < 0.5 h, TEM measurements show an intensive sintering of platinum. After hydrogen reduction, H_2–O_2 titrations confirm the sintering of platinum, since the dispersion does not exceed 2%. Nevertheless, i.r. adsorption of nitric oxide shows that very small platinum crystallites (particle diameter 1 nm) are present on samples chlorinated by CCl_4 at 573 K. In addition, for the 0.1 wt% Pt/Al_2O_3

sample, no sintering was observed after CCl_4 treatment at 573 K. Since the sintering of platinum appears to be due to the accumulation of $PtCl_2 \cdot 2AlCl_3$ on the support, it can be postulated that minute amounts of this complex can be immobilized by interaction with the stronger Lewis acid sites generated by the chlorination under CCl_4.

Subsequent hydrogen reduction would be expected to lead to the small platinum crystallites evidenced by NO adsorption. For larger Pt contents, the strongest Lewis sites would be saturated (as evidenced by pyridine adsorption measurements), the agglomeration of the $PtCl_2$, $2AlCl_3$ molecules on the support occurs leading to the observed sintering.

Previous works have already suggested or concluded that the sintering of platinum can occur *via* chlorine containing compounds of platinum. Burnonville and Martino[21] have evidenced a very rapid platinum sintering under $Ar+CCl_4$ mixtures. Goble and Lawrance[22] mentioned that a good isomerization catalyst is obtained when contacting Pt/Al_2O_3 with CCl_4 and oxygen (or nitrogen, or air); no isomerization activity is observed by using CCl_4+H_2 mixtures; they also reported a loss of platinum for severe conditions of chlorination. Birke *et al.*[23] have postulated a chemical transport of platinum in the form of $Pt(CO)_2Cl_2$ in the presence of $AlCl_3$. More recently Smith *et al.*[24] concluded that oxidizing or inert atmospheres favour the platinum sintering of Pt/Al_2O_3 catalysts, whereas CCl_4+H_2 mixtures lead to a more limited sintering. Similar observations were reported by Delannay *et al.*[25]

Neopentane and n-Butane Isomerization

These reactions have been performed at 473 K and 573 K on the samples resulting from the chlorination process. In this temperature range volumetric measurements have shown a reduction of the platinum chloride complexes into metal. In addition, when the chlorinated Pt/Al_2O_3 catalysts are reduced under hydrogen for 1 h at 573 K prior to the reaction, no changes in activity and selectivity were observed. The observations allow the exclusion of participation of oxidized forms of platinum in the conversion of neopentane and n-butane.

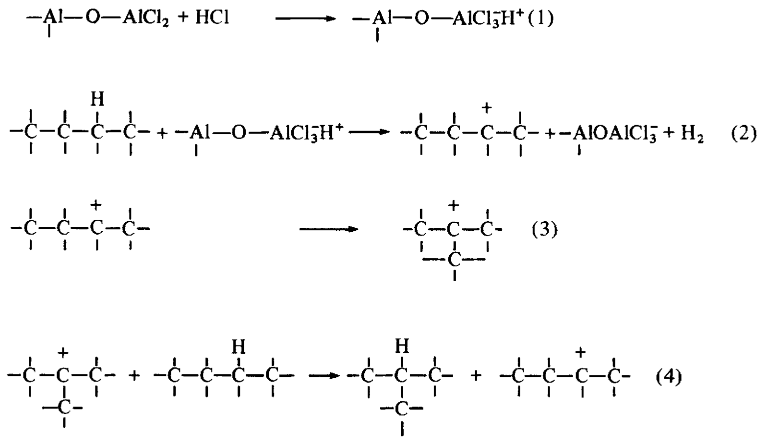
For neopentane conversion, the changes in activity and selectivity observed after chlorination are explained by a sintering of the platinum particles. The overall activity expressed per gram of catalyst decreases when the metal dispersion decreases, whereas the selectivity towards isomerization (isopentane formation) increases.

For samples chlorinated at 473 K, n-butane is converted at 473 K into isobutane and hydrogenolysis products. The initial rate of isomerization is very close to that of chlorinated alumina free of platinum, suggesting that the metal is not involved in the isomerization mechanism. Moreover, the deactivation is limited for platinum-containing samples, probably because the metal can hydrogenate the coke precursors responsible for the ageing. The hydrogenolysis activity is due to the remaining metal particles of moderate dispersion.

For Pt/Al_2O_3 samples chlorinated at 573 K, n-butane is converted at 473 K into isobutane with a selectivity close to 100%. Hydrogenolysis is weak because of the too low dispersion of the sintered metal particles. It can be also postulated that the very small crystallites ($d \approx 1$ nm) are not able to give hydrogenolysis products since they do not exhibit the multiple adsorption sites required for the reaction.[26]

For reactions performed at 573 K on samples chlorinated at 573 K, hydrogenolysis of butane is also very limited. By contrast with chlorinated alumina free of platinum, butenes were not detected. The small platinum clusters could be responsible for the hydrogenation of olefinic hydrocarbons, which are at the origin of polyaromatic compounds (precursors of coke). Thus the slow deactivation of chlorinated Pt/Al_2O_3 catalysts by comparison with pure alumina is certainly due to the hydrogenating activity of these small platinum clusters.

If we compare the isomerization of n-butane at 573 K over chlorinated Al_2O_3 and



Scheme 1. n-Butane isomerization over chlorinated Pt/Al_2O_3 samples involving the presence of superacid sites. (1) Conversion of Lewis sites into Brönsted centres; (2) hydride abstraction from n-butane; (3) carbocation isomerization; (4) isobutane formation and propagation.

chlorinated Pt/Al_2O_3, the isomerization activity is greatly enhanced by the presence of platinum (12×10^{-4} mol h^{-1} g^{-1} for Pt/Al_2O_3 instead of 0.4×10^{-4} mol h^{-1} g^{-1} for Al_2O_3 free of platinum). In addition, the rate of isomerization expressed per gram of catalyst does not depend on the metal loading in the 0.1–5.0 wt% range.

In a bifunctional catalyst, like platinum supported on chlorinated alumina, the metal has been assumed to favour the butane–butene equilibrium.[27–29] The role of scavenger has been also assigned to platinum towards the formation of coke precursors.[30] Platinum can also favour the dechlorination of the support in presence of hydrogen. As a matter of fact, a chlorinated Pt/Al_2O_3 catalyst treated under hydrogen at 573 K for 24 h becomes inactive towards butane isomerization. Mass-spectrometric studies have evidenced the formation of great amounts of hydrogen chloride during this treatment.[12]

So during the (nC_4+H_2) reaction over chlorinated Pt/Al_2O_3 catalyst, a similar dechlorination of the support assisted by the metal can be expected. By reaction of hydrogen chloride with the strong acid Lewis sites previously identified with Al—O—$AlCl_2$ groups,[2] superacid species like Al—O—$AlCl_3$—H^+ may be formed. Such sites have already been obtained by reaction of $EtAlCl_2$ with the hydroxyl groups of alumina; they have been found to be sites responsible for the isomerization of saturated hydrocarbons.[31] These centres are able to produce hydride abstraction from a n-butane molecule.[32] The obtained carbonium ion isomerizes itself into t-butyl one. Hydride abstraction from another butane molecule leads to isobutane and regenerates the first carbocation. The reaction could obey to the scheme described in scheme 1.

In the case of chlorinated alumina free of platinum, smaller amounts of hydrogen chloride are formed at the beginning of the reaction. Consequently the number of superacid species is lower and the rate of isomerization is weaker. In addition butenes were detected on alumina;[2] since the catalyst does not possess any hydrogenating function, butenes polymerize leading to polyaromatic compounds which adsorb on the strong acid Lewis centres of the surface. Such poisoned sites cannot be further converted into superacid centres by subsequent action of HCl.

In the case of samples chlorinated by CCl_4 at 473 K, the Al—O—$AlCl_2$ groups are not formed and the creation of superacid species by HCl addition is not possible. In accordance with this hypothesis involving superacid groups as active sites, the initial activity in butane isomerization is the same for chlorinated alumina, whether it contains platinum or not. For such samples, the effect of platinum is restricted to a limitation of the deactivation rate (hydrogenating function).

The participation of superacid species in the mechanism of alkanes isomerization is not in contradiction with industrial processes, since traces of chlorinated hydrocarbons are injected in the feed in order to continuously produce hydrochloric acid. HCl so formed is then able to generate additional superacid groups. Further experiments are needed for a better understanding of the role of hydrogen chloride in the catalysts of alkanes isomerization.

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