Journal of Catalysis **212,** 173–181 (2002)
doi:10.1006/jcat.2002.3765

Surface and Subsurface Platinum in Sulfated Zirconia Catalysts: Relation with Toluene Hydrogenation and *n*-Hexane Isomerization

J. van Gestel,[1] Vu T. Nghiem, D. Guillaume,[2] J. P. Gilson, and J. C. Duchet

Laboratoire de Catalyse et Spectrochimie, CNRS-ISMRA—Université de Caen 6, bd. du Maréchal Juin, F-14050 Caen, France

Received April 24, 2002; revised June 20, 2002; accepted July 10, 2002

DEDICATED TO THE MEMORY OF ALAN PETERS, FORMERLY RESEARCH MANAGER
AND SENIOR SCIENTIST AT GRACE-DAVISON

Surface platinum of sulfated zirconia has been characterized by hydrogenation of toluene at 150°C and by carbon monoxide adsorption on a series of catalysts containing 0.025–0.8 wt% Pt. The variation of the hydrogenation rate with the Pt content showed two linear domains with a sharp increase at 0.15 wt% Pt. A very good correlation between hydrogenation activity and CO adsorption indicates that the low activity at low loading results from a lack of accessible platinum. We suggest that part of the platinum migrated to the subsurface of the zirconia matrix. After the saturation of the subsurface platinum sites, additional platinum is located on the surface with a constant particle size of about 1 nm. Combination of these results with those of the isomerization of *n*-hexane at 150°C indicates that very active surface platinum does not play the key role in isomerization. The influence of hydrogen on the isomerization activity nicely correlates with the estimated amount of platinum inserted in the subsurface of zirconia. Reduction of the catalysts at higher temperatures (up to 250°C) diminishes strongly the toluene hydrogenation activity of the samples, while *n*-hexane isomerization is hardly affected. This is further proof of the importance of subsurface platinum in isomerization and supports the kinetic model based on Lewis acid sites, where desorption of the isocarbenium ion is assisted by hydrides formed on subsurface platinum.

Key Words: **sulfated zirconia; *n*-hexane isomerization; platinum; reduction; toluene hydrogenation.**

INTRODUCTION

Pt supported sulfated zirconia catalysts are known to isomerize linear alkanes at low temperatures (1, 2). Their importance will further grow with the strong demand for the production of isoparaffin molecules from the C5–C6 cut (high octane number). They comply with the environmental regulations for clean processes and therefore are good candidates to substitute the corrosive halogenated alumina catalysts and the lower activity zeolitic catalysts. Active and stable catalysts require the presence of a noble metal, generally platinum, and the presence of hydrogen to prevent "coke" formation (2–4).

The vast literature on sulfated zirconias reports a strong influence of hydrogen on the isomerization activity. Most of the publications deal with *n*-butane at atmospheric pressure and temperatures higher than 200°C. Positive (5, 6) or negative (6, 7) hydrogen orders are observed, depending on the hydrogen/hydrocarbon ratio and temperature. A maximum in activity is observed when working over a wide range of H_2/C_4 ratio (8, 9). Under pressure, the order changes from zero to negative, depending on temperature (10, 11).

Higher alkanes (C5 to C7, methylcyclohexane) are generally isomerized under pressure and at lower temperatures (100–200°C) than butane. Typical catalysts containing 0.5 wt% Pt show a positive (5, 12–14) or zero order with respect to hydrogen (10). A maximum is found for *n*-hexane isomerization at atmospheric pressure and much higher temperatures (270–330°C) on a catalyst highly loaded (3%) with platinum (15). Most authors explain their results qualitatively: hydrogen is activated on platinum and is a source of protons and hydride species. The positive effect of hydrogen at low pressure is due to increased concentrations of either Brønsted acid sites (5, 16) or hydride species assisting the desorption of the isocarbenium ions (12, 16). In turn, excess hydrogen inhibits the reaction by competing with the intermediates on the active sites. These studies, however, deal with catalysts loaded with only one, relatively high, platinum concentration.

We recently reported a systematic study on the influence of the hydrogen partial pressure (5–45 bars) independently of the hexane pressure (1–5 bars) in a series of platinum-loaded catalysts (as low as 0.025 wt% and as high as 0.8 wt% platinum) (17). In all cases, the rate first increased with hydrogen pressure, reached a maximum, and finally decreased slowly. The reaction conditions used in this latter study were in the range used in the commercial practice of these

---

[1] To whom correspondence should be addressed. Fax: (+33) 02 31 45 28 22. E-mail: vangestel@ismra.fr.

[2] Present address: Institut Français du Pétrole, F-92506 Rueil Malmaison.

0021-9517/02 $35.00

catalysts. Changing the platinum loading considerably affected the influence of hydrogen on the isomerization rate: below 0.15 wt%, the rate increase with hydrogen slowed progressively, and the position of the maximum shifted toward higher hydrogen pressure as the loading decreased. There was no influence of platinum content on the shape of the curves above 0.15 wt%.

Kinetic modeling gave valuable insight into the isomerization mechanism, especially on the roles of hydrogen and platinum. The model was based on an acid mechanism in which a Lewis acid–base pair of sites promotes carbenium ion formation. The presence of strong Lewis acid sites was shown by FT–IR spectroscopy of adsorbed carbon monoxide. Desorption of the isomerized carbocation is assisted by hydrides associated with the platinum–hydrogen pair. The parameters of the rate equation (α, related to the platinum–hydrogen couple, and β, related to the acid strength of the sulfated zirconia) fitting the whole range of data quantified modifications of the catalyst functions: while the Lewis acidity remained constant in the series, the efficiency of the platinum–hydrogen couple first increased with loading and then leveled at 0.15 wt%. Such a plateau is intriguing and prompts us to characterize the surface platinum by means of its activity in toluene hydrogenation.

The first goal of the present paper is to determine if hydrogen species involved in *n*-hexane isomerization need platinum with a high hydrogenation activity. This was examined on the whole series of catalysts loaded with 0.025–0.8 wt% Pt. Furthermore, in the presence of sulfates, the state of platinum may be strongly affected by the temperature of reduction. Reduction generally occurs in the presence of hydrogen at the reaction temperature used for isomerization. At 150°C, platinum oxide is reduced to metal, as shown by carbon monoxide adsorption (17). Higher temperatures may affect the activity of platinum and the sulfated zirconia as well. Changes occurring in *n*-hexane isomerization upon reduction between 150°C and 250°C were studied on two samples containing 0.1 and 0.3 wt% Pt. The platinum loadings were chosen to be substantially below and above 0.15 wt% Pt, the breakpoint in isomerization behavior as found earlier (17). Results will be interpreted using the same kinetic parameters of the rate equation proposed earlier.

EXPERIMENTAL

Catalysts

Zirconium hydroxide was precipitated from an aqueous solution of zirconium oxychloride by ammonium hydroxide. The powder was sulfated with 0.5 M H_2SO_4 and then shaped as extrudates with an alumina binder (20 wt% Al_2O_3), followed by calcination at 650°C. The zirconia crystallized in the cubic form, with a small fraction of monoclinic phase. The sulfur content amounted to 2.0 wt%. Platinum was loaded at 0.025, 0.05, 0.1, 0.15, 0.3, 0.5, and 0.8 wt% by incipient wetness impregnation with an H_2PtCl_6 solution. The final catalyst was calcined at 480°C. Further details on the preparation are described elsewhere (17).

Activity Measurements

The catalyst (0.3 g of extrudates) was activated in the reactor at 400°C for 2 h in a flow of dry air, then purged by passing a dry helium flow while cooling down, and subsequently reduced with flowing hydrogen at 150°C (standard conditions) or 175–250°C during 2 h. Dry *n*-hexane (3 and 5 bars) was vaporized in the dry hydrogen–helium mixture at 50 bars total pressure and 150°C. The hydrogen partial pressure was varied from 5 to 45 bars. Conversions were kept low (<30%) to calculate initial rates, assuming first-order kinetics. Great care was taken to work with a very low (<0.15 ppm) moisture level. Under these conditions, the catalyst was stable for more than one week. Toluene hydrogenation rates were measured in a differential reactor under atmospheric pressure (0.026 bar of toluene) at 150°C on catalysts (about 50 mg) activated according to the same procedure as that used for *n*-hexane isomerization. Steady-state activity was achieved after 2 h.

Infrared Characterization

Infrared spectra were recorded on a Nicolet Magma 550 spectrometer equipped with a DTGS detector. The catalyst extrudates were crushed and pressed into self-supported wafers. The pellet was activated *in situ* in a flow cell under air at 400°C for 2 h cooled down to 150°C under nitrogen, and contacted with flowing hydrogen for 1 h. The cell was finally evacuated at room temperature before the FTIR measurements were started. The metallic function was characterized by stepwise adsorption of small doses of carbon monoxide at room temperature.

RESULTS AND DISCUSSION

Toluene Hydrogenation and Carbon Monoxide Adsorption: Platinum Accessibility

Hydrogenation of toluene at atmospheric pressure was measured at 150°C on the series of Pt/SZ (0.025–0.8 wt% Pt) catalysts reduced at 150°C. Under these experimental conditions, at low conversion, the reaction was totally selective into methylcyclohexane. Neither isomerization nor ring-opening products were observed. Apparently, the acidic function of the catalysts was not activated, probably due to traces of moisture. Moreover, hydrogenolysis on the metal was not observed. The variation of the hydrogenation rate with platinum content is plotted in Fig. 1. Two linear domains are clearly distinguished: catalysts with a low platinum loading are poorly active, while hydrogenation develops in the second domain, above 0.15 wt% Pt. The

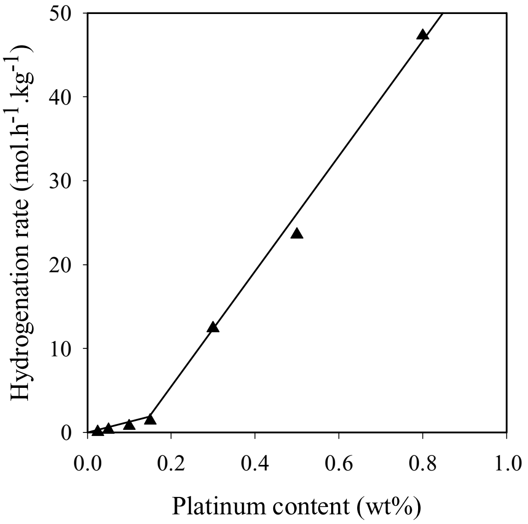


FIG. 1. Influence of platinum loading on the toluene hydrogenation rate at 150°C over the Pt–SO_4–ZrO_2 catalysts.

observed straight lines indicate a constant dispersion within each domain. The quasi-turnover frequency per atom of platinum in the catalyst (QTOF) increases from 0.04 s^{-1} for the 0.1 wt% Pt sample to 0.22 s^{-1} for 0.3 wt% Pt. Such a sharp change is remarkable for supported metals. Since the catalysts are shaped as extrudates of sulfated zirconia powder with an alumina binder, preferential location of platinum on the alumina binder might occur. However, impregnating the xerogel alumina calcined at 650°C with 0.15% Pt, activation at 400°C in air and reduction at 150°C, showed a negligible activity for toluene hydrogenation at 150°C. In any case, preferential platinum location on the binder should be a continuous phenomenon, without such a sharp change. Also samples with 0.05–0.6% platinum supported on pure nonsulfated zirconia powder crystallized at 500°C before platinum impregnation showed the two domains in hydrogenation. We conclude that platinum located on the alumina binder (if any) plays a negligible role compared to that supported on the zirconia. Therefore, the two platinum domains, below and above 0.15 wt%, are characteristic of the platinum–zirconia system, and we can exclude shielding of the platinum by sulfates.

Infrared spectroscopy of adsorbed carbon monoxide is often used to measure the dispersion of platinum (18). For instance, Fig. 2a gathers the IR spectra recorded after adsorption of incremental small doses of CO at room temperature on the 0.3 wt% Pt sample reduced at 150°C. The band at 2080 cm^{-1} near saturation is characteristic of linear adsorbed CO species on metallic platinum. At higher doses, a band at 1863 cm^{-1} appears, usually attributed to bridged species. The other catalysts examined, containing 0.1, 0.5, and 0.8 wt% Pt, showed the similar IR features of the fingerprint of metallic platinum. Quantitative analysis of the data by the saturation method allows us to determine the number of platinum adsorption sites. According to (18), the breakpoint in the plot of the IR signal versus the quantity of CO introduced (Fig. 2b) corresponds to the amount of CO adsorbed at saturation, which is equal to the amount of accessible platinum. For the four catalysts studied by FT–IR, the results of the titration of accessible platinum with CO are plotted in Fig. 3 against the toluene hydrogenation activity. A very good correlation between these two characterizations is obtained. This validates toluene hydrogenation as a model reaction to probe the accessible surface platinum of our sulfated zirconia catalysts. Such a good correlation was already shown for the reverse reaction over ceria–alumina supported Pt catalysts (19), and for toluene hydrogenation over zeolite supported Pt and Pd catalysts (20). From this figure, the real turnover

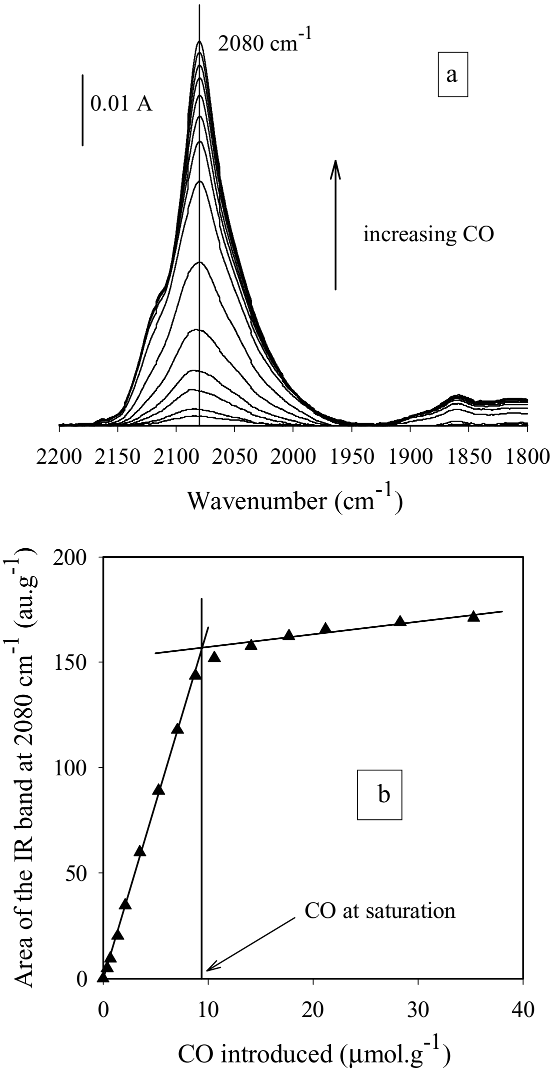


FIG. 2. (a) Infrared spectra of incremental amounts (smallest dose 0.007 μmol up to about 0.7 μmol) of adsorbed CO at room temperature on the 0.3 wt% Pt catalyst. (b) Determination of the platinum dispersion according to (18).

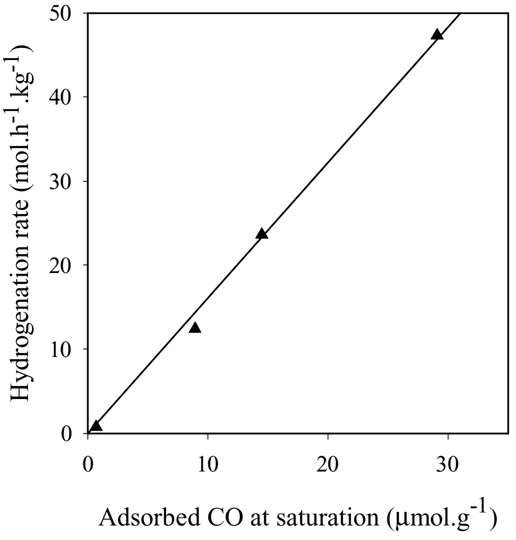


FIG. 3. Relation between the amount of CO adsorbed at saturation and the hydrogenation activity at 150°C for the catalysts containing 0.1, 0.3, 0.5, and 0.8 wt% Pt.

frequency for toluene hydrogenation over Pt is calculated to be 0.45 s^{-1}, a very reasonable value for a temperature of 150°C. Both hydrogenation and CO characterizations fully agree in that the mediocre activity of the low-loaded catalysts in the first domain is the result of a lack of accessible platinum. At first glance, this could result from a low platinum dispersion. From CO adsorption, the dispersion of platinum ($D =$ number of accessible Pt atoms/number of total Pt atoms in the catalyst) on the 0.1 wt% catalyst was estimated to be 15%, a surprisingly poor result for such a low loading. For the other samples containing 0.3, 0.5, and 0.8 wt% Pt, falling in the second domain in hydrogenation, the calculated dispersion increases but remains poor, 58, 57, and 71%, respectively. This change in dispersion would mean an unrealistic decrease in particle size from 6.1 to 1.2 nm with increasing platinum content from 0.1 to 0.8 wt%. This change contrasts with the linear variation of the hydrogenation rate. A cause other than a particle size effect must therefore account for the lack of accessible platinum below 0.15 wt%.

We propose that a fraction of the platinum is embedded in the subsurface of the zirconia, and not accessible to either toluene or carbon monoxide. Zirconia is known to accommodate various cations, such as yttrium, to stabilize its cubic structure (21). Yamamoto *et al.* corroborated by XAFS insertion of Fe ions in the zirconia bulk (22). Manoli *et al.* (15) proposed this from XPS embedding of platinum in the bulk of zirconia. However, in that study 3 wt% Pt was loaded on an uncalcined sample. Upon calcination, large particles of platinum were covered by zirconia. In our case, platinum was impregnated on the already crystallized zirconia. The calcination temperature of the platinum precursor (480°C) was far below the crystallization temperature of the sulfated zirconia (650°C). So, any changes of the zirconia can be excluded. The diffusion of metal ions into the zirconia matrix is shown by EPR to be an equilibrated process at high temperatures (23). Therefore, at a given calcination temperature, the amount of inserted platinum should depend on the total platinum content, reaching a limit when the zirconia subsurface is saturated. This limit can be determined from the two branches of the toluene hydrogenation rates in Fig. 1. Indeed, at constant particle size, the observed reaction rate is proportional to the amount of external (i.e., on the accessible surface) platinum, $\mathrm{Pt_{Ext}}$. For catalysts below the saturation level, a fraction x of total platinum, $\mathrm{Pt_{Tot}}$, is inserted, and $\mathrm{Pt_{Ext}} = (1 - x)\ \mathrm{Pt_{Tot}}$. Saturation occurs at $\mathrm{Pt_{Tot}} = \mathrm{Pt_{Sat}}$, and subsequent platinum will be external. So, in the second domain, $\mathrm{Pt_{Ext}} = (1 - x)\ \mathrm{Pt_{Sat}} + (\mathrm{Pt_{Tot}} - \mathrm{Pt_{Sat}})$. Optimization of the unknowns reveals that the zirconia of our samples accommodates as much as 82% of total platinum at low loading and is saturated for a total loading of 0.15 wt% Pt.

Subsurface (cationic) platinum is not active for hydrogenation, as in the case of nickel in γ-alumina (spinel). Accordingly, the QTOF is very low for catalysts with platinum content below 0.15 wt%, due to the very low levels of $\mathrm{Pt_{Ext}}$. We verified that even after reduction under 10-bar hydrogen, the 0.1 wt% Pt sample remained poorly active for toluene hydrogenation.

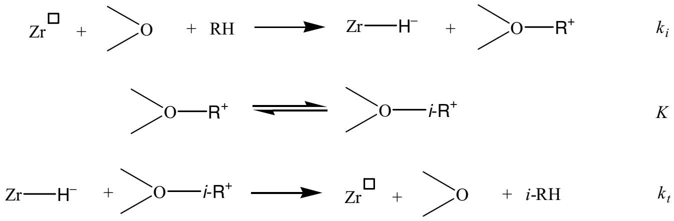
It is worth mentioning that the occurrence of such "buried" platinum species explains why hydrogen, or carbon monoxide, hardly adsorbs on low-loaded samples (24–27), while adsorption is substantial at higher loading. This phenomenon is very frequently ascribed to the SMSI effect. However, the calculation of meaningful particle sizes from adsorption measurements are erroneous if part of the platinum is not located on the surface but migrates to the subsurface of the support. The good correlation between toluene hydrogenation and CO adsorption in this study allows us to determine the particle size of surface platinum. For all samples studied, we found a constant particle size of 1.0 nm. This value is much more realistic than the very high values obtained when all platinum was considered as surface Pt. So, the sharp change in hydrogenation at 0.15 wt% Pt is not the result of sintering or SMSI effects.

Efficiency of Platinum: n-Hexane Isomerization versus Toluene Hydrogenation

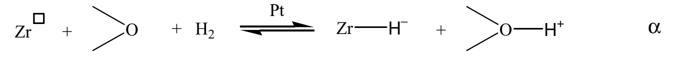
We can now compare the efficiency of platinum supported on the sulfated zirconia for toluene hydrogenation and *n*-hexane isomerization. As far as isomerization is concerned, the general features of the influence of platinum at various hydrogen and hexane pressures and the proposed mechanism have been recalled in the Introduction. More details were reported in (17). We recall briefly, however, the elementary steps of the reaction mechanism that allowed a very satisfactory kinetic modeling of the data.

We proposed to combine two reaction sequences: a sequence (a) involving Lewis acid–base sites, dealing with the isomerization itself and a second sequence (b) relative to the hydrogen–platinum couple.

(a) Isomerization sequence



(b) Hydrogen–platinum sequence



Our results (17) showed that the closed isomerization sequence (a) does not operate without hydrogen; i.e., the hydride species created from the hydrocarbon at the initiation step were not as efficient as those produced in the platinum–hydrogen sequence (b) to assist the desorption of the isocarbenium ions. Indeed, fitting the data in the whole range of hydrogen and hexane pressures yielded a negligible contribution of the hydrides generated in the isomerization sequence itself. The resulting rate equation is (17)

$$r = \frac{k \cdot P_{\mathrm{RH}}}{\left\{1 + \alpha \cdot P_{\mathrm{H}_2} + \frac{\beta}{\alpha} \cdot \frac{P_{\mathrm{RH}}}{P_{\mathrm{H}_2}}\right\}^2},$$

where

$$k = L \cdot k_i \qquad (L = \text{number of acid–base sites})$$

$$\alpha = \frac{(\mathrm{O}-\mathrm{H}^+)\cdot(\mathrm{Zr}-\mathrm{H}^-)}{(\mathrm{Zr})\cdot(\mathrm{O})\cdot p(\mathrm{H}_2)}$$

$$\beta = \frac{k_i}{k_t}\left(1 + \frac{1}{K}\right).$$

In addition to the rate constant k, two independent parameters characterize the catalyst: α is related to the efficiency of the platinum–hydrogen couple, and β is representative of the acid strength of the sulfated zirconia sites in the isomerization sequence. This equation accurately modeled all the features of the influence of hydrogen (positive and negative orders, shift of the maximum with increasing hexane pressure) on the isomerization rate for the series of catalysts with various platinum loadings (17).

The variation of the kinetic parameters with platinum content was informative about the changes in the functions of the isomerization catalyst. As expected, the parameter β, associated with acidity, remained constant in the series, indicating that the strength of the Lewis acid–base sites was not influenced by platinum. Only the number of sites, represented by the rate constant k, was slightly decreased with platinum loading. Most significant was the variation of the parameter α in the series: it showed that the hydrogen influence on the isomerization rate was remarkably governed by the efficiency of the platinum–hydrogen couple.

Figure 4a recalls the variation of parameter α in the *n*-hexane isomerization with platinum loading (17). Comparing the variation of α with that of toluene hydrogenation (Fig. 1), it is clear that both sets of experiments highlight an abrupt change in catalytic activity at about 0.15 wt% Pt. Strikingly, α increases only for low-loaded catalysts. Beyond 0.15 wt% Pt, α reaches a plateau, while toluene hydrogenation activity increases rapidly with the concentration of accessible platinum. This implies that platinum located on the accessible surface, $\mathrm{Pt}_{\mathrm{Ext}}$, does not play a key role

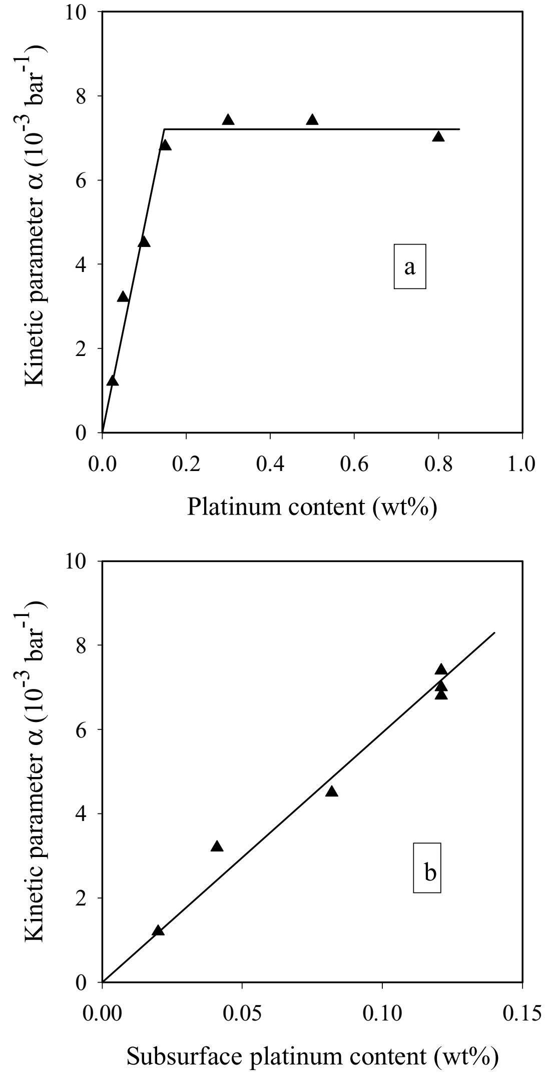


FIG. 4. (a) Variation of the kinetic parameter α for isomerization with platinum content. (b) Relation between α and the amount of inserted platinum.

for *n*-hexane isomerization. The most important platinum species are those inserted into the zirconia matrix. This is suggested by the strong correlation with the kinetic parameter α (Fig. 4b). In our previous paper (17), we hypothesized, on the basis of kinetic arguments, that only some specific platinum species were involved in *n*-hexane isomerization. The present comparison with the activity of platinum in hydrogenation strongly suggests that these species are related to subsurface platinum. The major role of hydride species originating from the platinum–hydrogen sequence in the mechanism is thus confirmed.

Unfortunately, direct spectroscopic or TEM evidence for subsurface platinum is not presently available. However, this hypothesis can be validated indirectly by measuring the reactivity of catalysts where the level of accessible platinum, Pt_{Ext}, has been modified by reduction at higher temperatures. Such results are reported in the following section.

Influence of the Reduction Temperature on the Catalytic Properties of Pt/Sulfated Zirconia

Two samples, containing 0.1 and 0.3 wt% Pt were chosen as representative of the two domains observed in *n*-hexane isomerization and toluene hydrogenation.

Characterization of accessible platinum: hydrogenation of toluene, adsorption of CO. The variation of the toluene hydrogenation rate at 150°C on catalysts reduced at various temperatures is shown in Fig. 5. The hydrogenation activity of the 0.3 wt% Pt sample strongly decreases with the reduction temperature in the range of 150–200°C and then stabilizes at a very low level. The effect appears so dramatic that it cannot be attributed to a loss in dispersion of the metallic particles. More plausible is the sensitivity of metallic platinum to sulfur (28). At a reduction temperature of 150°C, the external platinum is present in the metallic state, as shown by the IR band of adsorbed CO at 2080 cm^{-1}. According to the literature (2), a fraction of the metal can be formed already during the calcination of the platinum precursor. The remaining PtO_2 is readily reduced. At high reduction temperature (above 200°C), hydrogen sulfide was detected by mass spectrometry analysis of the exit gas, indicating sulfate reduction. Hence, it is quite likely that the low hydrogenation activity is due to sulfur poisoning of the metal, in agreement with the literature (29–31). Poisoning of platinum by sulfur is fully supported by the infrared spectra of adsorbed CO. After reduction at 250°C, the band is now located at 2093 cm^{-1}. No signal at 2080 cm^{-1} observed for metallic platinum in the case of reduction at 150°C is further detected. This shift of 13 cm^{-1} is comparable to that observed on sulfur-poisoned Pt/Al_2O_3 (32). This is in line with the known effect of sulfur coverage of the platinum surface on the binding energy of adsorbates. In the case of carbon monoxide (and hydrogen), the decrease is attributed to repulsion with adsorbed sulfur (28). Moreover, the adsorption capacity is lowered on the sulfided metal and depends on the sulfur coverage. This hampers a correct determination of the particle size.

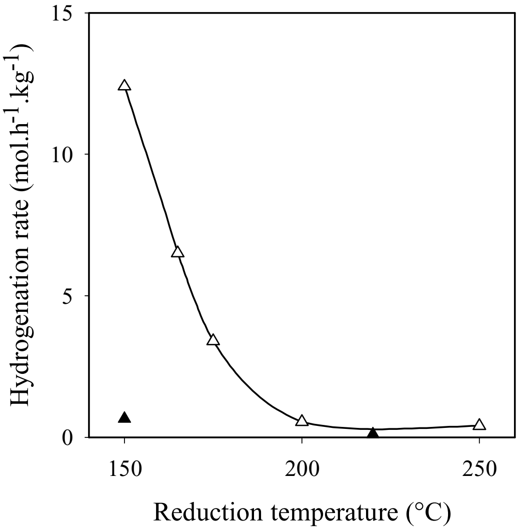


FIG. 5. Influence of the reduction temperature on the toluene hydrogenation rate at 150°C over $Pt–SO_4–ZrO_2$ catalysts. The catalysts were reduced at atmospheric pressure. Open symbols: 0.3 wt% Pt; filled symbols: 0.1 wt% Pt.

The main conclusion is that at 250°C hydrogen reduces some sulfates. Consequently, the Pt_{Ext} has been poisoned and lost its metallic properties. This may also occur during the isomerization conditions, under high hydrogen pressure.

The influence of the reduction temperature on the sample containing 0.1 wt% Pt is much more limited (Fig. 5). In fact, the sample contains a small amount of Pt_{Ext} and is therefore poorly active in toluene hydrogenation, even at the low reduction temperature of 150°C. It follows that poisoning by sulfur upon reduction at higher temperatures is not pronounced. Nevertheless, a decrease in hydrogenation activity can be measured upon reduction at 220°C.

Isomerization of n-hexane. Isomerization rates were measured at 150°C for 3- and 5-bar *n*-hexane at various hydrogen pressures on the 0.1 and 0.3 wt% Pt catalyst reduced *in situ* at a temperature in the range of 150–250°C. The activity of the two catalysts reduced at 150°C is compared in Fig. 6, showing the influence of the platinum content on the evolution of the reaction rate with hydrogen pressure. The position of the maximum is clearly dependent on the platinum loading, while both catalysts have the same maximum activity. At 10 bars of hydrogen, the 0.1 wt% sample appears more active than its 0.3% counterpart. It should be noted, however, that the response to hydrogen after standard reduction at 150°C is slightly different from that obtained one year earlier on the same catalyst (17): the catalyst lost 20% of its activity, and the maximum shifted to lower hydrogen pressures. We can discard any irreproducibility of the

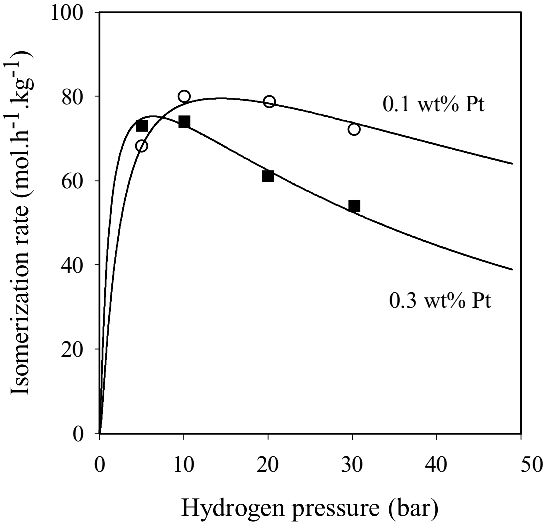


FIG. 6. Comparison of the isomerization rates at 150°C and 3-bar *n*-hexane over the two catalysts containing 0.1 (open symbols) and 0.3 wt% Pt (filled symbols). Reduction temperature is 150°C.

measurements. The sample did not lose sulfur, as checked by chemical analysis. We may suspect some structural change of the zirconia that would have spontaneously occurred during the period separating the two studies. However, XRD failed to detect such a modification. So, the reason for the catalyst change remains unclear but is not very relevant with respect to the main topic of this paper. Indeed, we studied the influence of the reduction temperature on these samples between 150°C and 250°C, so the internal comparison is correct.

Figure 7 gathers some of the isomerization results for 3-bar *n*-hexane measured at 150°C on the catalyst containing 0.3 wt% Pt, reduced *in situ* at the specified temperatures. Reduction at 220°C or 250°C is detrimental to the isomerization activity, whatever the hydrogen pressure. In all cases, the curves display the typical maximum reported earlier for sulfated zirconia catalysts.

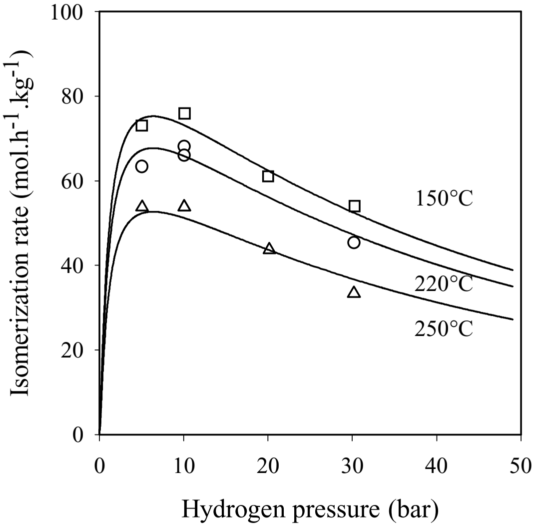


FIG. 7. Influence of the reduction temperature on the isomerization rate at 150°C and 3-bar *n*-hexane for the Pt–SO_4–ZrO_2 catalyst (0.3 wt% Pt).

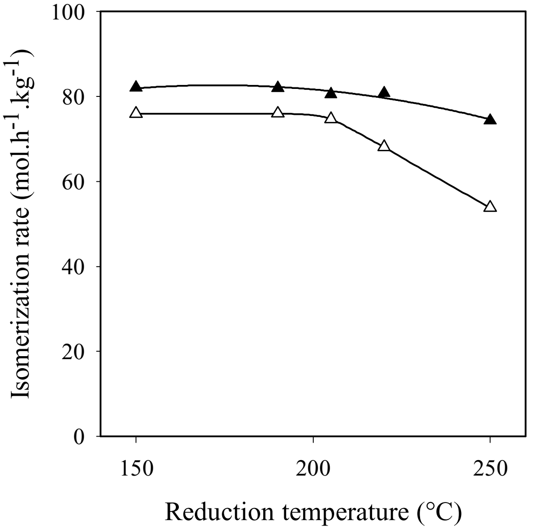


FIG. 8. Influence of the reduction temperature of Pt–SO_4–ZrO_2 catalysts on the isomerization rate at 150°C and 3-bar *n*-hexane and 10-bar hydrogen. Open symbols: 0.3 wt% Pt; filled symbols: 0.1 wt% Pt.

The isomerization rates measured at 10-bar H_2 and 3-bar hexane are plotted in Fig. 8 against reduction temperatures. An increase in the reduction temperature leads to a decrease in the isomerization activity. The effect is minor for the 0.3 wt% Pt sample reduced between 150°C and 205°C, but it is more dramatic at higher temperature. Reduction at 250°C results in a decrease of about 30% of the catalyst activity compared to that reduced at 150°C. However, the maximum rate is found at the same hydrogen pressure ($P_{H_2} = 6$ bars). If our hypothesis about inserted platinum is correct, the activity in isomerization for the catalyst containing 0.1 wt% platinum should be almost insensitive to reduction, because most of its platinum is located in the subsurface, i.e., incorporated into the zirconia. This is in fact the case, as shown in Fig. 8 for 3-bar hexane and 10-bar hydrogen. A slight loss in activity is observed for reduction at 250°C, amounting to no more than 8%, and contrasts with the 30% encountered on the 0.3 wt% catalyst. This confirms that very active surface platinum can diminish the isomerization activity of the catalyst much more by sulfate reduction. Moreover, the selectivity among isomers is not affected by reduction. The product distribution in Fig. 9 shows that methyl-2-pentane (2MP), methyl-3-pentane (3MP), and dimethyl-2,3-butane (23DMB) were formed in their internal thermodynamic ratios. In any case, these isomerization steps are very fast and all three isomers, even 23DMB, appear as primary products. Dimethyl-2,2-butane (22DMB) is formed consecutively. Such a behavior

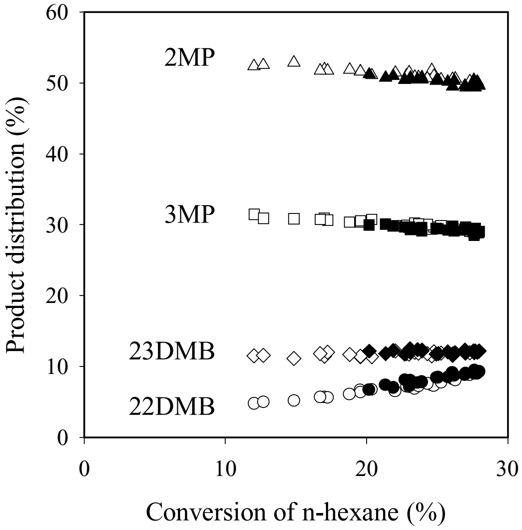


FIG. 9. Product distribution at 150°C for Pt–SO_4–ZrO_2 catalysts for various hydrogen pressures and reduction temperatures. Open symbols: 0.3 wt% Pt; filled symbols: 0.1 wt% Pt.

is typical of the Pt-sulfated zirconia catalysts (17). Similar features are observed at 5-bar *n*-hexane. Then, the reduction temperature only affects the activity of the catalyst, but not the shape of the curve (response to hydrogen) nor the selectivity.

All the data at 3- and 5-bar hexane for the catalyst reduced at various temperatures could be fitted by the kinetic rate equation already presented (17). The change in behavior with reduction temperature may then be quantified by the kinetic parameters.

The isomerization rate constant k is significantly decreased upon reduction of the 0.3 wt% sample: from 33 mol h^{-1} kg^{-1} bar^{-1} at 150°C to 23 mol h^{-1} kg^{-1} bar^{-1} at 250°C. This reflects a loss in the number of acidic sites. It is a further proof that platinum easily catalyzes the reduction of sulfate species in the presence of hydrogen. However, under our conditions, about two thirds of the active sites are preserved even after a hydrogen treatment at 250°C. Most probably, platinum becomes rapidly inactive for reduction due to strong poisoning by sulfur. This is in full agreement with the results of the toluene hydrogenation and CO adsorption.

The parameter β is almost constant at a value 0.002 bar^{-1} for both catalysts. Therefore, the acid strength is not influenced by reduction. Only the number of sites is decreased. This is in line with the internal isomer distribution, independent of the reduction temperature (Fig. 9).

Again, the most significant parameter is α, associated with the platinum–hydrogen efficiency in supplying hydride species to the Lewis acid sites. The parameter α remains remarkably constant ($\alpha = 0.012$ bar^{-1} for the 0.3 wt% Pt sample) whatever the reduction temperature. Hence, the activity of platinum for isomerization remains high, while the toluene hydrogenation rate decreases dramatically. The already lower value of α for the catalyst containing 0.1 wt% Pt ($\alpha = 0.005$ bar^{-1}) is also unaffected by the reduction temperature. This study of platinum reduction shows evidence that the active isomerization catalyst is not as "demanding" on the platinum–hydrogen couple as is hydrogenation. Therefore, platinum plays a different role in *n*-hexane isomerization than in toluene hydrogenation. This supports the proposal that subsurface platinum plays a major role in isomerization.

It is thus demonstrated that isomerization over sulfated zirconia may proceed even in the absence of metallic Pt_{Ext}, very active in toluene hydrogenation. The hydride species involved in isomerization require specific platinum entities. We propose to associate these specific entities to the fraction of platinum located in the subsurface of the zirconia structure. Given the low loading of our catalysts, it is highly improbable that this embedded platinum is present as large particles. Such large particles have been evidenced in highly loaded samples, prepared by impregnation of the amorphous zirconia followed by calcination at high temperatures (15, 33). In our case, platinum is deposited after crystallization of the sulfated zirconia further calcined at moderate temperatures. Under these conditions, migration into the zirconia matrix should yield isolated ionic species and not sintered particles. Platinum ions would thus strongly interact with the zirconia matrix and remain in close proximity of the acid–base pair. We believe that a minimum efficiency of metallic external platinum is necessary to dissociate the hydrogen molecule, while the specific cationic platinum species associated with the acid–base pairs play an essential role in the generation of hydrides. Direct identification of these specific platinum species is most difficult due to their very low concentration and accessibility to probe molecules bulkier than H_2. The relation between the kinetic parameter α and toluene hydrogenation rate proves here to be most informative.

CONCLUSION

This study reports on the activity of platinum (0.025–0.8 wt% Pt) supported on sulfated zirconia in the isomerization of *n*-hexane and the hydrogenation of toluene, both at 150°C. Both reactions show a characteristic breakpoint at 0.15 wt% Pt. For isomerization, the efficiency of the platinum–hydrogen couple increases strongly with platinum content, reaching a plateau above 0.15 wt% Pt. The hydrogenation activity of these catalysts shows an opposite trend: a low QTOF below 0.15 wt% and a strong increase above 0.15 wt% Pt. Characterization of the platinum by CO adsorption followed by FTIR indicates metallic Pt on all catalysts; in addition, the amount of adsorbed CO nicely correlates with toluene hydrogenation at 150°C. We conclude that the low QTOF at low loading results from a lack of accessible platinum, due to migration of platinum into the subsurface of the zirconia support. The good correlation between the estimated amount of inserted platinum ions and the kinetic parameter representing the platinum–hydrogen couple proves the involvement of subsurface platinum in the isomerization mechanism. Surface (metallic) platinum is necessary only for the dissociation of molecular hydrogen, but a very low hydrogenation activity is sufficient. This is further demonstrated by applying a higher reduction temperature of the catalyst: surface platinum is poisoned by sulfur, while the isomerization activity is hardly affected.

This study further highlights the potential of kinetic modeling as a tool for an in-depth understanding of the working catalyst as well as a method to a rational design of improved catalysts.

ACKNOWLEDGMENTS

We kindly thank M. C. Basset and J. Quillard for the activity measurements and S. Aiello for the construction of the low temperature IR flow cell. Total FinaElf is kindly acknowledged for their financial support.

REFERENCES

1. Arata, K., *Adv. Catal.* **37**, 165 (1990).
2. Song, X., and Sayari, A., *Catal. Rev.-Sci. Eng.* **38**(3), 329 (1996).
3. Chen, F. R., Coudurier, G., Joly, J. F., and Vedrine, J. C., *J. Catal.* **143**, 616 (1993).
4. Vaudagna, S. R., Comelli, R. A., Canavese, S. A., and Figoli, N. S., *J. Catal.* **169**, 389 (1997).
5. Ebitani, K., Konishi, J., and Hattori, H., *J. Catal.* **130**, 257 (1991).
6. Kim, S. Y., Goodwin, J. G., Hammache, S., Auroux, A., and Galloway, D., *J. Catal.* **201**, 1 (2001).
7. Sayari, A., Yang, Y., and Song, X., *J. Catal.* **167**, 346 (1997).
8. Garin, F., Andriamasinoro, D., Abdulsamad, A., and Sommer, J., *J. Catal.* **131**, 199 (1991).
9. Signoretto, M., Pinna, F., Strukul, G., Chies, P., Cerrato, G., Di Ciero, S., and Morterra, C., *J. Catal.* **167**, 522 (1997).
10. Liu, H., Lei, G. D., and Sachtler, W. M. H., *Appl. Catal., A* **137**, 167 (1996).
11. Tomishige, K., Okabe, A., and Fujimoto, K., *Appl. Catal., A* **194–195**, 383 (2000).
12. Iglesia, E., Soled, S. L., and Kramer, G. M., *J. Catal.* **144**, 238 (1993).
13. Comelli, R. A., Finelli, Z. R., Vaudagna, S. R., and Fígoli, N. R., *Catal. Lett.* **45**, 227 (1997).
14. Figueras, F., Coq, B., Walter, C., and Carriat, J.-Y., *J. Catal.* **169**, 103 (1997).
15. Manoli, J.-M., Potvin, C., Muhler, M., Wild, U., Resofszki, G., Buchholz, T., and Paál, Z., *J. Catal.* **178**, 338 (1998).
16. Shishido, T., and Hattori, H., *Appl. Catal., A* **146**, 157 (1996).
17. Duchet, J. C., Guillaume, D., Monnier, A., Dujardin, C., Gilson, J. P., van Gestel, J., Szabo, G., and Nascimento, P., *J. Catal.* **198**, 328 (2001).
18. Binet, C., Jadi, A., and Lavalley, J. C., *J. Chim. Phys.* **86**, 451 (1989).
19. Rogemond, E., Essayem, N., Frety, R., Perrichon, V., Primet, M., and Mathis, F., *J. Catal.* **166**, 229 (1997).
20. Chupin, J., Gnep, N. S., Lacombe, S., and Guisnet, M., *Appl. Catal., A* **206**, 43 (2001).
21. Duchet, J. C., Tilliette, M. J., and Cornet, D., *Catal. Today* **10**, 507 (1991).
22. Yamamoto, T., Tanaka, T., Takenaka, S., Yoshida, S., Onari, T., Takahashi, Y., Kosaka, T., Hasegawa, S., and Kudo, M., *J. Phys. Chem. B* **103**, 2385 (1999).
23. Sasaki, K., and Maier, J., *Phys. Chem. Chem. Phys.* **2**, 3055 (2000).
24. Coq, B., Walter, C., Brown, R., McDougall, G., and Figueras, F., *Catal. Lett.* **39**, 197 (1996).
25. Comelli, R. A., *Catal. Lett.* **40**, 67 (1996).
26. Yori, J. C., and Parera, J. M., *Catal. Lett.* **65**, 205 (2000).
27. Falco, M. G., Canavese, S. A., Comelli, R. A., and Figoli, N. S., *Appl. Catal., A* **201**, 37 (2000).
28. Barbier, J., Lamy-Pitara, E., Marecot, P., Boitiaux, J. P., Cosyns, J., and Verna, F., *Adv. Catal.* **37**, 279 (1990).
29. Ebitani, K., Konno, H., Tanaka, H., and Hattori, H., *J. Catal.* **135**, 60 (1992).
30. Xu, B.-Q., and Sachtler, W. M. H., *J. Catal.* **167**, 224 (1997).
31. Buchholz, T., Wild, U., Muhler, M., Resofszki, G., and Paál, Z., *Appl. Catal., A* **189**, 225 (1999).
32. Chang, J. R., and Chang, S. L., *J. Catal.* **176**, 42 (1998).
33. Paál, Z., Wild, U., Muhler, M., Manoli, J. M., Potvin, C., Buchholz, T., Sprenger, S., and Resofszki, G., *Appl. Catal., A* **188**, 257 (1999).