Mechanism for isomerization of *n*-hexane over sulfated zirconia: role of hydrogen

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Received (in Cambridge, UK) 20th July 1999, Accepted 9th August 1999

The complex influence of hydrogen on *n*-hexane isomerization over sulfated zirconia enriched with platinum has been kinetically modelled with a simple three parameter rate equation derived from a mechanism involving Lewis sites and hydride species.

Sulfated zirconias are acidic catalysts which are able to isomerize linear alkanes at low temperature.[1,2] In practice, hydrogen is added to the isomerization unit in order to saturate the aromatics contained in the C_5–C_6 fraction and to prevent coking of the platinum enriched catalyst. Some authors attribute participation of hydrogen in isomerization *via* activation on platinum by creating either Brønsted acid sites[3,4] or hydride species accelerating the desorption of the carbenium ions.[5,6] In the literature, analysis of the influence of hydrogen has been limited to low hydrogen pressures.[6,7] Here we report the influence of hydrogen over a wide range of partial pressures (0.5–4.5 MPa) independently of the hexane pressure (0.1–0.5 MPa). Insight into the isomerization mechanism is obtained from the kinetic treatment of the data.

The catalyst was prepared as follows: zirconium hydroxide was precipitated from an aqueous solution of zirconium oxychloride by ammonium hydroxide. The dry material was sulfated with 0.5 M H_2SO_4, and then crystallised at 923 K. The sulfur content amounted to 2.0 wt%. Platinum was loaded at 0.3 wt% by impregnation with an H_2PtCl_6 solution and the final catalyst was calcined at 753 K. The catalyst was activated in the reactor at 623 K for 2 h in a dry air stream and contacted with flowing hydrogen at 423 K during 1 h. Dry *n*-hexane (0.1, 0.3 or 0.5 MPa) was vaporised in a dry hydrogen–helium mixture at 5 MPa total pressure and 423 K. The hydrogen partial pressure was varied from 0.5 to 4.5 MPa. Conversions were kept low to calculate initial rates.

The reaction was not observed without hydrogen owing to rapid deactivation. With hydrogen, the catalyst was stable for >1 week and cracking was negligible. The distribution among isomers showed that 2-methylpentane, 3-methylpentane and 2,3-dimethylbutane were primary products formed in their thermodynamic ratio. The formation of 2,2-dimethylbutane was a consecutive reaction. The distribution was not influenced by hydrogen partial pressure.

The variation of the isomerization rate with hydrogen pressure is shown in Fig. 1. At a given hexane pressure, the rate strongly increases up to a maximum, then slowly decreases. The position of the maximum was shifted from 0.3 to 1.5 MPa pressure of hydrogen with increasing hexane pressure in the range 0.1–0.5 MPa. The reaction order with respect to *n*-hexane was slightly lower than unity at low hydrogen pressure, and reached unity beyond the maximum.

Any proposed mechanism should account for the change in reaction order for hydrogen, from positive to negative, so yielding a maximum isomerization rate. Kinetic modelling was used to infer the reaction sequence.

The maximum activity with hydrogen pressure has scarcely been reported in the literature dealing with isomerization of light alkanes over acidic catalysts. A classical metal–acid bifunctional mechanism has been developed on platinum–zeolite catalysts operating at 523 K. The detrimental effect of hydrogen was easily interpreted by the dehydrogenation step of the hydrocarbon into an alkene. However, further dehydrogenation into a diene is required to account for a positive effect at low hydrogen pressure, so yielding a maximum in the curves.[8] We found that the corresponding rate equation completely failed to fit our data in the whole range of hexane pressure. Indeed, a classical bifunctional metal–acid mechanism is improbable at 423 K. The alkene concentration is likely to be too low, and the catalyst more likely operates by an acidic mechanism. The acidity of sulfated zirconia is generally attributed to Brønsted sites[9] and accordingly, carbenium ions are formed *via* carbonium intermediates. However, reaction sequences based on this first step did not yield satisfactory rate equations. On the other hand, Lewis sites are readily created during the activation of sulfated catalysts at 923 K.[9] We propose a mechanism involving Lewis sites in which hydride abstraction from *n*-hexane (RH) on coordinatively unsaturated zirconium atoms creates carbenium ions which adsorb on Lewis basic sites (bridged oxygen atoms). The adsorbed carbenium ions are then rapidly isomerized and finally desorbed by the hydride species (Scheme 1). The isomerization step is not rate-limiting, as shown by the thermodynamic distribution of primary isomers.

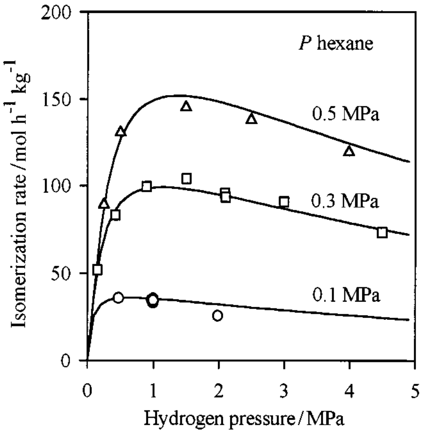
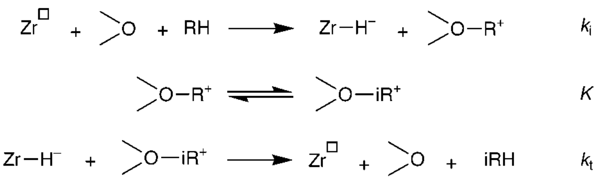


Fig. 1 Isomerization of *n*-hexane at 423 K and 5 MPa as a function of hydrogen pressure.

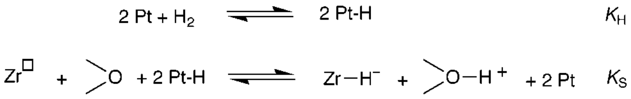
This scheme is fully consistent with the poisoning effect of water adsorbed on Lewis sites. The closed sequence isomerizes



Scheme 1 Isomerization sequence.

n-hexane in the absence of hydrogen but the catalyst rapidly deactivates by coking. Hydrogen prevents this coking.

The influence of hydrogen on the isomerization rate may be rationalised by a second sequence (Scheme 2) involving platinum. Molecular hydrogen is homolytically dissociated on the metal and the hydrogen atoms migrate by spillover to the sulfated zirconia where they are converted into hydride species (Zr–H$^-$) and protons (O–H$^+$).



Scheme 2 Hydrogen sequence.

In this manner, hydrogen increases the concentration of hydride species, accelerates the desorption of carbenium ions and thus the overall rate. This explains the positive order at low hydrogen pressure, while the decrease in activity at higher hydrogen partial pressure is simply owing to a competition between protons and carbenium species.

Kinetic treatment of this sequence yielded the rate eqn. (1)

$$r = \frac{kP_{\mathrm{RH}}}{\left\{1 + \alpha P_{\mathrm{H}} + \dfrac{\beta P_{\mathrm{RH}}}{\alpha P_{\mathrm{H}}}\right\}^2} \tag{1}$$

with $k = Lk_{\mathrm{i}}$ (L = number of adsorption sites), where $\alpha = K_{\mathrm{H}}K_{\mathrm{S}}$, $\beta = (k_{\mathrm{i}}/(k_{\mathrm{t}})[1 + (1/K)]$, P_{H} = pressure of hydrogen and P_{RH} = pressure of hexane.

Besides the rate constant k, which is related to the number of sites, two parameters, α and β, characterise the catalyst. Parameter α is associated with the sequence combining the capacity of platinum to adsorb hydrogen (K_{H}) and the transfer of hydrogen by spillover to the coordinatively unsatured zirconium and to the oxygen sites of the sulfated zirconia (K_{S}). The spillover is determined by the zirconia surface. The second parameter β is representative of the strength of the sulfated zirconia sites in the isomerization sequence.

The curves on the Fig. 1 were obtained after optimisation of the kinetic parameters. The fit is very satisfactory over the whole range of hexane pressure. This model has the advantage of involving two independent parameters that can be used as a guide to improve the catalysts. For instance, the hydrogen pressure at maximum isomerization rate is inversely proportional to α. Thus, to minimise the hydrogen pressure, α should be increased, either by increasing the platinum efficiency or the spillover rate.

The above mechanism demonstrates the importance of hydrogen in isomerization. For the first time, a complete reaction sequence is proposed, that offers a very good alternative for the classical bifunctional mechanism. Such a mechanism opens perspectives in the interpretation of the influence of hydrogen on various reactions.

Notes and references

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Communication 9/05855I