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New insights into the reaction mechanism and the rate-determining step of *n*-butane hydroisomerisation over reduced MoO₃ catalysts†

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The comparison of the proportions of the minor products formed during the hydroisomerisation of *n*-butane over reduced MoO₃ with thermodynamic data demonstrates that a bifunctional mechanism operates and that the rate-determining step is the isomerisation of the linear butene intermediates to *iso*-butene.

The need to tackle global warming has renewed the interest in alkane reforming for the production of more efficient and cleaner fuels. Catalysts based on molybdena reduced at mild temperatures, *e.g.* 623 K, are active for the hydroisomerisation of C₄–C₇ alkanes.^{1–5} These materials can be more selective than zeolite-supported platinum (in particular at high conversions), are more resistant to sulfur and nitrogen poisoning and do not catalyse the formation of significant levels of aromatics.^{3–5} However, industrial applications based on reduced MoO₃ are not yet viable, partly due to the low intrinsic activity of these materials.⁵ Further catalyst development has been hampered by the structural complexity of the material and by contradictory statements regarding the associated mechanism of reaction. Katrib *et al.*⁶ and Matsuda *et al.*⁵ have proposed that a traditional bifunctional mechanism operates, whereas Bouchy *et al.*⁷ have proposed a metallacyclobutane intermediate-based mechanism. In the case of the isomerisation of C₅–C₇ alkanes over reduced MoO₃, Matsuda *et al.*⁵ proposed that the dehydrogenation/hydrogenation process was the rate-determining step. The comparison of basic thermodynamic data with the proportions of reaction products, even at the trace level, has proven a valuable tool in unravelling reaction mechanisms.^{8,9} The data reported in the present article give a strong indication on the nature of the alkane isomerisation mechanism taking place over reduced MoO₃ samples and, moreover, suggest how the activity of these catalysts could be greatly improved.‡

The experimental details are available on-line as Electronic Supplementary Information.† The gradual increase of the activity of MoO₃ in *n*-butane conversion is shown in Fig. 1. The

yield of the main reaction product, *i.e.* *iso*-butane (right y-axis), follows a sigmoid-shape curve, similarly to the data based on other hydrocarbons.^{3,10} This behaviour can be explained by the time needed to form the reactive phase(s) from the reduction of MoO₃ (*e.g.* an oxycarbide MoO_xC_y phase⁷ or MoO₂⁶) and/or the increase in the surface area of the catalyst.¹¹ The steady-state value of the *iso*-butane yield (*ca.* 10%) was attained within 24 h under the experimental conditions used and corresponded to an *iso*-butane selectivity of *ca.* 90%. The main competitive reactions were cracking (*i.e.* C₃ + C₁ and 2 C₂), disproportionation (*i.e.* C₃ + C₅) and dehydrogenation (H₂ + butenes), with a selectivity of *ca.* 8, 1 and 1%, respectively.

The yields of the butene products (left y-axis) during the activation process are also reported in Fig. 1. Note that the total concentration of butenes is only about one hundredth that of *iso*-butane once steady-state conditions were reached. The concentration ratios of reactant and products at various times are given in Table 1. For the sake of clarity, the estimated error on the ratios (typically 10–15%) is only reported for the steady-state values. Interestingly, linear butenes were the first products to appear, after one hour on stream. After about three hours (not shown), but-1-ene was in thermodynamic equilibrium with *n*-butane. As the three linear butenes were also in equilibrium at this point, all the linear C₄ compounds were then equilibrated.

Is-butene was observed later than the linear butenes, *i.e.* after two hours, and the ratio *iso*-butene/but-1-ene always remained significantly below the corresponding thermodynamic value (see Table 1). The formation of *iso*-butene showed a maximum at *ca.* five hours, at which time the concentration of *iso*-butane started to increase sharply. The steady-state concentrations of *iso*-butane and *iso*-butene remained significantly below the thermodynamic limits associated with the isomerisation to the corresponding linear molecule (see values in bold font in Table 1). However, it is important to stress that the steady-state *iso*-butane/*iso*-butene ratio was that predicted by the thermodynamic calculation.

These results clearly show that the first catalytic function developed over the reduced and/or carburised MoO₃ is a metal-like function, which allows dehydrogenation/hydrogenation.

† Electronic supplementary information (ESI) available: experimental details. See <http://www.rsc.org/suppdata/cc/b3/b304978g/>

Fig. 1 *Is*-butane and C₄-alkene yields during the reductive activation of MoO₃ at 623 K. (a) *iso*-butane, (b) *trans*-but-2-ene, (c) *cis*-but-2-ene, (d) but-1-ene and (e) *iso*-butene.

Table 1 Ratios of the concentration of C₄ products during the activation of MoO₃ under an *n*-butane/H₂ feed at 623 K

	1h	2h	6h	Steady-state ^a	Thermodynamic ratio at 623 K
Dehydrogenation					
<i>n</i> -butane/but-1-ene	16000	8400	7000	6000 ± 800	6600
<i>iso</i> -butane/ <i>iso</i> -butene	0.045	0.91	17	500 ± 80	470
Double-bond isomerisation					
<i>trans</i> -but-2-ene/but-1-ene	2.51	2.72	2.60	2.7 ± 0.4	2.89
<i>cis</i> -but-2-ene/but-1-ene	1.63	1.77	1.75	1.8 ± 0.3	2.06
Skeletal isomerisation					
<i>iso</i> -butene/but-1-ene	0.27	1.63	3.3	1.2 ± 0.2	8.12
<i>n</i> -butane/ <i>iso</i> -butane	1.6 10 ⁶	5600	120	9.3 ± 1	1.73

^a The average value for the three data points after 20 h is reported.

Katrib *et al.* have shown by XPS studies that MoO₂, which is formed in such conditions, possesses a metallic character.⁶ Other experiments (to be reported elsewhere) have shown that a pure MoO₂ phase leads to the same equilibrium concentration of linear butenes, without any *iso*-butene being formed. Regarding this last point, Wehrer *et al.* have also shown that a pure MoO₂ phase is not active for *n*-hexane and hex-1-ene skeletal isomerisation.¹² The time-delayed formation of *iso*-butene and *iso*-butane shows that the isomerising function is developed subsequently, most likely related to the increase in sample Brønsted acidity, as Matsuda *et al.*¹¹ pointed out by propan-2-ol dehydration experiments. It is not yet clear from which phase the acidity originates, *e.g.* the oxycarbide or an amorphous oxidic phase. However, the acidity is unlikely to be associated with a pure MoO₂ phase.

The decrease in *iso*-butene yield at reaction times greater than five hours can probably be explained by the fact that the metallic character of the sample increases much faster than the acidity. The rate of formation of *iso*-butene is always slower than that of linear butenes, but, initially, it is probably of the same order of magnitude. Subsequently, the dehydrogenation/hydrogenation is so much faster that the *iso*-butene concentration is depleted at the benefit of that of *iso*-butane. This conclusion is supported by the fact that, at the steady-state, *n*-butane is in thermal equilibrium with the linear butenes and *iso*-butane is in equilibrium with *iso*-butene (see Table 1). The increased metallic character could be associated with the increase of the specific surface area of the MoO₂ and the oxycarbide phases (being an interstitial alloy, the MoO_xC_y could exhibit a metal-like character¹³). Therefore, the data reported here strongly suggest that the rate-determining step of *n*-butane isomerisation to *iso*-butane over this catalyst is the skeletal isomerisation of linear butenes to *iso*-butene. A schematic representation of the various equilibria and the rate-determining step taking place over the reduced MoO₃ at steady-state conditions is given below (see Scheme 1). The addition (as a mechanical mixture or as a support) of selective butene isomerisation catalysts such as the zeolite FER or CoAPO-11¹⁴ could lead to much increased reaction rates. This possibility is currently under investigation.

It is interesting to note that the rate-determining step in the case of the isomerisation of C₅–C₇ alkanes was proposed to be the dehydrogenation/hydrogenation process, as suggested by propan-2-ol conversion data.⁵ This discrepancy could be related to the difference of reactivity of the corresponding alkenes, *i.e.* the isomerisation of butene is less favourable, possibly because of the higher energy requirements associated with C₄ carbonium intermediates.¹⁴ Also, inferences on the rates of isomerisation and hydrogenation/dehydrogenation of an alkane from data on propan-2-ol conversion may not be fully quantitative. This underlines that the rate-determining step for the reaction of C₅+ chains may be different and needs to be further investigated.

In conclusion, this paper shows that the quantitative analysis of trace amounts of reaction products (the butene concentrations are in the order of hundreds of ppm) and the related thermodynamics is a powerful tool to elucidate reaction

Scheme 1 Reaction equilibria and rate-determining step taking place during *n*-butane reaction over reduced MoO₃ under steady-state conditions.

mechanisms and highlight rate-determining steps. In the present case, this may result in a step improvement of the activity of a most promising catalyst for alkane isomerisation.

Notes and references

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