Site Distinction in Reactions of Alkenes on Ga_2O_3 and γ-Al_2O_3. Selective Poisoning of Double Bond Migration by SO_2

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Summary The effect of SO_2 as a selective poison of double bond migration and other evidence from exchange and isomerization studies of alkenes on Ga_2O_3 and Al_2O_3 show that the sites responsible for double bond shift are distinct from those which catalyse direct *cis* $\rightleftharpoons$ *trans* interconversions of 2-alkenes.

Exchange reactions of a variety of alkenes and cycloalkenes with D_2 at 463—503 K on Ga_2O_3 activated by outgassing for 10 min at 563 K, clearly indicated that highly selective allylic and vinylic hydrogen exchange occurs without saturation and with very little concomitant movement of the double bond.[1] Separate studies at < 463 K agreed with this conclusion in that *cis*- and *trans*-but-2-enes and pent-2-enes interconvert rapidly on the same catalyst with little or no double bond shift. The results were explained by the novel suggestion that σ-bonded allyl, rather than the generally accepted symmetrical (π) allyl,[2] species are reversibly formed by dissociative adsorption, and that adsorbed vinyl species are responsible for both vinylic exchange and direct *cis* $\rightleftharpoons$ *trans* isomerization.

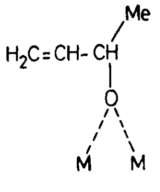
We have now confirmed this postulate by monitoring exchange reactions of several terminal alkenes at 453 K (using the system and conditions previously described[1]), quenching the reaction, and further analysing product samples by both n.m.r. spectroscopy and g.l.c. For example, in but-2-ene and 3-methylbut-1-ene, allylic hydrogens were exchanged in preference to vinylic with only minor amounts of double bond shift. Furthermore, the n.m.r. analyses also revealed a tendency for preferential exchange of the hydrogen on the substituted vinylic carbon compared with the terminal methylene hydrogens. This enhancing effect of electron-releasing substituents on the reactivity of the internal vinylic C-H bond was well demonstrated by the observation that one hydrogen in 3,3-dimethylbut-1-ene was preferentially and rapidly exchanged at 453 K while ethylene was virtually inert.

Table. Butene isomerizations[a]

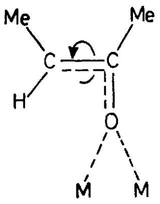
Reactant	Catalyst[b]	Initial product ratio	Rate constant $10^2k/s^{-1}\,g^{-1}$
		t-2-B/1-B[c]	
c-2-B[c]	G(A)	0·6	1·17
"	G(B)	14·0	1·17
"	A(A)	16·0	1·17
"	A(B)	6·0	1·50
		c-2-B/*t*-2-B	
1-B	G(A)	2·0	2·67
"	G(B)	3·0	0·07
		t-2-B/1-B	
c-2-B	G(B)[d]	$>50{\cdot}0$	0·67
"	A(A)[d]	$>50{\cdot}0$	2·00
"	A(B)[d]	$>50{\cdot}0$	1·67

[a] Reaction at 433 and 363 K for G and A samples respectively.
[b] G(A): Ga_2O_3 (B.D.H. Ltd., containing surface carbonate impurity) activated for 10 min at 573 K. G(B): Ga_2O_3 [Johnson-Matthey Ltd. ($<$ 10 p.p.m. metal impurities)] activated for 16 h at 773 K. A(A): Boehmite [Peter Spence Ltd. ($<$ 20 p.p.m. metal impurities)] activated for 16 h at 773 K. A(B): γ-Al_2O_3 [E. Merck Ltd. (99% pure)] activated for 16 h at 773 K. [c] 1-B = But-1-ene, *c*-2-B = *cis*-But-2-ene, *t*-2-B = *trans*-But-2-ene.
[d] Samples pre-treated with SO_2 (0·266 and 2·66 kN m^{-2} for G and A samples, respectively) for 30 min and pumped for 10 min at the appropriate reaction temperature.

Several other results on both Ga_2O_3 and Al_2O_3 clearly indicate that the sites responsible for double bond shift are distinct from those which catalyse the above reactions. For example, we frequently observed a four-fold increase in the rate of exchange of 1-alkenes in second runs over the Ga_2O_3 catalyst. However, in isomerization studies (using 0·1 g samples activated at 573 K for 10 min with 4·0 kN m^{-2} of alkene in the system described previously[1]), such enhanced activity was only observed for *cis* ⇌ *trans* interconversions, and not for double bond shift. Furthermore, one sample of Ga_2O_3 containing surface carbonate (revealed by i.r. and other analyses) which did not decompose during the usual activation, had no activity for exchange but was much more active for double bond shift than uncontaminated samples (Table). This particular sample has catalytic features very similar to those of γ-Al_2O_3 where CO_2 selectively poisons exchange but not isomerization.[3] Ga_2O_3 activated at 773 K also shows catalytic behaviour for isomerization similar to γ-Al_2O_3 (Table). Since double bond shift is usually considered to occur by formation of symmetrical (π) allyl species with anionic character on electron donor sites,[2] we predicted that SO_2 would be a selective poison for these sites. This was borne out by the fact that when SO_2 was pre-adsorbed on catalysts for reactions of but-1-ene and *cis*-but-2-ene, double bond shift was very severely retarded on both Al_2O_3 and Ga_2O_3 whilst *cis* ⇌ *trans* interconversions were virtually unaffected on Ga_2O_3 and actually enhanced on Al_2O_3 (Table).



(A)



(B)

In view of the stability of the σ-bonded allyl species and the site distinction observed for *cis* ⇌ *trans* isomerization, we now propose that the organic entities involved are bonded to oxide ions in the surface rather than to metal ions.[1,4] Species (A) and (B) are formed independently on the same type of site with reversible formation of (A) being responsible for preferential step-wise allylic exchange. Direct *cis* ⇌ *trans* isomerization is then a manifestation of keto–enol tautomerism in the surface vinylic complex (B). Chemisorbed SO_2 appears even to enhance the ease of formation or reactivity of such complexes on Al_2O_3 in view of the increased rates of *cis* ⇌ *trans* interconversions (Table). Species of this type have not been considered to date, but may be more generally significant in chemisorption of alkenes on oxides, especially with regard to selectivities in oxidative dehydrogenation.[5]

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