Accumulation of Potassium Oxide on Carbon and Enhancement of Catalytic Activity for Isomerization by O_2

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Summary The concentration of potassium oxide on a carbon surface is changed by contact with oxygen at room temperature, resulting in a marked enhancement in catalytic activity for the isomerization of but-1-ene to *cis*-but-2-ene.

OUR previous papers[1] gave *X*-ray photoelectron spectroscopic evidence proving that potassium carbonate is decomposed on carbon at rather low temperatures (650 °C) (reference decomposition temperature *ca.* 900 °C[2]) and the potassium oxide formed on the carbon is reduced to potassium atoms which dissolved into the carbon. However, it was also shown that the concentration of potassium atoms on the carbon surface returns to its former value on contact with O_2 at room temperature; that is, the potassium atoms which had penetrated into the carbon may re-accumulate on the surface as potassium oxide.

If this scheme is correct, the surface consitution of the evacuated surface of carbon doped with potassium carbonate should be changed by contact with O_2 and a marked change of catalytic properties would be expected. To confirm this

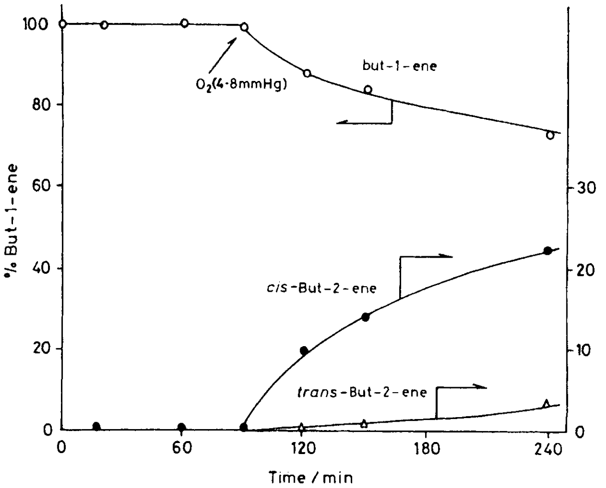


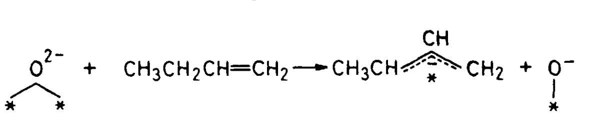
FIGURE. Effect of oxygen on the isomerization of but-1-ene on K_2CO_3 11·7 wt%–carbon at room temperature (but-1-ene: 186·9 mmHg).

TABLE. Effect of pre-evacuation of sample I[a] on the isomerization of but-1-ene (evacuation temperature: 740 °C).

	Evacuated[b]			Non-evacuated[c]		
Reaction temperature/°C	25	25	70	200	300	400
Reaction time/min	10	40	40	30	30	40
% But-1-ene	86·0	81·2	73·5	100	100	89·0
% *cis*-But-2-ene	11·0	14·8	21·2	0	0	5·4
% *trans*-But-2-ene	3·0	4·0	5·3	0	0	5·6
% Conversion	14·0	18·8	26·5	0	0	11·0
cis/*trans*-But-2-ene	3·7	3·7	4·0	—	—	0·96

[a] Sample 1: carbon doped with 11·7 wt% of K_2CO_3. [b] But-1-ene: 178·9 mmHg, O_2: 4·1 mmHg. [c] But-1-ene: 181·6 mmHg, O_2: 3·7 mmHg.

assumption the isomerization of but-1-ene was performed on carbon doped with 11·7 wt% of potassium carbonate (sample I) and evacuated *in vacuo* at 740 °C. The Figure shows the results for the isomerization of but-1-ene on this catalyst at room temperature. This pre-evacuated sample I has no catalytic activity for the isomerization of but-1-ene but the addition of O_2 markedly enhances the isomerization of but-1-ene. A high ratio of *cis*- to *trans*-but-2-ene reveals the presence of ionic intermediates which are characteristic of basic oxide catalysts.[3] Sample I, when O_2 was added, behaves as does MgO or CdO.[4] The intermediate in this isomerization therefore seems to be the allyl carbanion (Scheme).



SCHEME. * represents a surface potassium atom.

As shown in the Table, the sample I which was not evacuated at high temperatures is inactive for the isomerization, suggesting that potassium carbonate is decomposed to the oxide by evacuation at high temperatures.

It has been reported that alloy surfaces change their constitution by contact with gases, which explains some aspects of the catalytic activity of alloys as observed with Ni–Cu[5] and Rh–Pt.[6] As far as we know, the present work is the first example of the enhancement of catalytic activity for the isomerization of olefins by O_2, and this phenomenon is caused by the changes to the carbon resulting from contact with O_2.

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