Apparent Disproportionation of n-Butane on Alloy Films

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Summary During a study of the isomerisation of n-butane on Pt–Au films we found besides the usual products methane, ethane, propane, and isobutane, also an appreciable amount of n-pentane; pentane appears at 300 °C; below this temperature only cracking and isomerisation products are observed.

THE reactions were carried out in a closed system, usually with initial butane and hydrogen pressures of 4 and 50 Torr respectively. The glass apparatus had a volume of about 600 ml and was fitted with a circulation pump. The films were prepared by evaporation under ultra-high vacuum and sintering at 380 °C ($p < 10^{-8}$ Torr). For analysis small samples were taken from the reaction vessel and injected into a gas chromatograph.

TABLE

Pt–Au catalyst	T/°C	Overall conversion %	CH_4	C_2H_6	mol % products[a] C_3H_6 + C_3H_8	i-C_4H_{10}	n-C_5H_{12}
~ 1% Au	304	1	44	26	23	2	6
	376	5	2	10	57	1	31
~ 52% Au	408	5	2	4	61	1	31
	433	2	7	7	57	1	29
Pt	256	4	48	32	17	3	
	272	6	53	31	14	2	

[a] The sum of all alkanes and propene is set as 100%, quantity of butenes detected is 0·1—0·01% of butanes.

Because of self-poisoning of the catalyst by the reaction mixture, the activity of the film decreased by about a factor of 2 with repeated runs on the same catalyst. This did not influence the product composition. A typical composition of the reaction products over Pt and Pt–Au alloys is shown in the Table.

The increase in the amount of pentane was accompanied by an increase in C_3 products. The connection between C_5 and C_3 products suggests that pentane is formed by a disproportionation mechanism[1,2] such as is known for olefins, *viz.* two C_4 molecules disproportionate into a C_5 and C_3 molecule. To our knowledge alkane disproportionation has not been observed with any metal or alloy catalyst. Hydrocarbon products with a higher number of carbon atoms than in the reactants have been reported on metals only where unsaturated hydrocarbons (C_2H_4,[3,4] cyclo-C_3H_6[5]) formed adsorbed carbonaceous material which was subsequently hydrogenated.

Disproportionation of olefins is known to occur on transition-metal oxides[6] *via* π-complexed cyclobutane-like structures bound to one metal-ion site. It is not impossible that the alkane disproportionation observed by us is also due to a disproportionation of olefins. Only under the conditions where C_5 formation is observed did we find dehydrogenated species in the gas phase, *e.g.* but-1-ene and but-2-ene. The amounts of these butenes agree roughly with those expected for equilibrium at 350 °C (10^{-3}—10^{-4} of butane).

In order to check whether disproportionation is a typical reaction for the Pt–Au alloy and not for Pt alone we did some experiments on Pt at 350—400° C. At these temperatures the total activity fell off rapidly by a factor of about 20 with respect to the starting reaction rate. Once the catalyst was deactivated for cracking we were able to observe also a disproportionation in the high temperature range with, as main products, n-pentane and propane and some traces of hexane and cyclopentane. It is clear that in this case the catalyst is platinum poisoned with carbonaceous residues.

These results allow us to draw a parallel between the Pt–Au alloy and strongly poisoned Pt. In both cases we have a surface where numerous sites are inactive, either they are covered with carbon or they are Au-sites. It seems that isolation of active Pt-sites suppresses the cracking-isomerisation reaction and that isolated sites are still able to catalyse other reactions, in particular to form a complex with the alkenes (or alkanes) to give a disproportionation reaction.

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