Dissociative Adsorption of Hydrogen on Copper and the Mechanism of Butyric Aldehyde Hydrogenation

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It has been demonstrated that metallic copper of various (but not any) genesis can dissociatively adsorb hydrogen and that atomic hydrogen takes part in the hydrogenation of *n*- and isobutyric aldehydes on copper-containing catalysts.

The question of the ability of metallic catalysts to adsorb hydrogen and the nature of this adsorption is of great importance when the mechanism of many heterogeneous catalytic reactions is being determined. In the case of some catalysts, *e.g.*, metals belonging to Group VIII (Pt, Pd, Ni, *etc.*), it is clear that hydrogen is easily adsorbed even at relatively low temperatures. But with respect to other catalysts, *e.g.*, copper, there is contradictory data on the issue under consideration.[1,2] The resolution of this problem is important for the determination of possible mechanisms of catalytic transformations on the surface of copper-containing catalysts.

Our kinetic investigations of *n*- and isobutyric aldehyde (BA) hydrogenation into the corresponding alcohols on copper-containing catalysts[3] has demonstrated that the rate of these reactions is best described by the equation (1),

$$r = kP_{\mathrm{A}}P_{\mathrm{H}}/(P_{\mathrm{A}} + k_1P_{\mathrm{H}}^{0.5} + k_2P_{\mathrm{H}}^{0.5}P_{\mathrm{A}}) \tag{1}$$

where P_{A} and P_{H} are current partial pressures of aldehyde and hydrogen, respectively, and k, k_1 and k_2 are constants. It follows that hydrogen should be adsorbed on the catalyst in its atomic form, otherwise there would not have been a term $k_1P_{\mathrm{H}}^{0.5}$ in the denominator of the equation.

The participation of dissociatively adsorbed hydrogen in the reaction is confirmed by an intensive isotopic exchange between *n*-BA and deuterium: below 180 °C, when the degree of hydrogenation is 82%, 34% of BA molecules were subjected to exchange.[4] Because of the practical irreversibility of the total hydrogenation process at this temperature the isotopic exchange could take place only with the participation of atomic hydrogen (deuterium) in accordance with reaction (2),

$$\mathrm{C_3H_7CHOZ + DZ \rightleftharpoons C_3H_7CHDOZ + Z} \tag{2}$$

where Z is an active site.

A qualitative coincidence of all the relaxation curves obtained by the response method[5] both on multicomponent copper-containing catalysts and metallic copper has been seen. This means that it is the properties of copper as a catalytic active component that determine the BA hydrogenation mechanism in general and dissociatively adsorbed hydrogen participation in the reaction in particular.

However, the possibility of initial hydrogen adsorption on the microimpurities of other metals and transport towards active copper sites by spillover cannot be excluded. In addition, hydrogen adsorption could be made easier by the presence of BA, in the same way that the presence of CO (a compound chemically similar to aldehyde) promotes H_2 adsorption in methanol synthesis on a copper–zinc catalyst.[6]

A direct investigation of the possible dissociative adsorption of H_2 on copper samples of various origins containing different amounts of impurities was carried out. Isotopic exchange between H_2 and D_2 was used as a means of investigation, because according to both mechanisms of exchange reaction (so-called Bonhoeffer–Farcas or, less probably, Rideal–Eley[7]) atomic hydrogen exists on the surface.

Two sets of metallic copper samples were used. Those of the first set were prepared by thermal decomposition of different copper compounds at 300 °C. Some of their characteristics are given in Table 1. The other set was obtained from Cu-Al alloys of different composition.[8] To destroy the oxide film and to make metal and water interaction easier, 3%wt. of both gallium and indium were first introduced into the alloy. The samples of this set were marked as Cu(0.56), Cu(10) and Cu(40), the total amount of copper in percent being given in brackets. Before the experiments began all the samples were reduced with a mixture of H_2 and He (10% H_2). The temperature of the experiments was varied in the range 0–350 °C.

Table 1 Some characteristics of the copper samples (first set).

Sample	Original compound	S_{Cu}/m^2 g^{-1} (BET)	Impurity content (%wt.)			
			Fe	Ni	Co	Zn
$\mathrm{Cu_{carb}}$	$\mathrm{CuCO_3{\cdot}Cu(OH)_2}$	33.8	0.10	0.10	0.02	0.01
$\mathrm{Cu_{ac}}$	$\mathrm{Cu(OAc)_2}$	4.7	0.01	0.0003	0.03	0.01
$\mathrm{Cu_{ox}}$	CuO	0.1	0.50	0.001	0.05	0.01
$\mathrm{Cu_{nitr}}$	$\mathrm{Cu(NO_3)_2{\cdot}Cu(OH)_2}$	1.8	0.30	0.0005	0.01	0.05

Table 2 Catalytic activity of copper samples in H/D isotopic exchange at 100 °C.

Sample	Exchange rate/mmol g^{-1}s^{-1}	Activation energy/kJ mol^{-1}
$\mathrm{Cu_{carb}}$	355.0	34
$\mathrm{Cu_{ac}}$	1.65	36
$\mathrm{Cu_{ox}}$	0.40	40
$\mathrm{Cu_{nitr}}$	0.00	–
Cu(0.56)	3.6	15
Cu(10)	5.7	14
Cu(40)	8.1	11

To facilitate the comparison of different copper sample activities, D/H exchange rates were interpolated to a common temperature (Table 2). The copper obtained from hydroxonitrate did not manifest any activity.

The data in Table 2 allow us to conclude that, firstly, copper is capable of dissociatively adsorbing hydrogen at moderate temperatures and, secondly, this capability does not correlate with the content of other metal impurities (a more detailed analysis of the impurities is described in ref. 2).

The activity of the samples belonging to the second set grows with increasing copper content, which also confirms the fact that exchange takes place on the copper component. The absence of a linear dependence between copper content and exchange rate is explained by the fact that copper loading on the surface is not equal to its total content in the bulk. This is a typical phenomenon in copper-containing catalysts.[9]

There are some data[10] to suggest that dissociative adsorption of hydrogen can proceed even at room temperature on the high index faces of copper crystallites (211), (311) and (755). These faces most probably appear at catalyst high dispersion. The existence of such faces as well as adsorbed hydrogen dissociation on them were actually discovered[11] in a Cu/ZnO catalyst investigation. On the contrary, highly ordered (low-index) copper faces are not capable of dissociatively adsorbing hydrogen and are not active in benzene hydrogenation.[12]

We noticed that at the stage of $\mathrm{Cu_{nitr}}$ reduction a metallic mirror formed on the reactor walls. This might be because of the increased volatility of some copper precursors. In all probability, the same layer is formed on the sample surface. If one assumes that this layer is formed by low index copper faces, Cu_{nitr} inactivity becomes understandable. A mixed sample consisting of jointly reduced Cu_{ox} and Cu_{nitr} showed no activity at temperatures up to 350 °C, though one of the components, Cu_{ox}, was fairly active itself.

An experiment was later conducted in which inactive Cu_{nitr} was converted into Cu_{carb} through some chemical transformations. A high activity of Cu_{carb}, close to that of the original sample of Cu_{carb}, resulted. Reverse Cu_{carb} conversion into Cu_{nitr} made copper totally inactive in the isotopic exchange.

It is possible that the nature of the initial copper-containing compound and the conditions of its destruction determine not only metallic copper dispersion but also the degree of regularity of its surface and, consequently, the metallic copper exchange activity. It is known that most active copper-containing hydrogenation catalysts are obtained on the basis of copper hydroxocarbonate; by contrast the use of copper hydroxonitrate as a precursor essentially weakens the catalyst hydrogenation function.[13]

Studies of the mechanism of heterogeneous reactions with the participation of hydrogen on copper-containing catalysts require that one should take into consideration the fact that copper is able to dissociatively adsorb hydrogen at relatively low temperatures. In addition, hydrogen adsorption on copper depends to a great extent on the origin of the copper.

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