

Activity and Selectivity of Ni-Cu/Al₂O₃ Catalysts for Hydrogenation of Crotonaldehyde and Mechanism of Hydrogenation

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Received July 29, 1982; revised June 20, 1983

New catalysts, Ni-Cu/Al₂O₃, for the selective hydrogenation of the C=O bond of crotonaldehyde have been prepared. The maximum yield of crotyl alcohol achieved in the hydrogenation products of crotonaldehyde was about 54 mol%. The reaction network in which this reaction is implicated has been studied.

INTRODUCTION

Unsaturated hydrocarbons, for example, olefines, and organic compounds which contain a C=C double bond, for example, saturated aldehydes and ketones, are easily hydrogenated on catalysts like Raney Ni, transition metal Raney catalysts, Rh, Pt, Pd to the corresponding saturated hydrocarbons and alcohols (1-4). α,β -Unsaturated aldehydes (which have both C=C and C=O double bonds) are preferentially hydrogenated to saturated aldehydes in most cases in the first stage. Over palladium, for example, the reaction stops spontaneously when the saturated aldehyde is formed (3). It may be that this preference for C=C bond hydrogenation has to do with its bond energy (5) being smaller (615 kJ/mol) than that of the C=O bond (715 kJ/mol).

It is a challenging task to accomplish selective hydrogenation of the C=O bond. Only a few catalyst suitable for that purpose have been reported hitherto. In 1925 Tuley and Adams (6) hydrogenated cinnamaldehyde (C₆H₅-CH=CH-CHO) to cinnamyl alcohol (C₆H₅-CH-CH₂OH) in ethanol over an unsupported platinum-zinc-iron catalyst. In 1963 Rylander *et al.* hydrogenated crotonaldehyde to crotyl al-

cohol over the same catalyst system (7). In heterogeneous hydrogenation of crotonaldehyde, the platinum-zinc-iron catalyst described by Rylander *et al.* (3, 8) gave a high yield of crotyl alcohol. Yada *et al.* (9, 10) reported a yield of 50 mol% of crotyl alcohol at 225-250°C from crotonaldehyde at 80% conversion. Simonik and Beránek (11) found a silica gel-supported catalyst, which contained 1% Pt, 0.7% Fe, and 2% NaOH (by weight), to have high selectivity for C=O bond hydrogenation.

Yada and Kudo (9) reported catalysts of Cu with 3-7% Cd to have high selectivity for hydrogenation of the C=O bond of crotonaldehyde, whereas no such selectivity was observed by Simonik and Beránek (11) on kieselguhr-supported catalysts with similar composition of the metallic components.

Up to now, no Al₂O₃-supported catalyst has been reported, which contained Ni as a main constituent together with another transition metal and could hydrogenate crotonaldehyde selectively to crotyl alcohol. Such catalysts will be described in this paper. An attempt has been made to find the best conditions for the formation of crotyl alcohol and to obtain information about the reaction network in which the hydrogenation of crotonaldehyde is involved.

EXPERIMENTAL

Catalysts. The nitrates of nickel, copper,

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and aluminum were coprecipitated with aqueous ammonia. The precipitates were dried, modeled with a hand-modeling press and then calcined at 300°C. Before hydrogenation, the catalysts were reduced with H₂ either at 200 or at 430°C. The composition of the catalysts was analyzed by means of atomic absorption spectroscopy and results are given in Table 1. The total surface area of the catalysts was roughly 250 m²/g.

Apparatus and procedure. A flow system was used. Hydrogen was passed through (liquid) crotonaldehyde (at about 20–22°C) and subsequently, from bottom to top, through the reactor, a vertical glass tube of about 0.8 cm inner diameter, which contained the catalyst between layers of glass fiber. Samples of gas were taken before and after the reactor and analyzed by means of gas chromatography (Perkin–Elmer F11 gas chromatograph with flame ionization detector). Column (0.33 cm × 2 m): Carbowax 20 M, 80–100 mesh. The same apparatus was used for the other reactants.

The reduction of the catalysts was carried out in the reactor after treatment with N₂ at 300°C for 2 h. Reduction conditions: either 200°C, 2.5 h, 45 ml H₂/min, or 430°C, 12 h, 26 ml H₂/min. For the results indicated in Table 2 the amount of catalyst in each run was 0.74 g (before reduction), which occupied about 1 ml. For the data given in Table 3, the amount of catalyst was 0.3 g.

RESULTS AND DISCUSSION

Influence of Composition of Catalysts and Temperature of Reduction upon Activity and Selectivity

Representative data are given in Table 2. In several instances, some smaller peaks, denominated "Rest" in the tables, appeared in the gas chromatograms. They could not be identified, except butane. As their peak areas in no case exceeded 5% of the total peak areas it should not seriously matter that no calibration factors could be taken into account in these "Rest" figures.

When the catalyst was reduced at 200°C, activity was found to increase with increasing content of copper. However, when reduction was carried out at 430°C, copper had the opposite effect.

Crotyl alcohol was only formed over catalysts 4, 5, and 6. The highest yield (54 mol%) was obtained with catalyst 4 when reduced at 430°C.

The above results may be discussed as follows. The temperature of 430°C was chosen for reduction because it is used for evoking the phenomenon denominated as "spillover" (12). As extensive reduction of NiO should be achieved already at the lower temperature (200°C) (13), it is possible that the increase of activity observed with catalyst 1 has to do with this phenomenon. On the other hand, as far as we know, spillover has not been observed with copper alone (14). Possibly the 430°C catalysts undergo sintering to some extent diminishing their activity, which in the case of copper would not be overcompensated by the spillover effect.

The decrease of activity on addition of a Group IB metal to a group VIII metal has often been described in the literature (15, 16). In some cases, however, activity was reported to increase (17). This discrepancy may be due to different methods of preparation: the activity of the 200°C catalysts is increased when copper is added, while that of the 430°C catalysts is decreased.

The selectivity for the formation of crotyl

TABLE 1
Composition of Catalysts, Weight Ratio

Catalyst	Al ₂ O ₃	NiO	CuO
1	10	2.0	0
2	10	2.1	0.11
3	10	2.9	0.69
4	10	3.0	1.4
5	10	1.3	2.9
6	10	0	2.9

TABLE 2

Conversion of Crotonaldehyde to Crotyl Alcohol, Butyraldehyde, and Butanol: Activity and Selectivity

Catalyst No.	Reduction temp. (°C)	Hydrogenation (°C)	Space velocity ^a ($10^4 \frac{\text{mol}}{\text{g min}}$)	Product composition (mol%)				
				Crotonaldehyde	Crotyl-alcohol	Butyraldehyde	Butanol	Rest
1	200	80	1.4	100				
	200	150	0.53	84		16		
	200	150	1.4	100				
	430	80	0.53			10	90	
	430	80	1.4			14	86	
2	200	150	0.53	76		24		
	200	150	1.4	90		10		
	200	200	1.4	77		23		
3	200	150	0.53			40	60	
	200	150	0.84			55	45	
	200	150	1.4	45		30	24	1
4	200	150	1.4				100	
	200	200	1.4		18		80	2
	430	80	0.53		42	15	41	2
	430	80	1.4		54	12	33	1
5	200	150	0.53				100	
	200	150	1.4		6	7	87	
	430	80	1.4	48		37	15	
6	200	100	1.4	69		31		
	200	150	0.53				100	
	200	150	1.4		8	3	84	5
	200	200	1.4		24	6	70	
	430	80	1.4	90		10		
	430	150	0.53	68		30	2	
	430	150	1.4	77		21	2	
	430	200	1.4	64		30	6	

^a Initial pressure of crotonaldehyde: 5260 Pa.

alcohol, i.e., C=O bond hydrogenation, was highest with catalyst 4 after reduction at 430°C. Smaller percentages of crotyl alcohol were obtained with catalysts 5 and 6. Copper appeared to favor this selectivity and some ideas to explain this effect of copper will be outlined. The coordination chemical approach to catalysis (18) will be used, which was developed for nonmetallic catalysts, but will be tentatively applied to metals here. An important feature of this approach is that all interactions are considered to take place between an electron pair

donor (EPD) and an electron pair acceptor (EPA).

Chemisorption of hydrogen has been found to be considerably stronger on *d* metals than on *sp* metals (19, 20).

The vacant *d* orbitals are considered to adopt EPA functions. Hydrogen, on the other hand, should be susceptible to function as an EPD. However, filled orbitals of the metal can probably adopt EPD capacity and this might mean that hydrogen interacting with them should adopt EPA function. Let us assume that, in the actual reaction,

TABLE 3

Conversion of Crotyl Alcohol, Butyraldehyde, and Butanol; Product Composition (mol%), Catalyst 4 (0.3 g), Reduction Temperature 430°C, Hydrogenation Temperature 150°C

Space velocity ^b ($10^5 \frac{\text{mol}}{\text{g min}}$)	Carrier gas	Crotonaldehyde	Crotyl alcohol	Butyraldehyde	Butan-1-ol	Butane	Rest
Crotyl alcohol							
0.72	H ₂		0	6	85	9	
3.2	H ₂		0	2	91	6	
4.1	H ₂		0	2	92	5	1
3.2	He	14	3	67	16		
Butyraldehyde							
49	H ₂		12 ^a	0	56 ^a		
49	He		0.2 ^a	0	0.2 ^a		
49	H ₂ ^c		0.7 ^a	0	59 ^a		
Butan-1-ol							
0.59	H ₂			3	88	9	
2.6	H ₂			1	92	7	

^a Further products not specified.

^b Initial pressure of reactants: crotyl alcohol, 658 Pa; butyraldehyde, 11,200 Pa; butan-1-ol, 526 Pa.

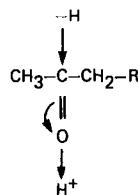
^c Catalyst reduced at 200°C.

one of the hydrogen atoms acts as an EPA, and the other one as an EPD; in other words, the H atoms might be in a more protonic or hydridic form, respectively.

Hydrogen can be chemisorbed on copper, but not so strongly as on nickel, because the EPA function of Cu (with its filled *d* orbitals) is weaker than that of Ni (with its partially vacant *d* orbitals). On the other hand, the EPD strength of chemisorbed hydrogen is greater on copper than on nickel because the (partially vacant) *d* orbitals of Ni withdraw more electrons from hydrogen than the (filled) *d* orbitals of copper.

This picture may now be connected with substituent effects observed in the hydrogenation of ketones. The reactivities of a number of open-chain ketones in the hydrogenation to alcohols over Raney nickel have been found (21) to decrease with the number of alkyl-carbon atoms, with minor differences between skeletal isomers. Introduction of an alkyl group into acetone diminished the rate of hydrogenation. Since alkyl groups provide electrons and thus diminish the EPA strength of the carbonyl group, we would deduce from this result that, in the rate determining step, an EPD

species, probably H⁻, attacks the C=O carbon atom.



The higher the EPD strength of hydrogen, the stronger its attack. If now copper has the effect of increasing the EPD strength of hydrogen in comparison with nickel, this should lead to higher selectivity for the hydrogenation of the C=O bond. When the EPD strength of hydrogen is low, hydrogen would rather react with the C=C bond, whose polarity is much lower than that of the C=O bond.

Influence of Flow Rate upon the Composition of Hydrogenation Products

Crotonaldehyde can be hydrogenated to butanol via butyraldehyde or crotyl alcohol (see Scheme 1 below). Furthermore, hydrogenation to butane can occur as well as

isomerization between butyraldehyde and crotyl alcohol.

For catalysts with high activity and high C=O bond selectivity (for example, catalyst 4 after reduction at 430°C), an increase in space velocity led to a higher percentage of crotyl alcohol (Table 2). It is in this way that the high yield of 54% crotyl alcohol was achieved. From the decrease of the percentage of butyraldehyde when space velocity was increased, it may be concluded that some isomerization of crotyl alcohol to butyraldehyde took place.

Influence of Hydrogenation Temperature upon the Composition of Hydrogenation Products

The increase of reaction temperature is usually expected to lead to higher conversion, because the rate of reaction is increased. However, it has been known for many years (22) that the rate of hydrogenation of olefins exhibits a maximum when temperature is raised. We would suppose that the appearance of such a maximum is characteristic for many, perhaps all, exothermic reactions. This should be taken

into account when the following results are discussed.

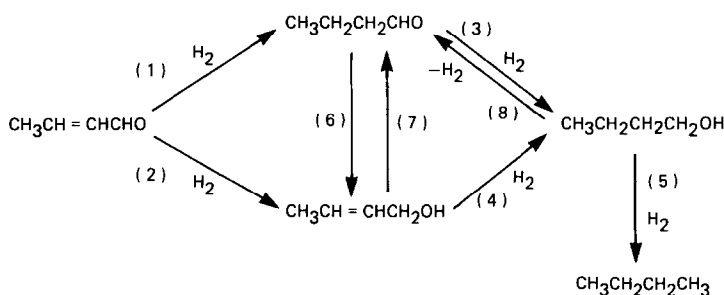
On the catalysts whose activity is not so high, for example, catalyst 2, conversion increases with temperature (Table 2).

With catalysts 4 and 6, which both have high C=O bond selectivity, the yield of butanol, which is the most important final product, is higher at 150°C than at 200°C. On the other hand, more crotyl alcohol is formed at the higher temperature. Perhaps 200°C is beyond the maximum of reaction rate and this is why the intermediates are more favored.

Reaction Network

From the products observed in the hydrogenation of crotonaldehyde over Ni-Cu/Al₂O₃, it may be deduced that we have to do with a parallel-consecutive reaction, as represented in Scheme 1.

On catalysts with low activity, for example, catalysts 1 and 2, only butyraldehyde was formed (Table 2), i.e., reaction 1 was the only one to proceed. On catalyst 3, which had higher activity, butanol was formed in addition to butyraldehyde. This showed reactions 1 and 3 to proceed.



SCHEME 1

On catalysts 4, 5, and 6, a further product, namely crotyl alcohol, appeared, demonstrating the occurrence of reactions 2 and 4. This reaction path was even more pronounced with catalyst 4 when reduced at 430°C. Furthermore, some butane was formed (reaction 5 in Scheme 1). This transformation could be (direct) substitution of OH by hydrogen or dehydration to butene

with subsequent hydrogenation. Butene, however, has not been found in the reaction products.

Isomerization and Dehydrogenation

Hydrogenation of crotonaldehyde over the catalysts with low activity (and low C=O bond selectivity) only led to butyraldehyde or to butyraldehyde and butanol

(Table 2). Isomerization of butyraldehyde to crotyl alcohol (reaction 6) was not observed. On the other hand, occurrence of reaction 6 could be shown directly when butyraldehyde and hydrogen were fed to the reactor, which contained catalyst 4 after reduction at 430°C: crotyl alcohol was formed in addition to butanol (Table 3). The yield of crotyl alcohol was lower when the catalyst was reduced at 200°C.

When crotyl alcohol was fed to the reactor with He as carrier gas large amounts of butyraldehyde were obtained (Table 3) and this showed reaction 7 to occur. Part of the crotyl alcohol was disproportionated to crotonaldehyde and butan-1-ol.

When crotyl alcohol and hydrogen were fed to the reactor, butanol and butane were obtained, which (again) showed the occurrence of reactions 4 and 5. In addition, small amounts of butyraldehyde were observed. It is possible that butyraldehyde is not only formed directly (reaction 7), but also via reactions 4 and 8. For instance, reaction 8 was shown to occur when butan-1-ol and hydrogen were fed to the reactor (Table 3). The indirect formation of butyraldehyde (via reactions 4 and 8) could account for the somewhat higher yield when space velocity was lowered.

No back reaction is indicated for reactions 1, 2, and 4 in Scheme 1. In principle all chemical reactions proceed also in the opposite direction. However, under the conditions of the present study, namely relatively low temperature and excess of hydrogen, the equilibrium is almost completely on the side of the hydrogenation products, so that these dehydrogenation reactions are negligible.

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