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Hydrogenolysis of Alcohols

II. Reduced Nickel Oxide—Its Intrinsic Acidity and Catalytic Activity in the Conversion of Alcohols to Ethers*

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The reactions of primary aliphatic alcohols over reduced nickel oxide catalysts were studied in a micropulse reactor at 160–200° at atmospheric pressure and in the presence of a flow of hydrogen. The nickel catalyst, which was obtained from nickel hydroxide by precipitating nickel nitrate with ammonia followed by calcination at 500°, contained after reduction with hydrogen at 300–400°, 3 to 1.5% nickel oxide.

The reduced nickel oxide is an effective catalyst for converting alcohols to the corresponding ethers with a selectivity up to 80%. The other reactions are dehydrogenation of alcohols to aldehydes, reductive dehydroxylation, and reductive dehydroxymethylation.

The formation of ethers from alcohols is attributed to intrinsic acidic sites of the nickel catalyst. The acidic sites are ascribed to the presence of nickel oxide in the catalyst. The presence in the catalyst of 0.05 wt % of sodium ions in the catalyst inhibits the formation of ethers, while the dehydrogenation and reductive dehydroxymethylation become the main reactions.

INTRODUCTION

In a previous paper (*1*) it was reported that primary alkanols in the presence of a nickel–kieselguhr catalyst and hydrogen undergo reductive dehydroxymethylation, reductive dehydroxylation, and ether formation:

$$\text{R-CH}_2\text{-CH}_2\text{-OH} \xrightarrow{2\text{H}_2} \text{R-CH}_3 + \text{CH}_4 + \text{H}_2\text{O}, \quad (1)$$

$$\text{R-CH}_2\text{-CH}_2\text{-OH} \xrightarrow{\text{H}_2} \text{R-CH}_2\text{-CH}_3 \text{ and } \text{R}^1\text{-CH}_2\text{-CH}_3 + \text{H}_2\text{O}, \quad (2)$$

$$2\text{R-CH}_2\text{-CH}_2\text{-OH} \longrightarrow (\text{R-CH}_2\text{-CH}_2)_2\text{O} + \text{H}_2\text{O}. \quad (3)$$

(R^1CH_2–CH_3 is the product of skeletal isomerization).

The reductive dehydroxymethylation proceeds most probably through decarbonylation of the intermediate aldehydes produced by the dehydrogenation of the alcohols (*1, 2*). Further evidence for this mechanism was obtained through the study of the infrared spectra of adsorbed alcohols on nickel and nickel–silica (*3, 5*).

The methods of preparation of nickel–kieselguhr catalysts can greatly influence the selectivity of the hydrogenolysis reactions. When ammonium carbonate was used as a precipitating agent, reactions (2) and (3) were favored (*1*). When potassium carbonate was used, reaction (1) predominated. Reactions (2) and (3) were related to the intrinsic acidic sites present in the nickel catalyst (*6–9*). It was also found (*10*) that nickel–kieselguhr modified by the presence of sulfide ions can promote reaction (2) at the exclusion of reaction (1).

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The present paper describes the effect of the preparation and reduction of nonsupported nickel oxide upon the reaction of primary alcohols. The alcohols chosen for this study are in *n*-butanol, 2-methyl-, and 3-methylbutanol, and 3,3-dimethylbutanol (neopentyl alcohol).

EXPERIMENTAL METHODS

Procedure

The experimental procedure and the micropulse reactor (*11*) were the same as described in the previous paper of this series (*1*). Powdered nickel catalyst, 200 mg, was placed in the middle of the reactor tube, between layers of glass wool, and the rest of the reactor was filled with glass beads of 20–30 mesh size. Separate runs proved that neither the glass beads nor glass wool had any catalytic activity. The temperature of the catalyst was measured by a fixed internal thermocouple. Ten μl of alcohol was injected in each run, and the hydrogen flow through the reactor and chromatographic column was 100 ml/min. Analysis of the products was done on a vapor-phase chromatograph using specially designed columns, and a liquid nitrogen trapping technique described previously (*11*). Four separate columns were used: (i) 25-ft column packed with 20% Ucon 75 H, 9000 polar on Chromosorb W 60/80 mesh. (ii) 35-ft column, packed with 15% L.P.—122 Silicone gum rubber phenylmethyl GE-SE-52 on Chromosorb W 60/80 mesh. (iii) 10-ft column, packed with 33% at 2,4-dimethylsulfolane on Limebrick-Gas-Pak P 80/100 mesh. (iv) 10-ft column, packed with 5% of tetraethylene pentamine on Chromosorb 102, 80/100 mesh (Styrene-Divinylbenzene polymer) supplied by Johns-Manville Co.

Column iii was used for the identification of low-boiling products. Column iv was employed for the quantitative estimation of the water produced from reduction of the nickel oxide.

Preparation of Nickel Catalyst

To a solution of 20 g of nickel nitrate hexahydrate in 100 ml of distilled water, was added while stirring 120 ml of 10 *M* ammonium hydroxide. The resulting deep blue solution was heated to 80° and a stream of steam was percolated through it for 4 hr. The precipitate of nickel hydroxide so obtained was filtered, washed free from ammonium ions, and dried at 110° overnight. The nickel hydroxide which was then decomposed to nickel oxide by heating it in a flow of helium at 500° for 4 hr. The nickel oxide, when reduced in a flow of hydrogen at 400° for 4 hr had a surface of 44 m^2/g.

Each fresh catalyst was prepared *in situ* by reducing the nickel oxide in the micropulse reactor by heating it in a flow of hydrogen at 250° for 1 hr, and then at 350° for 1 hr.

Preparation of Sodium Containing Nickel Catalysts

Nickel hydroxide, 15.8 g, prepared as described above, was added to two 15-ml solutions containing 0.43 and 0.21 moles of sodium hydroxide, respectively. The mixture was allowed to stand overnight and then was dried at 60° for several hours, and then at 110°. The doped nickel hydroxide contained 0.1 and 0.05 wt % of sodium ions, based on the nickel content.

Quantitative Determination of the Extent of NiO Reduction

The method used was based on the quantitative determination of water produced during the reduction of nickel oxide at various temperatures and time intervals, and was similar to that described previously (*12*). The nickel oxide prepared from 1.5 g of nickel hydroxide as described above, was reduced by hydrogen with a flow rate of 100 ml/min. The reduction was made at temperatures ranging from 200 to 485°. The temperature was increased in increments of about 50°.

The water formed from the reduction of the nickel oxide was trapped in a 2-ft copper column packed with Chromosorb 102 and immersed in liquid nitrogen.

The hydrogen used in these experiments was purified from traces of oxygen by the procedure described previously (*1*). It was then dried by passing it through a 15-ft × ¼-in. column packed with a molecular sieve X-13 and immersed in a liquid nitrogen bath. The amount of water collected during the liquid nitrogen trapping periods was estimated quantitatively, using methyl alcohol as an internal standard and calibration curves of synthetic mixtures of water and methyl alcohol. The trapping periods were of 15-min duration, arbitrarily chosen. When the amount of water produced in the last two periods was almost nil, the reduction temperature was raised.

TABLE 1

Hydrogenolysis of Alcohols in the Presence of Nickel Catalyst[a] Effect of Temperature

Temp (°C):	160	170	180	195
	Neopentyl alcohol			
Expt. no.	1	2	3	4
Conversion (%)	3	5	10	12
Selectivity (mole %)[b]				
Propane	—	—	1	3
Isobutane	—	2	2	7
Neopentane	—	2	5	8
Isopentane	—	Traces	Traces	1
1,1-Dimethylcyclopropane	Traces	0	1	Traces
Trimethylacetaldehyde	9	8	11	11
Dineopentyl ether	91	88	80	69
	2-Methylbutanol			
Expt no.	5	6	7	8
Conversion(%)	4	7	16	36
Selectivity (mole %)				
Butane	2	10	12	17
Isopentane	—	Traces	2	3
n-Pentane	—	Traces	Traces	1
Ethylcyclopropane	~0.5	~0.2	~0.4	Traces
2-Methylbutanal	9	9	7	4
Di-2-methylbutyl ether	88	81	79	74
	3-Methylbutanol			
Expt. no.	9	10	11	12
Conversion(%)	4	10	20	37
Selectivity (mole %)				
Isobutane	2	12	19	25
Isopentane	—	—	~0.5	2
3-Methylbutanal	6	3	4	4
Di-3-methylbutyl ether	92	85	76	69
	n-Butanol			
Expt. no.	13	14	15	16
Conversion(%)	6	11	23	36
Selectivity (mole %)				
Propane	4	13	19	23
Butane	—	—	1	3
n-Butyraldehyde	6	2	2	3
Dibutyl ether	90	85	78	71

[a] 200 mg of nickel oxide reduced at 350° for 2 hr. The reduced catalyst contained about 1.5% of nickel oxide.

[b] Expressed in moles per 100 moles of alcohol reacted.

RESULTS

Effect of Temperature

The effect of the reaction temperature upon the dehydration and hydrogenolysis of alcohols in the presence of unsupported nickel catalyst reduced at 350° is given in Table 1. At 160° the conversion of the alcohols amounted to less than 6%. At 195° the conversion of *n*-butanol, 2- and 3-methylbutanol increased to about 37% while that of neopentyl alcohol increased only to 12%. The main reaction product was ether, amounting to 88–91% at 160° and decreasing to 69–74% when the temperature was increased to 195°. At the higher temperatures the dehydroxymethylation reaction (2) greatly increased, producing hydrocarbons containing one carbon atom less than the original alcohol. The dehydrogenation of the alcohols to the corresponding aldehydes also occurred, and with the exception of neopentyl alcohol, the yield of the aldehydes decreased with the temperature.

It is interesting to note that small amounts of 1,1-dimethylcyclopropane and ethylcyclopropane were formed from neopentyl alcohol and from 2-methylbutanol, respectively. At 195° the same alcohols formed, respectively, about 1% of isopentane and *n*-pentane, products of reductive dehydroxylation accompanied by skeletal isomerization.

Effect of Sodium

Since the dehydration of alcohols to ethers is usually associated with acidic sites, it was deemed necessary to determine the effect of sodium ions on the reactivity and selectivity of reduced nickel oxide catalyst. For that purpose the precipitated nickel hydroxide was impregnated with sodium hydroxide, calcined and reduced *in situ* to obtain a catalyst containing 0.05 and 0.1% by weight of sodium. The experimental results are summarized in Table 2. Neopentyl alcohol, 2-methylbutanol, and *n*-butanol were used in this study. The presence of 0.05% of sodium in the catalyst influenced greatly the selectivity of the reaction, but had only little effect on the total conversion of the alcohols. With a sodium-free catalyst the main reaction product was ether, amounting to almost 80% of the reacted alcohols. However, in the presence of nickel, doped with sodium, the yield of ethers dropped to less than 8%, the main reaction being reductive dehydroxymethylation and aldehyde formation. A similar effect was observed after the catalyst was treated with dry ammonia at 150° (Table 3). However after desorption of the

TABLE 2

EFFECT OF SODIUM ON THE REACTION OF ALCOHOLS IN THE PRESENCE ON NICKEL CATALYST[a]

Sodium (wt %)	0	0.05	0.1
Neopentyl alcohol			
Expt. no.	3	17	18
Conversion(%)	10	9	2.5
Selectivity (mole %)[b]			
Isobutane	2	44	45
Neopentane	5	0	0
1,1-Dimethylcyclopropane	~1	0	0
Trimethylacetaldehyde	11	23	22
Dineopentyl ether	80	4	—
Unidentified[c]	—	29	32
2-Methylbutanol			
Expt. no.	7	19	20
Conversion(%)	16	15	10
Selectivity (mole %)			
Butane	12	70	74
Isopentane	2	~0.5	—
Ethylcyclopropane	~0.4	—	—
2-Methylbutanal	7	14	16
Di-2-methylbutyl ether	78	8	2
Unidentified[c]	—	7	7
n-Butanol			
Expt. no.	15	21	22
Conversion(%)	23	24	19
Selectivity (mole %)			
Propane	19	78	78
Butane	1	—	—
n-Butyraldehyde	2	10	15
Dibutyl ether	78	6	—
Unidentified[c]	—	6	6

[a] Reaction temp, 180°C.

[b] Footnote *b*, Table 1.

[c] Presumably products of condensation of aldehydes.

TABLE 3
EFFECT OF AMMONIA TREATMENT ON THE REACTION OF ALCOHOLS AT 170° IN THE PRESENCE OF NICKEL CATALYST

	Untreated catalyst	NH_3 treated catalyst	Catalyst after desorption at 400°
Neopentyl alcohol			
Experiment	2	41	42
Conversion(%)	5	3	4
Selectivity (mole %)[a]			
Isobutane	2	8	8
Neopentane	2	—	2
Trimethylacetaldehyde	8	81	10
Dineopentyl ether	88	11	80
Isopentane	Trace	—	—
2-Methyl-1-butanol			
Experiment	6	43	44
Conversion(%)	7	5	8
Selectivity (mole %)			
Butane	10	12	9
Isopentane	Trace	—	—
2-Methylbutanal	9	31	8
Di-2-methylbutyl ether	81	57	83
n-Butanol			
Experiment	14	45	46
Conversion(%)	11	9	11
Selectivity (mole %)			
Propane	13	27	12
Butyraldehyde	2	10	3
Dibutyl ether	85	63	85

[a] Footnote *b*, Table 1.

ammonia at 400° the catalyst recovered its activity.

Effect of Nickel Oxide

The experiments given in Table 1 were made using a "reduced" nickel oxide. Since this catalyst still contained some unreduced nickel oxide, it was decided to study the effect of the concentration of nickel oxide in nickel on the hydrogenolysis of neopentyl alcohol and 2-methylbutanol. Nickel oxide which was used as a starting material from which the reduced nickel catalyst was prepared, was made by heating nickel hydroxide at 500° in the presence of a flow of helium. The reduction was made by passing hydrogen over the nickel oxide at increasingly higher temperatures and for various periods of time. The amount of nickel oxide in the nickel catalyst was determined from the quantity of water produced from the reduction, as described above in Experimental Methods.

The nickel oxide content in the reduced catalyst, as a function of time and temperature is given in Table 4. After the reduction of the oxide at 250° for 5 hr only 3.0% of nickel oxide remained in the nickel catalyst. Further reduction of the catalyst at 300° for 1, 2, and 3 hr diminished its nickel oxide content to 2.56, 2.14, and 2.00%, respectively. In order to reduce the catalyst still further, higher temperatures were required. At 350° during the first hour of reduction the nickel oxide content was diminished from 2.00% to 1.50% while in the second hour it was reduced to 1.28%. After heating the catalyst for 1 hr at 485°

TABLE 4

Nickel Oxide Content in the Catalysts as a Function of Time and Temperature of Reduction[a]

Temp of reduction (°C)	Time of reduction (hr)	Mole % of NiO in Ni
250	5	3.0
300	1	2.6
	2	2.1
	3	2.0
350	1	1.5
	2	1.3
400	1	1.0
	2	0.5
485	1	0.05
	2	—

[a] In each experiment catalyst from a preceding experiment was used.

in a flow of hydrogen, no further evolution of water occurred, indicating the absence of nickel oxide in the nickel.

Table 5 and Fig. 1 summarize data concerning the effect of nickel oxide upon the hydrogenolysis of neopentyl alcohol and 2-methylbutanol. The experiments were made in a micropulse reactor charged with 200 mg of nickel oxide which was reduced as above and the approximate concentration of nickel oxide was estimated from the data in Table 4.

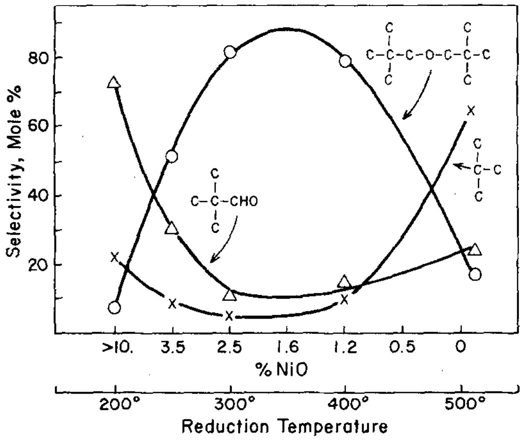


Fig. 1. The effect of temperature of reduction and of concentration of nickel oxide on the composition of products obtained from neopentyl alcohol at 180°.

The experimental results, Table 5, demonstrate that the distribution of the products changes with the concentration of nickel oxide in the catalyst. The optimum yields of ethers were obtained with a catalyst which was reduced at 300–400°. The estimated concentration of nickel oxide was >1.0% and <2.6%. When the catalyst was reduced at 520° and its nickel oxide concentration corresponded to 0.05%, the catalyst showed little activity towards ether formation; and dehydroxymethylation was the main reaction resulting in the respective formation of isobutane and *n*-butane, Expts. 28 and 40. (Tables 5 and 6, Fig. 1).

The selectivity of the reaction towards the production of ethers was more pronounced when the temperature was 170°, instead of 200°, Expts. 31–33. The yield of neopentyl ether was 49% at 200° while it was 79% at the lower temperature. On the other hand the yield of neopentane was higher at the higher temperature, Expts. 25, 31, and 32.

In the experiments listed in Table 6 the catalysts were exposed during the reduction to much higher temperatures than the temperatures at which the reaction with alcohols were made. At the high temperatures, 400–520°, at which the reduction of the catalyst was made (Table 5) two factors should be considered: conversion of nickel oxide to nickel and the possible sintering of the catalyst. Experiments were made to determine whether the exposure of the catalyst to high temperatures might have altered its catalytic properties.

In Expt. 39 the nickel catalyst which was previously reduced at 300° (Expt. 38) was heated at 500° for 1.5 hr in a stream of helium. This catalyst was only slightly altered during its exposure to high temperature. The yield of dineopentyl ether dropped from 80.6% to 70.4% while the yield of trimethylacetaldehyde increased from 8 to 20%. There was however a drastic change in the properties of the catalyst when it was heated at 500° in a stream of

TABLE 5

EFFECT OF NICKEL OXIDE IN NICKEL ON THE CATALYTIC CONVERSION OF ALCOHOLS

Temp of reduction (°C)[a]	200	250	300	300	400	520	250	300	400
Duration of reduction (hr)	2	1	1	2	1	1	1	1	1
Nickel oxide in catalyst(%)	>>3.0	>3.0	2.1	2.1	1.0	0.05	>3.0	2.6	1.0
Temp of reaction (°C)	170	170	170	170	170	170	200	200	200
			Neopentyl alcohol						
Expt. no.	23	24	25	26	27	28	29	30	31
Conversion(%)	4	5	5	5	6	7	16	17	17
Selectivity (mole %)[b]									
Propane						Traces	4	4	4
Isobutane	12	10	2	2	4	67	17	16	13
Neopentane	1	1[c]	1	1	1	0	15	20	21
Isopentane		Traces	Traces	Traces	0	0	Traces	2	1
Trimethylacetaldehyde	74	32	8	8	15	27	38	10	20
Dineopentyl ether	12	56	88	88	80	5	25	47	41
			2-Methylbutanol						
Expt. no.	32	33	34	35	36	37			
Conversion(%)	—[d]	7	7	7	8	8			
Selectivity (mole %)									
Butane	28	17	10[e]	9	10	60			
2-Methylbutanal	26	12	9	9	10	17			
Di-2-methylbutyl ether	46	71	81	82	80	18			

[a] In Expts. 24–28 and 30–31, catalyst from the preceding experiment was used.

[b] Footnote *b*, Table 1.

[c] Small amount of 1,1-dimethylcyclopopane was present.

[d] Not estimated.

[e] Small amounts of ethylcyclopropane were detected.

TABLE 6

EFFECT OF HEAT TREATMENT OF THE CATALYST UPON THE REACTION OF NEOPENTYL ALCOHOL

Expt. no.[a] Catalyst	38 —[b]	39 —[c]	40 —[d]
Conversion	5	4	4
Selectivity (mole %)[e]			
Propane	—	—	3
Isobutane	5	5	7
Neopentane	4	2	1
1,1-Dimethylcyclopropane	1	1	—
Isopentane	2	1	—
Trimethylacetaldehyde	8	20	69
Dineopentyl ether	81	70	13

[a] 200 mg of nickel hydroxide were used. The temperature of the reaction was 175°, and the flow of gas (helium of hydrogen) was 100 ml/min.

[b] The nickel hydroxide was heated for 2 hr at 500° in a stream of helium. The nickel oxide thus formed was reduced at 300° for 1 hr.

[c] The catalyst from Expt. 38 was heated in a stream of helium for 1.5 hr at 500°. After it was cooled to 300°, hydrogen was passed over it for 1 hr.

[d] A fresh catalyst was treated as in Expt. 38 and tested with neopentyl alcohol. The results were very similar to Expt. 38. The catalyst was then heated at 500° in a stream of hydrogen for 1 hr.

[e] Footnote *b*, Table 1.

hydrogen, Expt. 40. The yield of the ether dropped to 13% while that of the aldehyde increased to 68%.

DISCUSSION

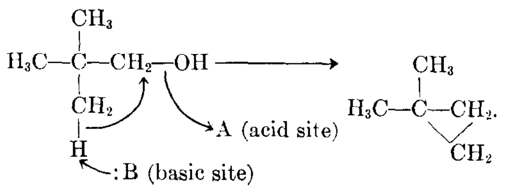
The reactions of primary alcohols in the presence of hydrogen over reduced nickel catalysts can be divided into two types: (a) ionically catalyzed elimination reactions leading to the formation of ethers and of reductive dehydroxylation products, and (b) dehydrogenation reaction leading to the production of aldehydes and to hydrocarbons resulting from the reductive decarbonylation of the aldehydes. Reactions of Type (a) occur preferentially on reduced nickel catalyst with an optimum concentration of nickel oxide between 2.6 and 1.0% (Table 5). The yield of (a)-type products is of the order of about 89% at 170° and ~65% at 200°. At the lower temperature the product consisted of almost all ether, while at 200° the Type (a) product was composed, in the case of neopentyl alcohol, of 2 moles equivalent of dineopentyl ether and 1 mole of neopentane.

When the nickel oxide content of the catalyst was reduced to 0.05%, Type (b) products were predominant and amounted to 94 and 83% in the case of neopentyl alcohol and 2-methylbutanol, respectively. The dehydrogenation to the aldehydes accompanied by reductive decarbonylation was the main reaction. Also a higher concentration of aldehydes was detected, when the nickel oxide increased above 3%. The results with the catalyst containing high concentration of nickel oxide were not too reliable because, under the conditions of the reaction, part of the nickel oxide was reduced to nickel.

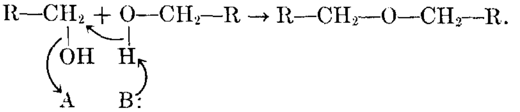
The formation of ethers and of hydrocarbons obtained from the reductive dehydroxylation of the alcohol, Type (a) products, can best be explained by a concerted mechanism, involving the cooperative effect of a base and an acid. For that reason we are compelled to assume the presence of intrinsic acidic and basic sites on the catalyst. Since the presence of 1.0 to 2.6% of nickel oxide in the catalyst is essential, it appears that these sites were generated on the interphase of the nickel and nickel oxide. The metal part of the catalyst acts an electron acceptor (Lewis acid), while the oxide as an electron donor. The situation is somewhat reminiscent of the calcined alumina catalysts in which Lewis acidic and basic sites were postulated as being produced through the cleavage of the aluminum–oxygen bond (13). Peri had postulated the presence of Lewis acidic sites created by Ni^{2+} ions incorporated into the silica lattice (*9*).

That the intrinsic acidic sites of the nickel catalyst are responsible for the conversion of the alcohols to the corresponding ethers was demonstrated by the experiments listed in Table 2 and 3. The inclusion of 0.05% by weight of sodium ions into the nickel catalyst containing about 1.5 mole % of nickel oxide drops the yield of ethers from an average of 79 to about 6%. With 0.1% of sodium, partically no ether was produced; a sharp decrease of ether yield was also observed after treatment of the catalyst with ammonia.

The neutralization of acidic sites by sodium ions inhibits also the reductive dehydroxylation reaction. The latter could be considered as a dehydration reaction followed by hydrogenation. The formation of 1,1-dimethylcyclopropane from neopentyl alcohol and of ethylcyclopropane from 2-methylbutanol could be interpreted by a concerted γ-participation reaction as in the case of alumina (*13–15*).



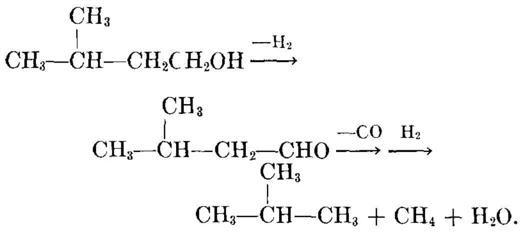
The production of neopentane from neopentyl alcohol could be explained by the hydrogenolysis of the 1,1-dimethylcyclopropane catalyzed by nickel (*16*). The dehydration of the alcohols to the ethers proceeds most probably through a concerted mechanism, whereby the basic sites remove the proton and the acidic sites the hydroxyl group.



$$\underset{OH}{R{-}CH_2} + \underset{H}{O}{-}CH_2{-}R \rightarrow R{-}CH_2{-}O{-}CH_2{-}R.$$

The possible formation of the ethers through an intermediate formation of hemiacetals also was considered in a previous publication (*1*), but in the meanwhile no evidence to support this intermediate could be found.

When the nickel oxide content of the nickel catalyst drops to about 0.05%, or when the ether producing catalyst contains 0.05% by weight of Na^+, the reductive dehydroxymethylation becomes the predominant reaction (Tables 2 and 5). This reaction results from the dehydrogenation of the alcohols to the aldehydes followed by the elimination of carbon monoxide, e.g.,



$$CH_3{-}\overset{CH_3}{CH}{-}CH_2CH_2OH \xrightarrow{-H_2} CH_3{-}\overset{CH_3}{CH}{-}CH_2{-}CHO \xrightarrow{-CO} \xrightarrow{H_2} CH_3{-}\overset{CH_3}{CH}{-}CH_3 + CH_4 + H_2O.$$

The mechanisms for the decarbonylation of aldehydes in homogenous (*17, 18*) and heterogenous (*3, 19*) systems have been discussed recently.

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