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Reactions of Alcohols

V. Conversion of Alcohols to Ethers Over Nickel and Other Transition Metal Catalysts in the Presence of Hydrogen*

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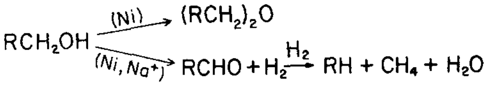
The reactions of primary alkanols have been investigated over reduced nickel oxide and other transition metal oxides and metals in the presence of a flow of hydrogen in a micropulse reactor.

The temperature of reduction of nickel oxide greatly affects its catalytic activity and selectivity for the conversion of *n*-butanol to dibutyl ether. After 20 hr of reduction at 190° or after 1 hr of reduction at 300° the catalyst shows 50% reactivity and 90% selectivity for the conversion of butanol to dibutyl ether. The ether forming properties of the reduced nickel oxide were correlated with the intrinsic acidic sites of the catalyst.

Both the activity and selectivity of the catalyst are impaired by the presence of pyridine. The selectivity of the nickel catalyst towards ether formation is also influenced by the amounts of butanol injected. An injection of at least 2–6 μl of butanol per 200 mg of catalyst is required for 80% selectivity for dibutyl ether formation.

Of the transition metal catalysts, Ni, Ir, and Pd show good properties for the conversion of alcohols to ethers. Rh and Ru, under similar conditions act as dehydration and dehydrogenation catalysts, while cobalt acts only as a dehydrogenation catalyst.

Previous studies from this laboratory have shown that primary and secondary alcohols undergo dehydration to form ethers when passed in the presence of hydrogen over reduced nickel oxide containing catalysts (*1–4*). The dehydration properties of the catalysts were ascribed to the existence of intrinsic acidic sites in the nickel. It was also reported that when the acidic sites were neutralized by sodium ions the nickel loses its ether formation abilities and becomes a dehydrogenating and dehydroxymethylating catalyst:



$$RCH_2OH \xrightarrow{(Ni)} (RCH_2)_2O$$
$$RCH_2OH \xrightarrow[(Ni,\,Na^+)]{} RCHO + H_2 \xrightarrow{H_2} RH + CH_4 + H_2O$$

The present study was also carried out in a micropulse reactor and was extended to a more detailed investigation of the effect of the extent of reduction with hydrogen of nickel oxide–kieselguhr catalyst on the reactivity and selectivity of the reaction of alcohols. The effect of nitrogen bases on nickel was also investigated, as well as the effect of variation of the amount of butanol used in each injection on the composition of product resulting from its reaction.

The present paper also describes the

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effect of other transition metals or their oxides on the reaction of butanol.

EXPERIMENTAL METHODS

1. *Apparatus and Procedure*

The experiments were made in a micropulse reactor described previously (*2*, *3*, *5*). The product from the reactions was analyzed by vpc using an analytical procedure and chromatographic columns reported already (*3*).

Nickel. Nickel catalyst was prepared by precipitation of about 15% aqueous solution of reagent grade nickel nitrate hexahydrate with gaseous ammonia in plastic bottle. This procedure was used to assure that no silica from glassware is added to the catalyst. The nickel hydroxide was then converted to nickel oxide by heating it in a flow of helium at 500° for 4 hr (*3*).

Iron, cobalt, and copper. The oxides of the title metals were prepared from $Fe(No_3)_2 \cdot 9H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, and $Cu(NO_3)_2 \cdot 3H_2O$ (Mallinckrodt, Analytical Reagent).

Platinum and palladium. A powder-like metal or oxide was obtained by thermal decomposition of diamminoplatinum dinitrite (Alfa Inorganics, Inc.) and palladium nitrate (Fischer Scientific, Inc.), respectively.

Iridium. Iridium dioxide (Alfa Inorganics, Inc.) was directly used as a catalyst.

Rhodium and ruthenium. These two metals (Alfa Inorganics, Inc.) 99.9%, ~ 60 mesh, were used as such.

2. *Surface Determination*

The metallic surface areas of three of the catalysts were determined by gas chromatography. For nickel, the adsorbing gas was oxygen (*6*); and for palladium and platinum, carbon monoxide was used (*7*). Before making the measurements, the catalysts were reduced for 1 hr at 400° with hydrogen, followed by a stream of helium for 1 hr at 400°. They were then allowed to cool to room temperature and several injections of the respective gases were made until the heat conductivity cell of the gas chromatograph (no column was used) showed a constant signal, indicating that no additional gas was adsorbed. The injections have to be done within a short time, otherwise, as stated in the literature (*8*), migration of oxygen from the surface into the bulk of the nickel can occur.

For the calculations the following values have been used: Ni, $1\ m^2 = 0.48$ ml of O_2 (*6*); Pd, $1\ m^2 = 0.31$ ml of CO (*8*), Pt, $1\ m^2 = 0.42$ ml of CO (*9*). The accuracy of this method is about 5–10% of the determined surface, for small surfaces it is about 15%.

RESULTS

1. *Nickel Catalyst: Effect of Temperature and Time of Reduction on the Selectivity of the Reaction of Butanol*

The temperature of the reduction of nickel oxide can greatly affect its catalytic activity and selectivity for the reaction of alcohols (*3*). Therefore, the purpose of this study was to determine the minimum temperature for the preparation of an active nickel catalyst for the conversion of *n*-butanol to dibutyl ether and compare these results with those obtained with catalysts reduced at previously reported much higher temperatures (*3*).

At the reduction and reaction temperature of 150° the conversion of butanol shows the first detectable products. Within the first hour of reduction the main product was butyraldehyde, but the overall conversion was small. After 18 hr of reduction at 150° the distribution of products showed a changed picture. The main product was propane, 77 mole %, while the ether amounted to 17%. The propane was formed by decomposition of the aldehyde. At 170° there was only a small change in product distribution, but at 190° ether formation was the main reaction, starting with the first injection.

The product distribution obtained after 20 hr at 190° remained almost unchanged up to a reduction temperature of 400°. A sharp change was observed after the reduction at 500°, the main products were

TABLE 1

ACTIVITY AND SELCECTIVITY OF REDUCED NICKEL OXIDE CATALYST FOR THE REACTION OF *n*-BUTANOL AS A FUNCTION OF TIME AND TEMPERATURE OF REDUCTION[a]

Expt:	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Temp (°C):	150	150	150	150	170	170	170	190	190	190	190[b]	190[c]	190[d]	190[e]	190[f]
Time [min (hr)]:	5	35	(4)	(18)	5	(1)	(3.5)	5	(1)	(20)					
Conversion (%):	0.5	0.7	1.8	2.8	5.0	5.6	7.5	26	31	59	51	41	45	26	1.8
Composition of converted alcohol (rate %)															
Propane	7	21	84	77	79	80	72	35	26	12	9	12	10	8	52
Butane	0	0	0	0	1	0	1	<1	<1	<1	<1	<1	<1	<1	0
Butyraldehyde	85	76	12	6	7	6	5	2	2	<1	<1	2	1	<1	44
Dibutyl ether	8	3	4	17	13	14	22	62	72	87	90	85	88	91	<5

[a] Conditions: 200 mg of nickel oxide; 7.2 liters of H_2/hr; 10 μl of *n*-C_4H_9OH/injection.

[b] Injection of 10 ml of NH_3.

[c] Flow of ammonia over the catalyst for 20 min.

[d] Fresh nickel oxide after reduction at 300° for 1 hr.

[e] As in (*d*) after reduction at: 400° for 1 hr; [f] 500° for 1 hr.

propane and butyraldehyde. The total conversion also decreased from 26% to 1.8% (Expts. 14 and 15). The decrease in the total conversion could be ascribed to sintering of the catalyst, resulting in decrease of the accessible surface. This explanation was supported by determining the nickel surface by adsorption of oxygen. A nickel catalyst reduced at 190° had a surface of 10 m^2/g but after reduction for 1 hr at 500° its surface was 1 m^2/g and the activity of the catalyst also decreased (Table 1). This sintering also caused the formation of channels in the catalyst powder. Nickel removed from the reactor after an experiment made at 500° was in the form of a lump and its catalytic activity was not restored after grinding it to a powder and reducing it with hydrogen.

2. *Effect of Ammonia, Aniline, and Pyridine*

It was shown in our previous studies that reduced nickel oxide has intrinsic acidic sites which are responsible for the conversion of alcohols to ethers (*1–4*). It was therefore of interest to determine the effect of nitrogen compounds on the composition of product obtained from the conversion of *n*-butanol.

Nickel catalyst reduced at 190° was subjected to the action of ammonia (Table 1, Expts. 11 and 12). The injection of 10 μl of gaseous ammonia did not affect the ether formation. Even a continuous flow of ammonia through the catalyst showed little effect on its activity and selectivity.

Aniline was also injected over the nickel catalyst in an amount of 20 μl. Ten minutes after the injection, the conversion to the ether amounted to 3.2% compared to 45% before injection. After 2 hr, however, with the usual stream of hydrogen, the activity of the catalyst was restored.

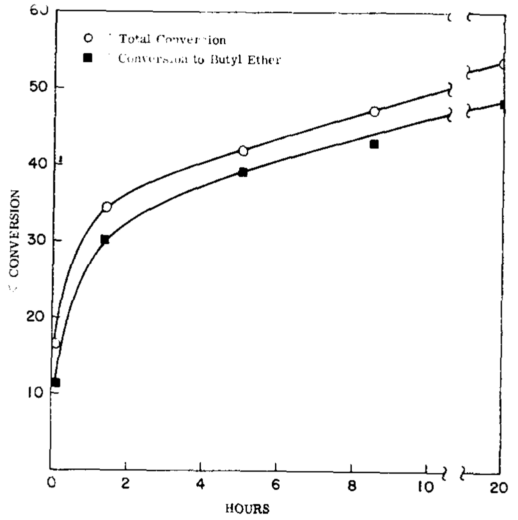


Fig. 1. Reactivation of nickel catalyst with hydrogen (7.2 liters/hr) after deactivation with pyridine. Original activity of the catalyst: total conversion, 56%; conversion to ether, 51%.

The "poisoning" and reactivation of nickel catalyst after an injection of 0.2 μl of pyridine is given in Fig. 1. This amount equals 4×10^{-6} moles or 2.4×10^{18} molecules. Considering an area of ~30 $Å^2$/molecule, the by-this-injection covered surface is equal to about 0.72 m^2, assuming that all the injected pyridine is adsorbed. Using the already mentioned surface area value of nickel as 10 m^2/g, the available surface of this catalyst (125 mg of Ni) being 1.25 m^2. From this rough estimate, a remaining activity of $100 \times [1 - (0.72/1.25)] = 42\%$ should be expected. The experiment shows a remaining activity of 25% which is not in good agreement, but this estimate did not consider an additional decrease of available sites by statistical poisoning in such a way that the remaining sites might be too small to permit ether formation.

The reactivation curve (Fig. 1) shows two remarkably different parts. A sharp increase of activity within 1 hr and a slow long-lasting increase of activity, which can probably be attributed to different active sites on the surface.

Table 2 contains a comparison of the formation of ethers from *n*-butanol, isobutyl alcohol, and neopentyl alcohol at six different stages of poisoning of the nickel. The experiments were repeated several times to be certain of their reproducibilities.

Experiment 1 in Table 2 was made without pyridine. In all the subsequent experiments 0.2 μl of pyridine was used; and,

TABLE 2
COMPARISON OF THE CONVERSION OF ALCOHOLS TO ETHERS AT VARIOUS RELATIVE CONCENTRATIONS OF PYRIDINE ON NICKEL[a,b]

	n-Butanol			Isobutyl alcohol			Neopentyl		
	% Conversion		% Selectivity to ether	% Conversion		% Selectivity to ether	% Conversion		% Selectivity to ether
Expt.	Total	to Ether		Total	to Ether		Total	to Ether	
1[c]	62	56	90	35	30	85	3.0	~1.8	60
2	55	51	92	29	25	87	2.3	~1.3	55
3	47	43	91	16	13	80	1.7	~0.5	28
4	42	38	90	12	9	71	1.4	~0.2	14
5	35	30	87	10	7	67	1.0	~0.1	10
6	16	11	70	8	4	56	1.0	<0.1	3
7	7	1	20	4	0.2	4	1.3	<0.1	1

[a] See Table 1 footnote *a*; the nickel oxide was reduced at 400° for 1 hr (Table 1, footnotes *a* and *c*.)

[b] Experimental conditions: temp of reactor, 190°; 10 μl of alcohol/injection; hydrogen, 7.2 liters/hr.

[c] Pyridine was not used in this experiment. In each subsequent experiment an increment of 0.2 μl of pyridine was injected.

for each alcohol, a new batch of catalyst was employed. The time lag between experiments was about 30 min, 20 min of which was required for the analysis of the product. The experiments show that there is a progressive poisoning of the catalyst as the total amount of pyridine injected is increased. After the fifth injection, the yield of ether dropped from 56% to 11% or a relative drop of about 80%. This is best presented in Fig. 2 where the drop of the relative yields of ether from isobutyl and neopentyl alcohol are plotted against the relative yield of butyl ether. If all three reactions would be influenced by pyridine in the same way, a straight-line dependence would be expected. Figure 2 shows concave shaped curves under straight broken line and the curve for neopentyl alcohol is always under that of isobutyl alcohol.

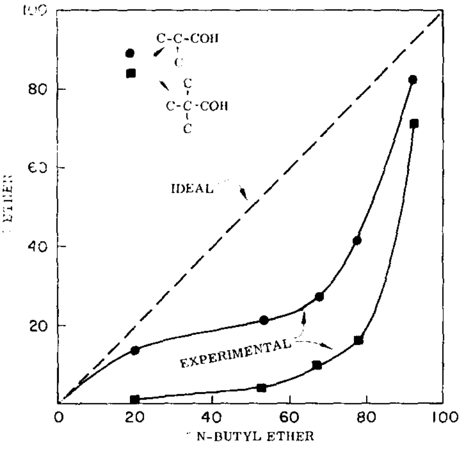


FIG. 2. Relative activity of nickel catalyst containing variable amounts of pyridine towards the formation of isobutyl and neopentyl ether vs the formation of *n*-butyl ether.

This can be explained by a homogeneous statistically distributed pyridine on the surface of the catalyst which decreases gradually the remaining active area and by this also the size of the remaining catalytic sites. The required size of an active site to form dineopentyl ether due to steric effects (*10*) should be larger than for diisobutyl ether or dibutyl ether.

3. *Effect of the Amount of Injection on Product Distribution from Butane*

There is a dependence of the amount of alcohol used in each injection, and the yield of ether. This is illustrated by passing butanol at 190° over reduced nickel oxide catalyst, Table 3. When small amounts, up to 0.5 μl, of the alcohol are injected, the main product is propane, from the decomposition of butyraldehyde. The injection of 2 μl of alcohol already shows a preference for ether formation. The bimolecular reaction is favored when the concentration of the substrate on the catalyst is in-

TABLE 3

EFFECT OF AMOUNTS OF BUTANOL INJECTED ON THE CONVERSION AND SELECTIVITY OF PRODUCTS[a,b]

Expt:	1	2	3	4	5	6	7
n-C_4H_9OH (μl)	0.1	0.5	2	5	10	20	50
Conversion (%)	92	80	78	66	59	57	57
Composition of product (mole %)							
Propane	99	64	38	16	12	6	5
Butane		1	0.1	<1	<1	<1	<1
Butyraldehyde		<1	0.1	<1	<1	<1	<1
Dibutyl ether	<1	34	60	83	87	93	94

[a] 200 mg of NiO was used, reduced at 400° for 1 hr (Table 1 footnote *a*).

[b] The experiments were made at 190°; H_2 flow 7.2 liters/hr.

creased. This is conceivable because the formation of an ether molecule requires 2 mole equiv of alcohol, but for propane formation only 1 mole equiv is required. The preferential formation of butyraldehyde and/or propane, and the high total conversion when a small amount of alcohol is used in injection, can be explained by an almost complete adsorption of the alcohol by the catalyst, and by the lack of the presence of the required two neighboring alcohol molecules for the formation of the ether.

4. *Effect of Hydrogen*

To obtain additional information regarding the effect of hydrogen upon the formation of dibutyl ether, n-butanol was passed over nickel catalyst at 190° using helium as the carrying gas, Table 4. Expts. 2–4 show that, in the absence of hydrogen, dibutyl ether is also produced; but with each successive injection, the total activity of the catalyst and its selectivity towards ether formation is diminished. However, after rerunning the flow of hydrogen the selectivity for ether is restored from 13 to 93%.

TABLE 4

EFFECT OF HELIUM ON THE REACTION OF n-BUTANOL OVER NICKEL CATALYST[a,b]

Expt.	Carrying gas	Total conversion (%)	Selectivity (mole %)
1	H_2	61	90
2	He	29	30
3	He	57[c]	21
4	He	19	15
5	H_2	35	93

[a] Table 3, footnote *a*.

[b] Experiments were made at 190°; gas flow, 7.2 liters/hr; injection, 10 μl.

[c] Injection, 1 μl.

The deactivation and loss of the selectivity of the catalyst in the absence of hydrogen is attributed to the formation of aldehyde condensation products on the catalyst.

Transition Metals as Catalysts

A survey of the effect of some of the transition metals and metal oxides on the reaction of n-butanol and of neopentyl alcohol are given in Tables 5 and 6. In most of the experiments, the catalysts were introduced into the reactor in the form of oxides and reduced *in situ* at 190° for 24 hr by a stream of hydrogen. In the case of rhodium and ruthenium, metal powder was used and treated the same way as the oxides. No attempt was made to make a thorough study of the optimal conditions for the preparation of the catalysts to make them most effective for the dehydration of alcohols to ethers.

Neopentyl alcohol being a solid was dissolved in n-hexane and several injections were made with different concentrations of hexane to be assured that the presence of the diluent does not influence the composition of the resulting product. The following metals or their oxides gave the highest selectivity for the formation of dibutyl and dineopentyl ether, respectively: nickel, irid-

TABLE 5

CONVERSION AND SELECTIVITY OF *n*-BUTANOL OVER TRANSITION METALS[a]

Expt:	1	2	3	4	5	6	7	8	9
Metal:	Fe	Ru[b]	Co	Rh[b]	Ir	Ni	Pd	Pt	Cu
Conversion (mole %):	8	3	9	2	26	12	15	6	<1
Composition of reaction product (mole %)									
Propane	19	45	64	58	14	12	15	6	10
Butane	72	2	20	3	7	<1	18	<1	0
Butyraldehyde	8	23	10	2	<1	<1	<1	93	90
Dibutyl ether	0	30	6	37	78	87	66	0	0

[a] Catalyst: 200 mg of the oxide in powder form; flow rate of hydrogen, 7.2 liters/hr temp of reaction, 190°; alcohol injected, 10 μl.

[b] Powdered metal, 200 mg.

ium, and palladium. Of these three catalysts iridium causes the highest reactivity of the alcohols. Unlike palladium, platinum causes dehydrogenation exclusively, the alcohols are converted to the aldehydes, and, through a subsequent decarbonylation reaction, to the corresponding alkanes. Iron and cobalt convert neopentyl alcohol to neopentane without at the same time forming isopentane, an indication that dehydration of the alcohol to an olefin is not a precursor for this reaction.

Ruthenium and rhodium can be classified as catalysts having both dehydration and dehydrogenation properties.

The relative selectivity of the catalyst toward ether formation is as follows: Ni, Ir, Pd > Rh, Ru > Co. The difference in the activity between platinum and palladium can be ascribed to the greater ease for the former to undergo a complete reduction to metallic platinum. It is known from the previous experiments with nickel that small amounts of oxide are required for the nickel to become a dehydration catalyst, and a similar requirement might also hold for platinum.

A more detailed study with iridium revealed that although this catalyst undergoes deactivation with use, it can nevertheless be reactivated by oxidation with air followed by reduction with hydrogen, Table 7.

Ammonia gas has little effect on the activity of iridium; pyridine mixed with alcohol has a poisoning effect on the iridium for the formation of ethers. The activity of the catalyst can, however, be restored by passage of hydrogen over the catalyst for 30 min.

TABLE 6

CONVERSION AND SELECTIVITY OF NEOPENTYL ALCOHOL OVER TRANSITION METAL OXIDES[a]

Expt.:	1	2	3	4	5	6	7
Metal:	Fe	Co	Ir	Ni	Pd	Pt[b]	Cu
Conversion (mole %):	3.4	5.0	25	7.4	5.7	0.7	1.3
Composition of reaction product (mole %)							
Propane	<1	7	<1	7	10	0	2
Isobutane	<1	4	<1	2	24	0	0
Neopentane	76	73	4	8	0	0	0
Isopentane	0	0	18	0	<1	0	0
Pivaldehyde	22	16	6	16	11	100	98
Ether			77	67	54	0	0

[a] See Table 5 footnote *a* for experimental conditions.

[b] Only 65 mg of PtO_2 was used.

TABLE 7

INFLUENCE OF AIR TREATMENT ON REDUCED IRIDIUM OXIDE CATALYST[a]

Expt.	Conversion of butanol (%)	Dibutyl ether in reaction product (mole %)
1	27.2	79
2[b]	12.8	38
3[c]	5.1	76
4[d]	14.2	80
5[e]	7.6	79
6[f]	21.0	57

[a] Catalyst: 200 mg of IrO_2; *n*-butanol injection, 10 μl; hydrogen flow, 7.2 liters/hr; temp 190°.

[b] After 20 injections.

[c] After 17 injections.

[d] Air was passed over a period of 0.5 hr, followed by nitrogen and hydrogen.

[e] After 27 injections.

[f] Air was passed for 1.25 hour, followed as in *d*.

DISCUSSION

It has been shown that special conditions have to be fulfilled to obtain a reasonable acting metal catalyst to convert an alcohol to an ether. Besides the obvious necessity to transport the alcohol through the gas phase to the active centers and the also obvious necessity to desorb the ether, there are three different stages involved in ether formation which all can become rate determining by themselves:

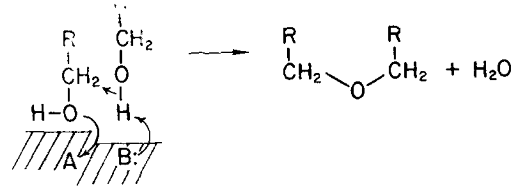
1. The two alcohol molecules have to react on the catalyst differently: (a) One molecule has to lose its hydrogen; and (b) the other one its hydroxyl group.
2. The alkyl and the alkoxy groups have to react to form ether.
3. The hydrogen and the hydroxyl group adsorbed by the catalyst have to form water which can then be desorbed from the catalyst.

The most uncomplicated way to fulfill these steps and the requirements therein involved, is to adsorb two alcohol molecules on two neighboring sites which are offering different characteristics. For simplicity, these OH-attracting sites are called in the following pages acid sites and the H-attracting sites are called basic sites. In extending the description of these sites the OH-accepting site can also be visualized as a coordinative unsaturated electron pair-accepting site [e.g., Al in the Al_2O_3 picture given by Peri (*11*)], and the H-accepting site might be, e.g., very well located on the metal surface (especially of a hydrogenation-dehydrogenation catalyst), which adsorbs an alcohol molecule dissociatively. This has been observed in exchange experiments between deuterium and alcohols. In confirmation of earlier work, Anderson and Kemball (*12*) found that, in the vapor phase reaction on metals, the monodeuterated alcohol was invariably the most abundant product. Therefore, it was also concluded (*13*) that for a ready exchange of the hydroxylic hydrogen the following species is most likely:

$$R\text{-}OH + 2^* \rightarrow \underset{*}{R\text{-}O} + \underset{*}{H}.$$

The activity order based on the temperature required to effect a rate of 5% exchange min^{-1} is given as $Pt > Rh > Pd > Ni > Fe = W > Ag$.

For the dehydration of butanol to its ether, only those metals in the middle of the series are active (Rh → Ni). Therefore, it has to be concluded that the loss of the hydrogen from the hydroxyl group alone is not a sufficient criterion for ether formation. Simultaneously a hydroxyl group from another molecule of the alcohol has to be removed. This reaction seems to occur on those metals which form relatively stable oxides or hydroxides. Regarding the stability of the oxides the following information is available (*14*): platinum oxide decomposes at 550°, palladium oxide melts at 870°, and nickel oxide melts at 1990°. These data do not consider the influence of hydrogen, but they show the stability in the absence of hydrogen. In comparing the "affinity" of metals toward hydrogen and hydroxide in terms of the possibility to form a surface compound, nickel, giving the highest ether selectivity seems to occupy an ideal position. In the present meaning of the word, nickel can be called amphoteric with respect to the H and OH of alcohols. In favor of a concerted mechanism is the ease by which all the three demanding steps can occur at almost the same time.



The above-postulated two differently behaving adsorption sites can be thought to be present on nickel and nickel oxide. The activity of the catalyst would then depend mostly on the ratio nickel/nickel oxide. If it changes, also the ether selectivity should change.

This can be checked, e.g., in the dependence of the ether formation on the state of reduction. The big difference between Expts. 7 and 8 in Table 1 is astonishing. The main difference between those runs is the difference in the temperature, 170 vs 190°. After a short time at 190°, the catalyst acquires a product selectivity which is maintained up to a reduction temperature of 400°. If this ratio of oxide to pure metal is essential for the ether selectivity, then it should be expected to find a stronger dependence of the ether formation on the reduction temperature, and for that reason a systematic and quantitative study of the ratios of metals to metal oxides and their relation to ether formation is contemplated.

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