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Reactions of Alcohols

VI. Dehydration of Primary Alkanols to Ethers in a Flow System over Supported Nickel Catalysts in the Presence of Hydrogen. Effect of Supports*

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Catalysts composed of 6% nickel deposited on silica, Cab-O-Sil, and alumina were found to be very effective for the conversion of primary alkanols to ethers at 160–190° in a flow system and in the presence of hydrogen. Nickel on magnesia, under similar conditions, had no catalytic activity.

The effect of varying concentrations of nickel on Cab-O-Sil were investigated as catalysts for the conversion of butanol to dibutyl ether. Catalysts containing 7 to 37% nickel were found to be the most active and selective for this reaction.

At 190°, alumina as such was inert towards the conversion of neopentyl alcohol; however, in the presence of 6% nickel on alumina, 23% of the alcohol reacted and the product of the reaction contained 69% of dineopentyl ether and 2% of 1,1-dimethylcyclopropane. Nickel on Cab-O-Sil was found to be the most effective catalyst for the formation of ethers.

The mechanism of dehydration is discussed.

In previous papers of this series (*1–5*), it was demonstrated that reduced nickel oxide as such deposited on kieselguhr and other supports is one of the most effective catalysts known for the conversion of primary alkanols to ethers. These reactions have been made in a pulse reactor (*6*) at temperatures varying from 150–200° and using hydrogen as a carrier gas. Hydrogen was found to be essential for the production of ethers and for maintaining the activity and selectivity of the catalyst (*4*).

The purpose of the present investigation was to determine the effect of supports on the activity of nickel catalysts for the conversion of alcohols to ethers. The supports studied were kieselguhr, silica (Cab-O-Sil), alumina, and magnesia. The supported catalysts contained about 4 to 7% by weight of reduced nickel oxide. A study was also made to determine the effect of varying amounts of nickel deposited on Cab-O-Sil on the activity and selectivity of the catalysts for the conversion of alcohols.

Since the dehydration of alcohols to ethers over nickel catalysts was assumed to be due to the presence of intrinsic acidic sites on the catalyst, an investigation was made to determine the effect of added sodium ions on the conversion and the type of products formed from *n*-butanol.

EXPERIMENTAL PROCEDURE

The experiments were conducted in a micropulse reactor developed in this laboratory (*6*) and modified to adapt it for a continuous flow type operation. The flow of the alcohols was regulated by means of a calibrated all stainless steel displacement pump. The flow of hydrogen was controlled

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by a microprecision valve and monitored by a microrotameter and measured with a soap bubble gas meter. The temperature was maintained constant throughout the experiment within ±0.5°.

An 1/8 in. o.d. transfer line connected the reactor outlet to a pneumatic activated diaphragm sampling valve. The latter was attached to a gas chromatographic column. A liquid nitrogen trapping technique was used to collect samples for analysis (*3*, *6*, *7*). The quantitative evaluation of the product from gas chromatography was determined by measuring peak areas using an electronic integrator with an attached printer, and making allowances for the peak area retentions. The analytical columns consisted of 15% Ucon 754,8000 on 80/100 Chromasorb W. The columns were 30 ft long.

The catalyst in the form of granulated powder, 300 mg, was placed in the center of the reactor tube between layers of glass wool. The rest of the reactor was filled with glass beads of 20–30 mesh size. Neither the glass wool nor the beads acted catalytically.

SUPPORTS AND CATALYSTS

Alumina A. It was prepared from aluminum isopropoxide and calcined at 700° as reported previously (*8*).

Cab-O-Sil M 5. It consisted of silica in the form of a fine powder (Cabot Corporation, Boston, MA). Before use it was wetted, broken into 20–50 mesh size, dried, and calcined at 400°.

Magnesia. The magnesium oxide was prepared by calcination of magnesium nitrate at 500°, followed by hydrogen treatment at 400° for 1 hr.

Silica. It was prepared by hydrolysis of tetramethylsilicate according to the procedure described previously (*4*).

Nickel on supports. Nickel in the form of $Ni(NO_3)_2 6H_2O$, 12 g, was precipitated in the presence of 20–25 g of the supports listed above, according to the description given previously (*4*). The catalyst after reduction at 300° contained about 6% nickel.

Nickel–alumina catalysts containing 0.1, 1.0, and 5.0% nickel were prepared by impregnating the alumina with concentrated solution of the nitrate. The solution was evaporated, dried, and the solid placed in the reaction tube was decomposed by heating in a flow of hydrogen. The temperature of reduction was raised slowly from 150 to 400° and maintained at the latter temperature for 2 hr.

The sodium containing catalysts were prepared as described previously (*4*).

RESULTS

Effect of supports. Supported nickel catalysts, containing 6–7.5% nickel by weight were used for the reactions of *n*-butanol (Table 1). The experiments were made at 160 and 190° with the exception of the

TABLE 1

REACTIONS OF *n*-BUTYL ALCOHOL OVER SUPPORTED NICKEL CATALYSTS[a]

Expt.		Temp. (°C)	Conversion (%)	Composition (mole %)			
				Ether	Aldehyde	Propane	Butane
1	6% Ni on Al_2O_3	160	17	98	<1	2	
2		190	29	79	<1	20	
3	6% Ni on silica	160	33	97		3	
4		190	68	77		23	
5	7.5% Ni on Cab-O-Sil	160	47	99	1		
6		190	83	86		10	4
7	6% Ni on MgO	190	1		48	52	

[a] Conditions: flow of hydrogen, 0.275 moles/hr; flow of alcohol, 0.0398 moles/hr; molar ratio of H_2/alcohol = 6.9:1.0; catalyst, 300 mg.

magnesia supported catalyst in which temperatures of 190° were used.

At 160° alumina, silica, and Cab-O-Sil supported nickel catalysts showed 17 to 47% conversion of *n*-butanol with 97 to 99% selectivity for ether formation. At 190° the conversion was from 70 to 100% higher than at 160°, but the selectivity for ether was somewhat lower. Dehydrogenation resulting in the formation of propane was the competing reaction. The total conversion at both temperatures was increasing in the order alumina, silica, Cab-O-Sil. Because both the total and the metallic surface of these catalysts was not determined, it is difficult to say whether there is a correlation between this parameter and ether formation.

The lack of activity of nickel on magnesia towards the formation of dibutyl ether from *n*-butyl alcohol is probably due to the neutralization of the intrinsic acidic sites of the nickel.

Effect of varying concentrations of nickel. A series of experiments were made with nickel on Cab-O-Sil containing increasing amounts of nickel, Table 2.

A marked difference in the selectivity and also in the stability of the catalysts was observed in the region between 0.1 and 5% nickel. The catalyst with the lowest nickel concentration showed the smallest selectivity for ether formation and the lowest catalytic activity. At 190° the conversion of *n*-butanol was 3.1% with a 38% selectivity for ether. After 20 min on stream, both the activity of the catalyst dropped and the selectivity for ether was only 1%. Propane and butyraldehyde, products of dehydrogenation, were the main compounds formed. Greater stability and selectivity was encountered with a catalyst containing 1% nickel.

Catalysts containing 5 to 37% of nickel demonstrated over 94% activity and of 85% selectivity for butyl ether formation. All these catalysts showed good stability without any appreciable deterioration during the 5 hr period on stream. When the concentration of the nickel was increased to 61%, a small decrease of its activity with time was observed.

The metallic surface of the catalyst was determined by the method previously described (*1*) and the average particle size was estimated by assuming that the catalyst was in the form of cubes with one face covered by the support.

The experimental data showed that there was a relation between the nickel surface and the reactivity and stability of the catalyst. With nickel surface of 1.42 m^2/g or

TABLE 2

REACTION OF *n*-BUTYL ALCOHOL AT 190° OVER NICKEL ON CAB-O-SIL CONTAINING VARYING CONCENTRATIONS OF NICKEL[a]

Expt.	Catalyst	Ni (%)	Conversion (%)	Composition				Ni surface (m^2/g)	Av particle size (Å)
				Ether	Aldehyde	Propane	Butane		
1	Impregnated	0.1	3.1	38	9	53		0.43	13
1[b]			1.9	1	19	80			
2	Impregnated	1.0	33.3	88	1	11		1.42	39.8
2[c]			5.7	56	10	34			
3	Impregnated	5	97.3	85		10	5	8.27	
4	Precipated	5	82	85		13	2	3.50	
5		10	95	84		16	1	18.2	30.9
6	Precipitated	37	94	84		13	3	35.4	59.5
7	Precipitated	61	89	94		6		15.7	21.8

[a] For experimental conditions see footnote[a] Table 1.

[b] Catalyst from Expt. 1 was used. The product for analysis was taken after the catalyst was on run for 20 min.

[c] Catalyst from Expt. 2 was used. Sample was taken after 8 hr on run.

lower, the catalyst loses rapidly its activity and selectivity. The nickel surface depends on the method of preparation of the catalyst, with 5% nickel on Cab-O-Sil the surface amounts to 8.27 m^2/g, when the catalyst is prepared by impregnation, and 3.50 m^2/g when it is made by precipitation.

EFFECT OF SODIUM

In the previous papers of this series, it was postulated that nickel oxide present in the reduced nickel had intrinsic acidic sites which were responsible for the dehydration of alcohols to ethers *(1–5)*. These acidic sites were influenced by the presence of alkali metals and of organic bases. It was of interest therefore to determine the effect of varying amounts of sodium ions on the activity and selectivity of a 6% nickel on Cab-O-Sil catalyst. The experiments were made at 160 and 190° in a continuous flow in the presence of hydrogen and using *n*-butyl and isobutyl alcohol as model compounds (Table 3). The catalyst contained 0.0, 0.1, 0.5, and 1.0% by weight of sodium ions based on the nickel.

Both the total activity and selectivity for ether formation dropped with the increase of sodium ion content. The reactivity decreased substantially when the sodium content was 0.5%; with a catalyst containing 1% of sodium, the conversion of butanol dropped at 160° from 28.5 to 2.9%, and at 190° from 76.6 to 14.4%.

The selectivity towards dehydrogenation increased with increase in concentration of sodium content as evidenced by the formation of aldehydes and of propane. The latter was produced by the decarbonylation of the aldehydes formed. The absolute yield of propane increased from 2.2 to 3.8 and 7.3% when the concentration of sodium changed from 0.0, 0.1, and 0.5%. When the concentration was increased to 1.0%, the catalyst was greatly deactivated and the absolute yield of propane dropped considerably. The results are very similar to those obtained by the pulse technique *(4)*.

NEOPENTYL ALCOHOL OVER Ni-Al_2O_3 AND Ni-Cab-O-Sil

It was previously reported that neopentyl alcohol formed isopentane and neopentane with small amounts of dineopentyl ether, when pulse injected over nickel–alumina catalyst *(4)*. The conversion of the alcohol could not be ascertained because part of the neopentyl alcohol was chemisorbed on the catalyst. This reaction was presently reinvestigated in a continuous flow system, using 6% nickel on alumina and 6% nickel on Cab-O-Sil as catalysts (Table 4).

It was found that, at 190° under conditions where alumina is practically inert

TABLE 3

EFFECT OF SODIUM IONS ON THE REACTION OF BUTYL ALCOHOL OVER 5% NICKEL ON CAB-O-SIL[a]

Temp (°C):	160				190			
Sodium (wt %):	0.0	0.1	0.5	1.0	0.0	0.1	0.5	1.0
				n-Butanol				
Conversion (%)	28.5	28.5	17.1	2.9	76.6	76.6	50.5	14.4
Product distribution (mole %)								
Dibutyl ether	91.6	85.1	56.9	24.2	73.0	64.4	37.0	9.7
Butyraldehyde	0.5	0.6	1.2	3.1	0.2	0.3	1.4	3.8
Propane	7.9	13.3	42.8	72.6	26.8	35.3	61.6	86.2
				Isobutyl alcohol				
Conversion (%)	23.0	17.3	8.9	1.5	60.9	53.8	29.0	10.9
Product distribution (mole %)								
Diisobutyl ether	97.0	91.0	53.8	12.0	75.3	69.9	41.0	6.4
Isobutyraldehyde	0.5	0.4	0.3	0	0.3	0.2	0.2	0
Propane	2.5	8.6	45.9	88.0	24.4	29.9	58.8	93.6

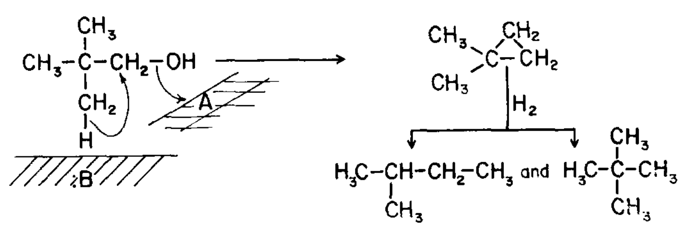
[a] Molar ratio of alcohol to hydrogen = 1:4.6; catalyst, 0.3 g, flow of alcohol, 8.36 ml/hr.

TABLE 4
Reactions of Neopentyl Alcohol[a]

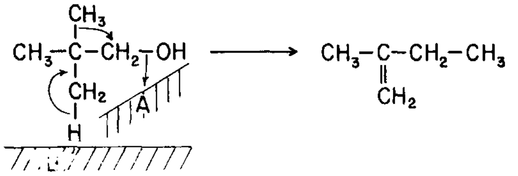
Catalyst:	6% Ni-Al_2O_3		6% Ni-Cab-O-Sil	
Temp (°C):	160	190	160	190
Conversion (%):	6.5	23.5	20.8	58.5
Composition of product (mole %)				
Isobutane	4.0	20.0	6.7	15.1
Neopentane	—	0.6	0	0.1
Isopentane	0.4	1.2	0	0.5
1,1-Dimethylcyclopropane	0	2.2	0	0
Pivaldehyde	16.5	6.7	0.5	1.1
Dineopentyl ether	83.0	68.9	92.8	83.2

[a] Catalyst, 600 mg; flow of hydrogen, 0.275 moles/hr; molar ratio alcohol/hydrogen = 1:4.6.

towards the reaction of neopentyl alcohol, alumina containing 6% nickel gives 23.5% conversion. At 160°, only 6.5% of the alcohol reacted with a selectivity towards dineopentyl ether of 83%, the remainder being pivaldehyde and isobutane. At 190° in addition to the above compounds, 2.2% of 1,1-dimethylcyclopropane was produced, which proves that the dehydration occurs with γ-hydrogen participation as in the case of alumina alone, but at much higher temperature, 300–400° (*9*). The formation of neopentane is intriguing and most likely it was produced by the hydrogenolysis of the cyclopropane ring. The passage of 1,1-dimethylcyclopropane over this catalyst and under similar experimental conditions produced a mixture of isopentane and neopentane, the latter predominating. The course of the reaction can be presented as follows



The formation of isopentane can proceed also *via* an intermediate formation of an olefin.



B: and A represent basic and acidic sites of the catalyst. The elimination of the elements of water can be considered as a concerted *trans* elimination reaction, similar to that occurring, but at much higher temperatures, on alumina catalysts (*9*).

Nickel on Cab-O-Sil is a more selective catalyst than nickel on alumina, and the only major secondary reaction is dehydrogenation followed by reductive decarbonylation with the formation of isobutane.

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