JOURNAL OF CATALYSIS 17, 384–393 (1970)

Hydrogenolysis of Alcohols

III. Effect of Supports on Reduced Nickel Oxide for the Conversion of Alcohols to Ethers*

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Received August 15, 1969

Catalysts prepared from nickel oxide deposited on kieselguhr, silica, silica-alumina, and alumina were reduced and studied for the conversion of primary alcohols. The alcohols studied were *n*-propanol, *n*-butanol, 2-methylbutanol, and 2,2-dimethylbutanol (neopentyl alcohol). The exepriments were made in a pulse reactor in the presence of a flow of hydrogen, at atmospheric pressure and at about 190°.

Three main reactions occur in the presence of a nickel-kieselguhr catalyst: (1) reductive dehydroxymethylation, (2) reductive dehydroxylation, and (3) ether formation. The last two reactions are related to the intrinsic acidic sites of the catalyst. Nickel-kieselguhr catalyst containing 6–10% of nickel gave in the case of *n*-butanol 73% conversion, with 72 mole % of di-*n*-butyl ether in the product. The presence of Na^+ in the catalyst inhibits the formation of ethers, while the dehydroxymethylation reaction increases.

A continuous flow reaction at 190° demonstrated that nickel-kieselguhr catalyst containing 6% of nickel shows no deterioration after 16 hr of use. At 170°, with a hydrogen to alcohol ratio of 10 and LHSV of 2, *n*-butanol reacted to the extent of 89%, with 91% yield of di-*n*-butyl ether.

INTRODUCTION

In previous papers of this series (*1*, *2*), it was reported that alcohols undergo various reactions when passed at 100–200° over a reduced nickel oxide catalyst in the presence of hydrogen. The main reaction products obtained from primary aliphatic alcohols were ethers and two types of hydrocarbons, one resulting from the reductive dehydroxylation and the other from the reductive dehydroxymethylation of the alkanols (see page 385).

Evidence was given that reactions I and II were catalyzed by the intrinsic acidic sites of the nickel catalyst, while reaction III involved a prior dehydrogenation of the alcohol to an aldehyde, with a subsequent decarbonylation of the aldehyde to carbon monoxide and alkanes, followed by the reduction of the carbon monoxide to methane.

The preparation method of the nickel catalyst, the reduction temperature of the nickel oxide, and the presence of sodium ions greatly influence the reactivity and selectivity of the catalyst (*1*).

The purpose of the present study was to investigate the influence of supports and the nickel concentration on the kieselguhr support on the distribution of the products obtained from the reaction of primary alcohols over these catalysts. A further aim of this study was to determine the effect of sodium ion content in the catalyst and the effect of pressure on the selectivity of the reaction.

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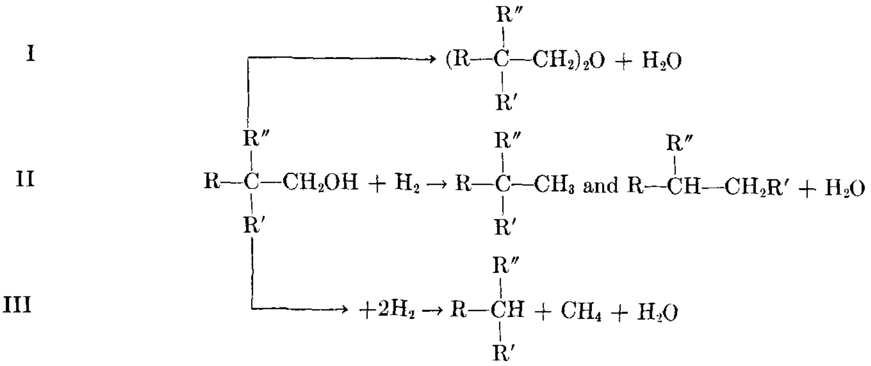
* This research was supported by the Atomic Energy Commission, Contract AT(11-1)-1096. The financial assistance of W. R. Grace & Co. is also appreciated.



R = H or CH_3 R′ = CH_3
R″ = CH_3, C_2H_5, or i-C_3H_7

Experimental Procedure

All the experiments were carried out in a pressure micropulse reactor (*1*, *3*) using a ⅜-in.-diameter reactor tube. The amount of catalyst used in each experiment was 200 mg, the hydrogen flow was 100 ml/min, and the amount of alcohol injected was 10 μl.

Continuous flow experiments were carried out in the same reactor tube. The amount of catalyst was 400 mg. Alcohols were fed using the pressure displacement pump at a minimum flow rate of 0.5 ml/hr. A remote control sampling valve immersed in an heated oil bath was used to inject samples into the analytical column.

A trapping technique was used to collect samples for the analysis (*1*, *2*, *3*). The liquid nitrogen trap was maintained for 6 min 45 sec, the Dewar flask was then removed, and the coil was warmed to room temperature. Finally, the chromatographic column was programmed starting at 40° at a rate of 35°/min up to 150°C. A 30-ft × ⅛-in. column was used; it was packed with 20% Ucon 75 H (supplied by Chemical Research Services, Inc., Addison, Illinois) and deposited on 60–80 mesh Chromosorb W. Catalysts containing nickel have been reduced in the reactor at 400° in the hydrogen flow.

Catalysts and Supports

Nickel kieselguhr. This catalyst was prepared according to the method described previously (*2*). The kieselguhr was supplied by Harshaw Chemical Company, Cleveland, Ohio, and its composition was described previously (*2*). Nickel nitrate hexahydrate, in amounts of 32, 20, 12, and 2 g, was precipitated on 25 g of kieselguhr with a slight excess of an aqueous solution of ammonium carbonate monohydrate, thus giving catalysts containing 16, 10, 6, and 1 wt % of nickel on kieselguhr.

Nickel–kieselguhr–sodium. To 10 ml of an aqueous solution of sodium carbonate which contained 0.0066, 0.0132, 0.0340, 0.1356, and 0.770 mmole of sodium carbonate, respectively, was added 10 g of dry nickel carbonate on kieselguhr, obtained as described above, and containing 6 wt % of Ni. The mixtures were allowed to remain overnight and then dried at 110°. The catalysts contained 0.05, 0.1, 0.3, 1.04, and 5.9 wt % of sodium ions, based on the nickel content.

Silica. A solution composed of 473 ml of tetraethylsilicate, 250 ml of 1 *M* hydrochloric acid, and 250 ml of 95% ethanol was slowly neutralized while stirring with about 250 ml of 0.1 *M* ammonium hydroxide. The precipitated silica gel was allowed to stand overnight and then washed thoroughly, dried at 150°, washed twice, dried at 175°, and calcined at 550°. Its surface area was 346 m^2/g, and its pore volume was 1.08 ml/g.

Silica–alumina. The same procedure was used as described for silica except that to the solutions of tetraethylsilicate were added 0.11, 0.55, and 5.5 g of $Al(NO_3)_3\cdot$

$9H_2O$, respectively. The resulting silicas contained 0.02, 0.1, and 1.0 wt % of alumina.

Nickel–silica–alumina. The nickel was precipitated on the silica-aluminas in the form of nickel carbonate, using the procedure described for nickel–kieselguhr. Catalysts containing 6 wt % of nickel were prepared.

Nickel–alumina. The aluminas used consisted of alumina A, prepared from aluminum isopropoxide as reported previously (*4*). The Harshaw alumina was the same as described in a previous paper (*5*).

The procedure for depositing the nickel was the same as given for nickel–kieselguhr. Alumina A contained intrinsic acidic sites, while Harshaw alumina contained sodium ions and was nonacidic.

RESULTS

Effect of Nickel Concentration

Table 1 summarizes the experimental conditions and results using nickel–kieselguhr catalysts having from 1 to 16% of nickel. Additional experiments are listed with a nonsupported reduced nickel oxide catalyst and with a nickel–kieselguhr cata-

TABLE 1

REACTION OF ALCOHOLS AT 190° IN THE PRESENCE OF NICKEL–KIESELGUHR CATALYSTS OF VARIOUS NICKEL CONCENTRATIONS

(Temperature, 190°; hydrogen flow, 100 ml/min; injection, 10 μl)

Ni (%)	0	1	6	10	16	100[a]	6[b]
n-Butanol							
Conversion (%)	0	19	73	66	63	16	13
Selectivity (mole %)[c]							
Propane		18	25	43	48	23	10
Butane		6	3	4	5		2
Dibutyl ether		76	72	53	45	65	66
Butyraldehyde						12	22
2-Methylbutanol							
Conversion (%)	2	19	77	77	66		
Selectivity (mole %)[c]							
n-Butane		15	20	29	40		
Isopentane	85[d]	18	9	14	17		
n-Pentane	15[e]	7	5	6	8		
Di-2-methylbutyl ether	Trace	60	66	51	35		
Neopentyl alcohol							
Conversion (%)	1	9	43	47	48	8	9
Selectivity (mole %)[c]							
Propane		6	1	1		4	1
Isobutane	Trace	3	6	9	11	42	1
Neopentane		2	2	4	5	4	0
Isopentane	99[f]	66	28	24	40		26
Dineopentyl ether		22	63	61	42	4	24
Trimethylacetaldehyde	Trace					46	47

[a] 200 mg of $NiCO_3$, reduced *in situ* at 400° (see Experimental Procedure section).

[b] 200 mg of catalyst contining 6% $NiCO_3$ mechanically mixed with kieselguhr and heated at 400° for 2 hr.

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

[d] The hydrocarbons consisted of 16% 2-methyl-1-butene and 84% 2-methyl-2-butene.

[e] Consisted of 1- and 2-pentenes.

[f] The hydrocarbons contained 15% 2-methyl-1-butene, 70% 2-methyl-2-butene, and 14% isopentane.

lyst which was prepared by mechanically mixing finely divided nickel oxide and kieselguhr and reducing the oxide in a flow of hydrogen. The nickel oxide was prepared from nickel nitrate and ammonium hydroxide according to the method described previously (*1*).

n-Butanol, 2-methylbutanol, and 2,2-dimethylpropanol (neopentylalcohol) were used in this study. The temperature chosen for the reaction was 190°, which was found most suitable for the optimum yield of the ethers (Table 1).

Kieselguhr alone has practically no effect on the conversion of alcohols. Nickel–kieselguhr catalyst containing as little as 1% of nickel gives 19% of an overall conversion of butanol, 76% of which is dibutyl ether. The optimum selectivity of ethers, 62 to 71%, was obtained when the concentration of nickel in kieselguhr was 6 wt %. The ether formation as well as the reductive dehydroxylation reactions, leading to the formation of butane in the case of *n*-butanol and to isomeric pentanes in the case of neopentyl alcohol, are acid-type reactions and were ascribed to the presence of intrinsic acidic sites in the catalyst (*1*). The extent of the reactions which can be attributed to the acidic sites of the catalyst containing 6% of nickel range from 75% in the case of butanol to about 92% in the case of neopentyl alcohol.

As the concentration of nickel in kieselguhr is increased to 10 and 16%, respectively, the acid-type reactions diminish and the dehydroxymethylation increases. Reduced nickel oxide in the absence of kieselguhr showed acid properties in the case of butanol, as indicated by a substantial formation of dibutyl ether; however, only a small amount of ether was produced when neopentyl alcohol was used. With the latter alcohol, dehydrogenation and dehydroxymethylation were the principal reactions. However, a mechanical mixture of finely divided kieselguhr and nickel oxide heated at 400° in hydrogen for 2 hr imparted acidic sites to the catalyst, and the product from neopentyl alcohol contained 26% of isopentane and 24% of dineopentyl ether.

Effect of Pressure

The effect of pressure upon the conversion of neopentyl alcohol has been studied in the range of 1 to 50 atm (Table 2). The rate of conversion drops with increase of pressure. The yield of dineopentyl ether also drops from about 66 to 53%, while the yield of isopentane increases from about 23 to 46%. Isobutane is formed at the lower pressures, but it is not produced at 50 atm. This is not unexpected, since the formation of isobutane would require prior dehydrogenation of the neopentyl alcohol to the corresponding aldehyde, a reaction which is not favored by pressure.

TABLE 2

EFFECT OF PRESSURE UPON THE CONVERSION OF NEOPENTYL ALCOHOL

(200 mg of nickel–kieselguhr catalyst was used containing 6% by wt of nickel; temperature, 195°; hydrogen flow, 100 ml/min; injection; 10 μl)

Pressure (atm)	1	16	30	50
Conversion (%)	40	15	13	11
Selectivity (mole %)[a]				
Propane	2	1		
Isobutane	4	2	<1	Trace
Neopentane	5	1		
Isopentane	23	39	43	46
Dienopentyl ether	66	57	55	52

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

Effect of Sodium

Nickel–kieselguhr catalyst containing 6% nickel by weight was impregnated with aqueous solutions of sodium carbonate. Catalysts containing 0, 0.05, 0.10, 0.3, 1.04, and 5.9% sodium by weight were prepared. The experimental conditions and results are given in Table 3.

The presence of as little as 0.05% of sodium ions reflects some loss of acidic sites, as evidenced by the decrease in the formation of ethers from propanol, butanol, 3-methylbutanol, and neopentyl alcohol. When the sodium content was increased to 1.04%, the ether formation was greatly

TABLE 3

EFFECT OF SODIUM ON REACTIONS OF ALCOHOLS IN THE PRESENCE OF NICKEL–KIESELGUHR AT 195

(Catalyst contained 6% Ni by weight; temperature; 190°; hydrogen flow, 100 ml/min; injection, 10 μl)

Sodium (wt %)	0	0.05	0.10	1.04	5.9
n-Propanol					
Conversion (%)[a]	53	40	46	20	2
Composition of products (%)					
Ethane	53	57	62	88	~55
Propane	2	4	2	2	
Cyclopropane	2	2	2	1	
Dipropyl ether	43	35	32	5	
Propylaldehyde	0	2	2	4	~45
Ethane and aldehyde	53	59	64	92	~100
n-Butanol					
Conversion (%)	63	44	47	22	7
Composition of products (%)					
Propane	48	53	62	90	81
Butane	5	5	5	1	0
Dibutyl ether	45	40	31	4	0
Butyraldehyde	2	2	2	5	19
Propane and aldehyde	50	55	64	94	100
3-Methylbutanol					
Conversion (%)	58	58	54	22	6
Composition of products (%)					
Isobutane	32	36	52	83	90
Isopentane	8	5	6	2	0
Di-2-methylbutyl ether	59	57	41	10	0
3-Methylbutanal	1	1	1	5	10
Isobutane and aldehyde	33	37	53	88	100
Neopentyl alcohol					
Conversion (%)[a]	45	31	27	11	4
Composition of products (%)					
Propane	1	2	3	4	6
Isobutane	12	19	28	72	28
Neopentane	4	7	8	9	1
Isopentane	35	36	26	1	0
Neopentyl ether	45	30	31	1	0
Trimethylacetaldehyde	43	6	4	12	63
Isobutane and aldehyde	16	25	32	84	91

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

curtailed, while with 5.9% of sodium the formation of ether was completely inhibited. With the neutralization of the acidic sites of the catalyst, the products obtained were those resulting from the dehydrogenation reactions; namely, aldehydes and hydrocarbons derived from the decarbonylation of the aldehydes. With 0.10% of sodium ions, the extent of dehydrogenation was in the range of 32 to 64%, depending on the alcohol used; with 1.04% Na^+ the selectivity to form products of dehydrogenation was increased to 94%.

Effect of Silica and Silica–Alumina

Catalysts composed of nickel deposited on silica containing various concentrations of alumina have been tested for the conversion of alcohols (Table 4). The experiments were made at 190° in the presence of a flow of hydrogen.

Pure silica has practically no effect on the conversion of alcohols. The presence of only 0.02% of alumina imparts a catalytic effect on the silica, and it becomes a dehydrating catalyst. The extent of dehydration of the alcohols increases from 3 to 35% when the concentration of alumina is increased from 0.02 to 1.0%.

Nickel deposited on pure silica exhibits catalytic effect for the formation of ethers from *n*-butanol and 2-methylbutanol. The main reaction is, however, the reductive dehydroxymethylation, amounting from 55 to 75% of the overall conversion, depending on the alcohol used. The introduction of 0.1 to 1.0% of alumina into the silica modifies the properties of the catalyst, and reductive dehydroxylation becomes the major reaction in the case of neopentyl alcohol. The selectivity of the catalyst towards dineopentyl ether formation can be increased by calcining the silica–alumina support at 1000°.

Nickel Supported on Alumina

Two types of aluminas were used as supports: alumina A, which was prepared from aluminum isopropoxide and which

TABLE 4

HYDROGENOLYSIS OF ALCOHOLS IN THE PRESENCE OF SILICA–ALUMINA–NICKEL OF VARIOUS ALUMINA CONCENTRATIONS

(Temperature, 190°; hydrogen flow, 100 ml/min; injection, 10 μl)

Alumina (%)	0	0.02	0.1	1.0	0	0.02	0.1	0.1	1.0[a]	25[b]
Nickel (%)	0	0	0	0	6	6	6	6	6	6
n-Butanol										
Conversion (%)[c]	0			20	69	71	82	56		
Composition of products (%)										
Propane					61	48	46	59		
Butane				100[d]	1	1	2	5		
Dibutyl ether					38	51	52	36		
2-Methylbutanol										
Conversion (%)[c]	0.5	3	14	28	63	69	80	71		
Composition of products (%)										
Propane					5	3	3	6		
Butane					56	48	43	39		
Isopentane		98[e]	100[e]	100[e]	1	3	6	17		
n-Pentane						1	2	7		
Di-2-methylbutyl ether		1			38	44	46	31		
Neopentyl alcohol										
Conversion (%)[c]	0.5	3	13	35	29	34	34	48	32	22
Composition of products (%)										
Propane					17	23	11	10	Trace	Trace
Isobutane					75	57	52	18	31	25
Neopentane					3	2	2	<1	Trace	Trace
Isopentane		100[e]	100[e]	100[e]	1	13	28	62	43	23
Dineopentyl ether					4	5	7	9	24	31
Trimethylacetaldehyde					Trace	Trace	—	—	2	11

[a] Silica containing 1% of Al_2O_3, calcined at 1000°.

[b] Silica containing 25% of Al_2O_3, calcined at 1000°.

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

[d] *n*-Butenes.

[e] Methylbutenes.

was demonstrated to have relatively strong intrinsic acidic sites (*5*), and Harshaw alumina, which contains 0.36% sodium ions and in which the catalytic "acidic" sites were neutralized (*5*).

Aluminas in the absence of nickel do not catalyze the conversion of alcohols under the experimental conditions given in Table 5. In the presence of 6% of nickel deposited on the aluminas, however, the alcohols undergo predominantly a reductive dehydroxylation reaction. The dehydroxylation reaction was accompanied by methyl migration; i.e., *n*-pentane was formed from 2-methylbutanol and neopentyl alcohol produced isopentane. The relatively high yield of neopentane produced from neopentyl alcohol could be attributed to the hydrogenolysis of the unstable 1,1-dimethylcyclopropane. Cyclopropanes have been found in the products of the reaction of neopentyl alcohol over reduced nickel oxide catalyst (*1*). Experiments with 1,1-dimethylcyclopropane in the presence of nickel–alumina catalysts and hydrogen, which are to be reported separately, demonstrated the preferential formation of neopentane over isopentane (*6*).

TABLE 5

REACTION OF ALCOHOLS ON NICKEL ON ALUMINA[a]

(Temperature, 190°; hydrogen flow, 100 ml/min; injection, 10 μl)

	Alumina A 6% nickel	Harshaw alumina nickel
n-Butyl alcohol		
Selectivity (mole %)[b]		
Propane	8	17
Butane	69[c]	50[a]
Dibutyl ether	23.0	33
Butyraldehyde	Traces	Traces
2-Methylbutanol		
Butane	6	10
Isopentane	58	51
n-Pentane	18	12
Di-2-methylbutyl ether	17	26
2-Methylbutanal	<1	1
Neopentyl alcohol		
Isobutane	7	16
Neopentane	20	10
Isopentane	64[c]	46
Dineopentyl ether	8	26
Trimethylacetaldehyde	1	2

[a] Conversion of alcohols is not given because part of the alcohol was chemisorbed on the catalyst.

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

[c] Small amounts of the corresponding olefins are included.

The yield of ethers produced ranged from 8 to 33%, depending on the alcohols and the aluminas used in the reaction.

It was observed that the alcohols and/or their products were strongly adsorbed on the alumina A support. After the injection of 10 μl of the alcohols, the product desorbed slowly at 180°. By increasing the temperature, the trapped product from neopentylalcohol consisted of 32% neopentane, 51% isopentane, and 17% 1,1-dimethylcyclopropane. About 8% of ethylcyclopropane was estimated to be in the product from the desorption of 2-methylbutanol.

Continuous Flow Reactions

The micropulse reactor used in the experiments described above was adapted to the continuous flow reactions. This was accomplished by connecting the inlet of the pulse reactor to a displacement pump and the outlet of the reactor to a magnetic oil-heated sampling valve. The valve was connected to the chromatograph and samples were taken at predetermined intervals.

Table 6 summarizes the results of the effect of temperature, contact time, and ratio of hydrogen to alcohols on the conversion and composition of the products obtained from *n*-butanol and neopentyl alcohol. The duration of each of the experiments was about 1 to 2 hr.

The conversion of *n*-butanol increased from 62% to 86 and to 95% when the temperature was raised from 160° to 170° and 190°. The selectivity of the reaction towards dibutyl ether formation decreased from about 93% to 89 and 68%.

The yield of dibutyl ether was higher when the contact time between the alcohol and the catalyst was shorter. In the experi-

TABLE 6

Continuous Flow Reaction of Alcohols over Nickel–Kieselguhr Catalyst: Effect of Variables[a]

Temperature (°C)	160		170		190	
Hydrogen to alcohol ratio	5	10	5	10	5	5
Alcohol feed rate	4	2	4	4	4	10
	n-Butanol					
Conversion (%)	62	89	86	91	95	75
Products distribution (%)[c]						
Propane	7	8	10	25	28	20
Butane	0	<1	<1	5	4	2
Dibutyl ether	93	91	89	70	68	78
	Neopentyl alcohol					
Conversion (%)	16		41		52	
Products distribution (%)[c]						
Isobutane and neopentane	<1		7		9	
Isopentane	12		17		31	
Dineopentyl ether	87		76		60	

[a] 400 mg of 6% nickel on kieselguhr was used.

[b] Liquid hourly space velocity corresponding to volume of alcohol passed per volume of catalyst per hour.

[c] In all the experiments traces of aldehydes were found.

ment made at 190°, the selectivity for ether formation increased from 68 to 78% when the LHSV was increased from 4 to 10, while the selectivity for propane dropped from about 28 to 20%. These data suggest that part of the propane might have been produced from the hydrogenolysis of the ether. Independent experiments confirmed this hypothesis.

The rate of reaction of neopentyl alcohol was lower than that of *n*-butanol. The selectivity towards ether formation was

TABLE 7

Continuous Flow Reaction of Alcohols over Nickel–Kieselguhr: Effect of Catalyst Life

(Catalyst, 6% nickel on kieselguhr, 400 mg; hydrogen to alcohol ratio, 10; LHSV of alcohol, 4; temperature, 190°; flow type reactor was used)

Time (hr)	2	4	5	7	9	11	15	16
	n-Butanol							
Conversion (%)	91	91	92	92	91	90	89	88
Products distribution (%)[a]								
Propane	25	24	29	26	25	24	25	25
Butane	5	5	7	6	5	5	5	5
Dibutyl ether	70	71	64	68	70	71	70	70
	Neopentyl alcohol							
Conversion (%)	52	53	52	51		51		50
Product distribution (%)[a]								
Isobutane and neopentane	9	10	10	10		10		10
Isopentane	31	32	31	33		33		33
Dineopentyl ether	60	58	59	57		57		57

[a] In all cases traces of aldehyde have been found.

87% at 160° and only 59% at 190°. Isopentane was the main side product of the reaction.

Two continuous flow experiments of 16-hr duration were made (Table 7). The purpose of these experiments was to study the reactions under steady state conditions and to establish the durability of nickel-kieselguhr as a catalyst for the conversion of alcohols to ethers.

The nickel–kieselguhr catalyst showed practically neither deterioration in activity nor a change in selectivity after 16 hr in use at 190°. In the case of *n*-butanol, the conversion was 88–92% and the yield of ether was about 70%. Under similar conditions, neopentyl alcohol reacted to the extent of 51% and the yield of ether was 57–59%.

CONCLUSIONS

In the previous paper of this series, it was concluded that an unsupported reduced nickel oxide catalyst possesses intrinsic acidic sites which are responsible for the formation of ethers and for the reductive dehydroxylation of alcohols (*1*). It was also postulated that the acidic sites were created by the presence of small amounts of unreduced nickel oxides in the bulk or on the surface of the nickel catalyst.

The present study suggests that nickel catalyst "supported" on kieselguhr, silica, silica–alumina, and on alumina may contain additional and/or stronger acidic sites. This is indicated by a higher conversion of the alcohols to ethers and/or to hydrocarbons resulting from the reductive dehydroxylation of the alcohols, a reaction catalyzed by acidic centers. The presence of acidic sites created by depositing nickel on silica has been reported (*7*). It was postulated, on the basis of the infrared spectroscopic study of adsorbed ammonia and hydrogen chloride, that Lewis-type sites formed by the surface Ni^{2+} ions were incorporated in the silica lattice. This postulate is in agreement with the observation that the yield of ethers and of the reductive dehydroxylation drops substantially when a stream of ammonia is passed over nickel–kieselguhr catalyst prior to the reaction (*2*).

That acidic sites are responsible for the formation of ether and for the dehydroxylation reaction is clearly demonstrated in Table 3. Small amounts of sodium incorporated in the nickel–kieselguhr catalyst inhibit these reactions.

The presence of hydrogen is essential for the maintenance of the activity of the catalyst (*8*). The increase of hydrogen pressure from 1 to 50 atm, however, lowers the formation of dineopentyl ether, while the selectivity towards isopentane production increases. The reactivity of neopentyl alcohol drops from 24 to 11% at the higher pressure. This can be explained by the fact that hydrogen and the alcohol compete for the same catalytic sites. The lower selectivity for ether formation is probably due to the fact that some of the adjacent sites required for the adsorption of two molecules of alcohols are occupied by the adsorbed hydrogen molecules.

Kieselguhr seems to be an excellent support or "co-catalyst" for the production of ethers. Silica as such or silica containing 0.01 to 0.1% of alumina is also a satisfactory support for this reaction. In order to compare the effectiveness of the various supports it is imperative that flow-type experiments are made at steady state conditions. Meanwhile, it can be concluded that the nickel–kieselguhr catalyst is the most effective of all the catalysts studied for the conversion of alkanols to ethers. This catalyst has a very long lifetime and, under proper experimental conditions, a 100% selectivity of *n*-butanol to di-*n*-butyl ether can be achieved, with over 50% conversion (*8*). Some other transition metal oxides also show catalytic effects for the conversion of alcohols to ethers (*9*). Kinetic studies presently carried out in our laboratory should furnish a better understanding of this novel catalytic reaction.

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