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A Comparative Study of the Reactions of Alcohols over Nickel–Silica, Silica–Alumina, and Nickel–Silica–Alumina Catalysts in the Presence of Hydrogen

ELIAHU LICHT, YEHOSHUA SCHÄCHTER AND HERMAN PINES[1]

Department of Chemistry, Bar Ilan University, Ramat Gan, Israel

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Nickel–silica, silica–alumina, and nickel–silica–alumina catalysts were compared by investigating the dehydration of alcohols in the temperature range of 100–220°C and in the presence of a flow of hydrogen. Differences in activity were found between silica–alumina and silica–nickel. The main differences were:

a. Silica–alumina, unlike nickel–silica, catalyzes also the decomposition of ether to alcohol and olefin.

b. Silica–alumina is much more active than nickel–silica towards olefin formation.

c. Retardation by water is much more pronounced over silica–nickel.

d. 2-Propanol is more reactive than 1-butanol towards ether formation over silica–alumina, while the opposite is the case over nickel–silica.

e. The addition of 0.14 to 1.0% of alumina to the nickel–silica catalyst seems to create new catalytic acidic sites between the reduced nickel oxide and the silica–alumina. The observed differences can be explained on the basis of the difference in the character of the two types of catalysts: The catalytic activity of silica–alumina is mainly due to its strong acid sites, whereas nickel–silica catalyzes the dehydration of alcohols by the concerted action of both acid and basic sites of moderate and comparable strength.

In previous papers of this series the conversion of alkanols over reduced nickel oxide as such or deposited on silica was described (*1–10*). The experiments were made at 120–190°C in the presence of a flow of hydrogen. With primary alkanols two main reactions were observed: (a) dehydroxymethylation of the alkanols to alkanes and (b) dehydration of the alkanols to the corresponding ethers.

$$H_2 + [CO] + RH \leftarrow RCH_2OH \rightarrow (RCH_2)_2O + H_2O.$$

The dehydroxymethylation reaction was attributed to contact catalytic sites of the metal, while the formation of ethers was ascribed to intrinsic acidic and basic sites of the nonentirely reduced nickel oxide on silica catalyst.

Secondary alcohols under similar conditions underwent dehydrogenation to ketones and dehydration to olefins and ethers. The olefins, however, in the presence of the flow of hydrogen were reduced to alkanes.

It was found that the addition of small amounts of sodium ion to the nickel–silica catalysts neutralizes their intrinsic acidic sites and thus deactivates their dehydrating properties (*1,6*). The purpose of the present study was therefore to determine the effect of an increase in acidic sites of the nickel–silica catalyst on its activity and selectivity as a dehydrating agent for the formation of ethers and olefins. Since pure calcined silica does not have acidic sites it was decided to impart

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[1] The Ipatieff Catalytic Laboratory, Department of Chemistry, Northwestern University, Evanston, IL 60201.

to it acidic sites by incorporating into the silica 0.14–1.0% of alumina and to compare the effect of nickel deposited on this support with the conventional nickel–silica catalyst.

EXPERIMENTAL PART

The experiments were performed in a flow type apparatus described previously (*6*) and the product from the reaction was analyzed by gas chromatography. Silica and silica–alumina were prepared as described before (*3*). The silica–alumina was prepared in three concentrations of alumina: 0.02, 0.14, and 1% weight. Nickel–silica–alumina and nickel–silica were made by precipitating nickel carbonate on the silica–alumina and on the silica, respectively, as described before (*3*). The percentage of nickel was 7% by weight. The carbonate was then decomposed and reduced in a stream of hydrogen at 450°C. Catalysts containing nickel oxide on silica and on silica–alumina amounting to 7% nickel, were prepared in the same manner, but instead of being reduced they were calcined overnight under helium atmosphere at 450°C.

RESULTS

In order to determine the effect of alumina on nickel–silica it was deemed necessary to study the action of silica–alumina per se on the conversion of the alcohols, and to compare the results obtained with those derived from the action of nickel–silica and nickel–silica–alumina.

The results of the reactions over silica–alumina catalysts are summarized in Table 1. Over pure silica no conversion of alcohols was observed. Over silica containing alumina both dehydration of alcohols to ethers and to olefins took place and the results obtained were the same whether the carrier gas was hydrogen or helium. Neither dehydrogenation nor dehydroxymethylation was observed over the silica–alumina catalysts.

Table 2 summarizes the results obtained with silica–nickel and silica–alumina–nickel catalysts. Results with catalysts containing 0.02% alumina were omitted from Tables 1 and 2 because they were within the range of experimental errors obtained with catalysts which do not contain alumina.

There are significant differences between nickel deposited on silica and nickel deposited on silica–alumina. Part of the differences might be due to the catalytic properties of silica–aluminas per se. The latter not only catalyze the dehydration of alcohols to olefins and ethers but also the decomposion of ethers to alcohols and olefins. There are also significant differences between the supported nickel oxides reduced at 450°C and those used without prereduction.

The more significant differences between the various catalysts are as follows:

1. Over silica–alumina catalyst, 2-propanol is more reactive than 1-butanol, and it produces both ether and propene, while 1-butanol affords almost entirely butenes. However, over silica–nickel 1-butanol is more reactive than 2-propanol, and di-*n*-butyl ether is the predominant product of reaction.
2. Ether formation over silica–alumina is almost not retarded by water relative to the extent of its retardation over nickel–silica.
3. Water does not seem to inhibit the conversion of 2-propanol over silica–alumina. At 160°C and with 1% alumina the extent of reaction is 50% both in the presence or absence of water. Over nickel–silica catalysts the inhibition by water becomes less pronounced with the increase of alumina in the catalyst. With 0.14% of alumina the conversion of 2-propanol is 53% of the original, while in the presence of 1.0% of alumina the conversion increases to 75%.
4. The relative reactivity of 2-propanol and 2-pentanol over silica–alumina is the

TABLE 1

REACTIONS OVER SILICA–ALUMINA[a]

Reactants	Temp (°C)	% of alumina	Percentage of each organic reactant appearing as							
			Alcohols		Ethers			Olefin		
					Symmetric					
			I	II	I	II	Mixed	C_3	C_4	C_5
2-Propanol	100	1	98.9	—	0	—	—	1.1	—	—
	115	1	95.5	—	1.6	—	—	2.9	—	—
	130	1	78.5	—	8.3	—	—	12.9	—	—
	160	0.14	77.0	—	9.5	—	—	13.5	—	—
		1	50.4	—	7.2	—	—	42.4	—	—
	175	0.14	68.4	—	10.6	—	—	21.0	—	—
		1	29.5	—	3.9	—	—	66.6	—	—
	190	0.14	56.9	—	12.1	—	—	31.0	—	—
		1	1	—	0	—	—	99	—	—
1-Butanol	160	0.14	99.5	—	0	—	—	—	0.5	—
		1	98.0	—	0.6	—	—	—	1.4	—
	190	0.14	97.8	—	Tr	—	—	—	2.2	—
—		1	90.6	—	1.4	—	—	—	8.0	—
	220	0.14	83.8	—	Tr	—	—	—	16.2	—
		1	28.9	—	0	—	—	—	71.1	—
2-Pentanol	160	1	45.9	—	0.7	—	—	—		53.4
Neopentyl alcohol[b]	160	1	>99.0							<1.0[c]
	190	1	94.8		<0.1					5.2[b]
2-Propanol : H_2O 7 : 1 molar ratio	160	1	50.3	—	6.5	—	—	43.2	—	—
I 2-Propanol II 2-pentanol 1 : 1 molar ratio	160	1	50.7	47.7	6.6	0.6	2.5[d]	40.2	—	49.2
I 2-Propanol	160	1	79.5	98.0	0.5	0	3	18		0.5
II Neopentyl alcohol	175	1	74.0	97.0			2	25		2
I 2-Propanol II 1-butanol 1 : 1 molar ratio	160	1	55.8	88.4	3.3	0.7	9.7[d]	31.2	1.2	—
Di-2-propyl ether	160	1	11	—	40	—	—	49	—	—
Propylene : H_2O 1 : 1 molar ratio[e]	160	1	0.5[f]	—	0	—	—	99.5	—	—

[a] Carrier: H_2 or He, 11.8 ml/min; molar ratio carrier : reactant, 3.1 : 1; catalyst, 400 mg.

[b] The alcohol was mixed with 30% *n*-heptane.

[c] Isopentane.

[d] For each alcohol.

[e] Propylene being the carrier, 23.6 ml/min, water being introduced by the liquid feeder.

[f] 2-Propanol.

TABLE 2

REACTIONS OVER CATALYSTS OF 7% NICKEL SUPPORTED ON SILICA AND ON SILICA–ALUMINA[a]

Reactants	Temp (°C)	% of alumina	State of nickel	Percentage of each reactant appearing as[b]							
						Ethers					
				Alcohols		Symmetric			Alkanes		
				I	II	I	II	Mixed	C_3	C_4	C_5
2-Propanol	160	0	Ni	87.2	—	7.8	—	—	5.0	—	—
		0.14	NiO	98.7	—	0	—	—	1.3	—	—
			Ni	76.5	—	10.5	—	—	13.0	—	—
		1	NiO	95.0	—	0.5	—	—	4.5	—	—
			Ni	68.6	—	8.2	—	—	23.2	—	—
	190	0	Ni	73.7	—	16.8	—	—	9.5	—	—
		0.14	NiO	95.8	—	0.9	—	—	3.3	—	—
			Ni	58.4	—	19.6	—	—	22.0	—	—
		1	NiO	89.9	—	0	—	—	10.1	—	—
			Ni	46.3	—	18.5	—	—	35.2	—	—
1-Butanol	160	0	Ni	84.6	—	15.2	—	—	0.2	0	—
		0.14	NiO	99.9	—	0	—	—	0	0.1	—
			Ni	83.1	—	16.5	—	—	0.2	0.2	—
		1	NiO	99.7	—	0	—	—	0	0.3	—
			Ni	81.6	—	17.7	—	—	0.2	0.5	—
	190	0	Ni	19.3	—	74.0	—	—	6.5	0.2	—
		0.14	NiO	99.7	—	0	—	—	0	0.3	—
			Ni	15.6	—	76.8	—	—	6.7	0.9	—
		1	NiO	98.9	—	0.1	—	—	0	1.0	—
			Ni	6.1	—	84.2	—	—	6.7	3.0	—
2-Pentanol	160	0	Ni	78.6	—	5.9	—	—	—	—	15.5
		1	Ni	56.9	—	7.8	—	—	—	—	35.3
2-Propanol:H_2O 7:1 molar ratio	160	0	Ni	95.6	—	Tr	—	—	4.4	—	—
		0.14	Ni	87.5	—	1.0	—	—	11.5	—	—
		1	Ni	76.5	—	2.0	—	—	21.5	—	—
I 2-Propanol II 2-pentanol 1:1 molar	160	0	Ni	94.8	81.9	1.0	3.6	0.7[c]	3.5	—	13.8
		1	Ni	84.9	64.1	2.0	4.0	2.1[c]	11.0	—	29.8
I 2-Propanol II 1-butanol 1:1 molar	160	0	Ni	93.3	82.3	0.2	15.7	2.1[d] 1.8[e]	4.6[d]	0	—
		0.14	Ni	86.1	81.3	0.4	16.2	2.5[d] 2.2[e]	11.2[d]	0.1	—
Di-2-propyl ether	190	0	Ni	0	—	100.0	—	—	0	—	—
		1	Ni	9	—	71	—	—	20	—	—

[a] Carrier: H_2, 11.8 ml/min; molar ratio H_2:each reactant = 3.1:1; temperature of reduction or calcination (*in situ*), 450°C.

[b] For the secondary alcohols—on ketone-free basis.

[c] For each alcohol.

[d] Relative to 2-propanol.

[e] Relative to 1-butanol.

same whether they are reacted singly or in mixture, while over silica–nickel their order of reactivity is inverted.

5. In the reaction of mixture of 2-propanol and 1-butanol over silica–alumina, the formation of mixed ether is preferred. This is not the case over silica–nickel.

6. Hydration of olefins occur over silica–alumina, as it is shown in Table 1, but its extent is negligible.

7. The nickel–silica–alumina catalysts are somewhat more active than nickel–silica with respect to ether formation, and much more active towards olefin formation. The olefins appear in the products as alkanes because as a result of the flow of hydrogen they undergo instantaneous hydrogenation. This high activity towards olefin formation is, however, much lower than that in the presence of silica–alumina. In the cases of 1-butanol and 2-pentanol the yield of ether over nickel–silica–alumina is somewhat higher than the sum of its yields over the corresponding silica–alumina and nickel–silica catalysts.

8. The results with nonreduced nickel oxide show that the presence of nickel oxide reduces drastically the activity of silica–alumina.

DISCUSSION

The differences described in the previous section can best be understood on the basis that catalytic activity of silica–alumina is due mainly to relatively strong acidic sites, while the activity of nickel–silica is due to a concerted action of both acidic and basic sites of moderate and comparable strength. Pure silica has no catalytic sites for the dehydration of alkanols (*3*) or for the double bond migration of *n*-alkenes (*11*). The introduction, however, of 0.14% of alumina to the silica is sufficient to impart to the latter catalytic activity which is associated with acidic catalytic sites. This is in agreement with results reported previously (*12,13*).

TABLE 3
REACTIONS OF 2-PROPANOL OVER SILICA–ALUMINA[a] AT 160°C AT VARIOUS RATES OF FLOW[b]

Rate of flow ($ml\ H_2/min$)	Percentage of alcohol appearing as		Total conversion	Olefin/ether ratio
	Propane	Ether		
11.8	42.5	7.2	49.7	5.9
23.6	27.0	6.9	33.9	3.9
47.0	13.0	4.8	17.8	2.7
94.0	6.7	2.6	9.3	2.6

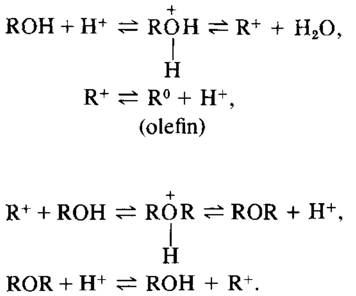
[a] 1% alumina.

[b] Hydrogen to alcohol molar ratio = 3.1:1.

The high propene:ether ratio obtained over silica–alumina compared with that over silica–nickel, can be ascribed to a cationic mechanism of elimination. This would also explain the relatively ready decomposition of the di-2-propyl ether over this catalyst and the reluctance of a primary alcohol, *n*-butanol, to undergo any appreciable reaction under the same experimental conditions. In contrast to the above, the dehydration of alcohols over nickel–silica catalysts proceed via a concerted *trans* elimination reaction (*4,7,10*), and for that reason the rate of reaction of *n*-butanol over these catalysts is much greater than that over silica–alumina. This difference in the two mechanisms would also explain the relative inactivity of the nickel–silica catalyst towards the decomposition of ethers.

As a consequence of the ready decomposition of di-2-propyl ether, the ratio of propene to ether formed from 2-propanol over silica–alumina catalyst depends on the contact time of reaction, Table 3. In the presence of nickel–silica catalyst, however, the ratio of ether to hydrocarbon formed is constant regardless of the conversion (*9*).

The mechanism of dehydration over silica–alumina catalysts can be presented by a cationic mechanism as follows:



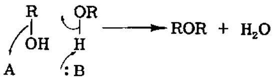
$$\mathrm{ROH} + \mathrm{H}^+ \rightleftharpoons \mathrm{R}\overset{+}{\underset{\mathrm{H}}{\mathrm{O}}}\mathrm{H} \rightleftharpoons \mathrm{R}^+ + \mathrm{H_2O},$$

$$\mathrm{R}^+ \rightleftharpoons \underset{\text{(olefin)}}{\mathrm{R}^0 + \mathrm{H}^+},$$

$$\mathrm{R}^+ + \mathrm{ROH} \rightleftharpoons \mathrm{R}\overset{+}{\underset{\mathrm{H}}{\mathrm{O}}}\mathrm{R} \rightleftharpoons \mathrm{ROR} + \mathrm{H}^+,$$

$$\mathrm{ROR} + \mathrm{H}^+ \rightleftharpoons \mathrm{ROH} + \mathrm{R}^+.$$

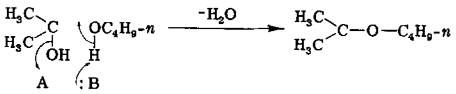
There are ample data to show from the previous work of these series that over nickel–silica catalysts the dehydration reaction proceeds via a concerted mechanism, in which both the intrinsic acidic and basic sites of the catalyst participate and as a result of it a substantial amount of the product formed consisted of ether:



The retarding effect of water over silica–nickel catalyst has been ascribed (*10*) to the competition between the proton of water and of the species of alcohol, which contain a partial positive charge on the carbon atom, $\mathrm{ROH}^{\delta+}$, for another molecule of alcohol carrying a partial negative charge on the oxygen atom (RO^- if complete dissociation would take place). Over silica–alumina, however, the positively charged alcohol species is much more abundant and the charge much stronger, so that it can overcome the competing influence of water.

The different behavior of 2-propanol by itself and in mixture with 2-pentanol when reacted over nickel–silica can be ascribed to competition for the acid sites of the catalyst, where the 2-pentanol has the upper hand due to its higher basicity. With silica–alumina which has stronger and more abundant acidic sites, the rate determining step is no longer the formation of the positively charged alcohol species so that the position of the two alcohols is similar to that exhibited by them when they react separately, where 2-propanol has an advantage over 2-pentanol.

It is of interest to note that 1-butanol as such does not undergo any appreciable reaction at 160°C when passed over a silica catalyst containing 1% alumina. However, when an equimolar solution of the above alcohol with 2-propanol is passed over the same catalyst, about 11% of the 1-butanol undergoes reaction to form primarily a mixed ether, 2-propyl 1-*n*-butyl ether, and a small amount of *n*-butane. The above results demonstrate that the $\mathrm{SiO_2}$–$\mathrm{Al_2O_3}$ catalyst does not contain strong enough acidic sites to polarize *n*-butanol to the corresponding *n*-butyl cation, which could react with another molecule of butanol to form di-*n*-butyl ether. However, 2-propanol can be adsorbed on the acidic sites of the catalyst to form isopropyl cation, which can then react with the more acidic primary alcohol to produce the mixed ether.



It is also worth noticing that the yield of di-2-propyl ether formed from pure 2-propanol is over twice as great as that produced from a solution of 2-propanol and 1-butanol. This can be interpreted by the fact that the primary alcohol is the more acidic of the two alcohols and therefore it is more readily adsorbed on the basic sites of the catalyst. The importance of both acidic and basic sites in the dehydration of alcohols over aluminas have been studied and reviewed (*13*), however, no such study has been undertaken on silica–alumina catalysts.

Similar results were obtained when a mixture of 2-propanol and neopentyl alcohol was passed over the same $\mathrm{SiO_2Al_2O_3}$ catalyst, Table 1. 2-Propanol alone yielded at 160°C 15% of ether and 85% propene with a conversion of 50%.

At 190°C the conversion was complete with a quantitative yield of the olefin. With neopentyl alcohol the conversion at 160°C was about 0.5% and at 190°C it was 5%. However, when an equimolar mixture of the alcohols was passed at 160°C, 3% of neopentyl alcohol reacted to afford a 75% yield of isopropyl neopentyl ether.

In the presence, however, of nickel–silica catalyst at 160°C, a mixture of 2-propanol and neopentyl alcohol yielded in addition to the mixed ether also 51% of dineopentyl ether, based on the converted alcohol (*10*). These results were interpreted as occurring via a concerted mechanism in which both the acidic and basic sites of the catalyst participate (*10*).

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