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Reactions of Primary and Secondary Alkanols over Platinum–, Iridium–, and Rhodium–Silica (Cab-O-Sil) Catalysts in the Presence of Hydrogen: Variables Affecting Ether Formation

ELIAHU LICHT,* YEHOSHUA SCHÄCHTER,* AND HERMAN PINES†

* *Department of Chemistry, Bar Ilan University, Ramat Gan, Israel, and* † *The Ipatieff Catalytic Laboratory, Department of Chemistry, Northwestern University, Evanston, Illinois 60201*

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Catalysts of platinum, iridium, and rhodium were prepared by precipitation of the oxide-hydrates on the Cab-O-Sil support and reduction with hydrogen. Gaseous mixtures of hydrogen with various primary and secondary aliphatic alcohols (alkanols) were passed over the catalysts at temperatures between 130 and 190°C in a continuous-flow system. All the catalysts show strong activity in dehydration of alcohols to ethers and olefins. The latter undergo hydrogenation under the reaction conditions. Primary alcohols are also dehydroxymethylated. Di-*sec*-ethers are decomposed and the corresponding hydrocarbons are obtained. Dehydroxymethylation is particularly pronounced with platinum. The dehydration reactions are attributed to a concerted mechanism in which intrinsic acidic and basic sites participate.

The use of reduced nickel oxide as such or on supports as catalysts for the conversion of primary and secondary aliphatic alcohols to the corresponding ethers in the presence of a flow of hydrogen was described (*1*). The use of a variety of nonsupported reduced transition metal oxides, such as Fe, Co, Ru, Rh, Ir, Pd, and Pt, as possible catalysts for the conversion of *n*-butanol and neopentyl alcohol to the corresponding ethers has also been reported (*2*). Of the reduced metal oxides studied Ir and Pd show high selectivity, 67 to 78%, toward ether formation. Ru and Rh at 190°C gave low conversion of alcohols with a selectivity toward ether ranging from 30 to 37%, the main reaction being reductive dehydroxymethylation of the alcohols. Reduced platinum oxide under similar conditions acted as a dehydrogenating catalyst, while reduced iron oxide converted *n*-butanol and neopentyl alcohol to *n*-butane and neopentane, respectively.

The aim of the present study was to determine the effect of supported and reduced transition metal oxide catalysts on the conversion of alkanols. The experiments were made in a continuous-flow-type system instead of pulse reactor as was done with the nonsupported catalysts (*2*).

The support used was a catalytically inert commercial silica, Cab-O-Sil, which was found to be an effective support for nickel (*3–5*). The present report deals with results obtained with reduced oxides of Rh, Ir, and Pt deposited on Cab-O-Sil. The study with Pd–SiO_2 was reported in a preceding publication (*6*).

PREPARATION OF CATALYSTS

a. Platinum on Cab-O-Sil. The concentration of platinum on the support was 20% by weight in order to obtain the same atomic percentages as with 7% nickel, which gave a catalyst with good activity for the conversion of alcohols to ethers (*4*).

The preparation consisted of dissolving chloroplatinic acid in water which contained dispersed Cab-O-Sil and precipitating the platinum onto the support by boiling the mixture with tetramethylammonium carbonate $[(CH_3)_4N]_2CO_3$ for 36 hr. The solid was filtered and finally reduced in a stream of hydrogen. The activity of the catalyst reaches its final level after passing hydrogen over it at 250–300°C for several

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days. This long time of activation may be due to the difficulty of removing the final traces of the residual chloride from the catalyst. The catalyst thereafter remained stable for any period of time it was used, several days up to a few weeks, without showing any decline in activity.

The platinum content of the original solution and of the mother liquor was determined by adding an excess of $SnCl_2$ to the sample containing 0.3 *N* HCl, reading the absorbance at 450 nm, and comparing it with a standard solution. The latter was prepared by dissolving a known amount of platinum wire in aqua regia (*7*).

b. Rhodium-Cab-O-Sil. Rhodium nitrate was dissolved in water and the solution was mixed with Cab-O-Sil. An aqueous solution of ammonium carbonate was added to the mixture while stirring. The mixture was boiled with continuous stirring for about 4 hr, until the rhodium was completely precipitated. The solution was filtered, the solid was washed with water, dried, and reduction with hydrogen at 300°C for as little as 10 min was sufficient. The catalyst contained 10% by weight rhodium.

c. Iridium-Cab-O-Sil. The catalyst was prepared from ammonium hexachloroiridate(III), $(NH_4)_3IrCl_6 \cdot xH_2O$ which was converted to hexachloroiridic acid by oxidation under reflux with aqua regia for 16 hr. The acid was separated by evaporation of the solution to dryness at 40°C under reduced pressure. The hexachloroiridic acid was dissolved in water, the solution was brought to a boil, and Cab-O-Sil was added, an equivalent amount of aqueous potassium hydroxide was introduced, and the mixture was refluxed for several hours. The iridium oxide deposited on Cab-O-Sil was filtered, washed with water and then with ethanol. The percentage of iridium was determined spectrometrically owing to the intense brown color of the hexachloroiridate anion.

This was done by treating a sample of the catalyst with aqua regia to dissolve the iridium metal. A small excess of ammonia was added to the solution, forming ammonium hexachloroiridate. This was determined colorimetrically against a standard.

The iridium oxide on Cab-O-Sil was reduced at 300°C for 2 hr to a constant activity with a flow of hydrogen. The catalyst contained 18% by weight iridium and less than 10 ppm potassium ions.

EXPERIMENTAL CONDITIONS AND RESULTS

The experiments were carried out in a continuous-flow microreactor attached to a gas chromatograph (*3, 8*). The reactor tube was charged with 200 mg of a 100- to 200-mesh size catalyst. "Standard conditions," unless otherwise indicated, consisted of passage of alcohol and 11.8 ml of hydrogen per minute with a molar ratio of hydrogen to alcohol equal to 3.1 to 1.0.

The experimental results obtained with Pt–, Ir–, and Rh–silica as the catalysts, and 2-propanol, 2-butanol, and 2-pentanol as the secondary alcohols, are summarized in Table 1. For purposes of comparison, the results with Pd–silica are also given (*6*).

Conversion of alcohols used in the reaction increases with temperature and with the length of the alkyl groups of the respective alcohols. Selectivity toward ether formation depends on the temperature, the catalysts, and the alcohols used in the reaction. In the presence of Ir–Cab-O-Sil catalyst the selectivity is less dependent on the alcohols used than in the presence of the other catalysts studied. The respective selectivities at 160°C for 2-propanol, 2-butanol, and 2-pentanol are 54.8, 44.1, and 39.5%. In the presence, however, of Pt–Cab-O-Sil under similar conditions the selectivities are 69.0, 31.4, and 21.1%, and in the presence of Rh–Cab-O-Sil they are 47, 40, and 8%. The greater selectivity of ethers formed using Ir–Cab-O-Sil as catalyst could be attributed to their greater stability toward hydrogenolysis in the presence of this catalyst. Only in the presence of Ir–SiO_2 in the temperature range between 160 and 190°C the selectivity of

TABLE 1

Reactions of *sec*-Alkanols in the Presence of Hydrogen over Silica-Supported Catalysts

Catalyst[a]	Conversion (%)		Mole% of alcohol converted appearing as			
	160°C	190°C	Ether		C_nH_{2n+2}[b]	
			160°C	190°C	160°C	190°C
			2-Propanol			
Pd–SiO$_2$	55	85	52	3.5	48	96.5
Pt–SiO$_2$	58	88	69	20.7	31	79.3
Ir–SiO$_2$	31	72	54.8	47.2	45.2	52.8
Rh–SiO$_2$	53	100	47	0	53	100
			2-Butanol			
Pd–SiO$_2$	58	88	34.5	20.7	65.5	79.3
Pt–SiO$_2$	70	81	31.4	3.7	68.6	96.3
Ir–SiO$_2$	34	—	44.1	—	55.9	
Rh–SiO$_2$	58	—		—	60	
			2-Pentanol			
Pd–SiO$_2$	62		19.4		80.6	
Pt–SiO$_2$	71	84	21.1	1.2	78.9	98.8
Ir–SiO$_2$	38		39.5		60.5	
Rh–SiO$_2$	65		8		92	

[a] Composition: 10% by wt Pd, 20% Pt, 18% Ir, and 10% Rh supported on Cab-O-Sil.

[b] From: 2-propanol, propane; 2-butanol, butane; 2-pentanol, pentane.

2-propanol toward diisopropyl ether drops moderately, from 54.8 to 47.2%, while the conversion of 2-propanol increases from 31 to 72%. The results indicate that the stability of the ether is both catalyst and temperature dependent.

In determining the selectivity of ether formation, it was taken into account that 2 moles equivalent of alcohol was required for 1 mole equivalent of ether. The yield of ethers formed has been studied as a function of temperature and structure and conversion of the alcohols (Table 2). The experiments were made under standard conditions using a molar ratio of hydrogen to alcohol equal to 3.1 to 1.0. The catalyst was Rh–SiO$_2$. At 130°C the conversion of alcohols increased with the length of the alkyl group in 2-alkanols. With 2-propanol the conversion was 17%, with 2-butanol, 25%, and with 2-pentanol, 46%. The selectivity of the alkanols toward ether formation dropped, however, with the increase in the alkyl group of the alcohols; it was 88% in the case of 2-propanol and 30% in the case of 2-pentanol. At 115°C the yield of ether increases to 68% while the conversion of 2-pentanol drops to 25%.

The presence of hydrogen in the reaction is required. When helium was substituted for hydrogen both the conversion of 2-propanol and the selectivity toward ether decreased. At 145°C the conversion diminished from 38 to 13%, and the selectivity toward ether dropped from 71 to 62%.

Table 3 summarizes the results obtained with 2-propanol as a function of contact time, which was accomplished by changing the flow of hydrogen over Rh–Cab-O-Sil at various temperatures. The results obtained demonstrate that with increasing contact time the conversion of 2-propanol increases and that the selectivity toward ether formation decreases while the yield of propane formed increases. It can thus be concluded that at least part of the propane produced is derived from hydrogenolysis of the ether and not directly from the alcohol.

TABLE 2

Reaction of 2-Alkanols over Rh-SiO_2:[a] Effect of Temperature on Composition of Products

Alkanol	Temperature (°C)	Conversion (%)	Mole% of Alkanol converted to			
			Ether	Propane	Butane	Pentane
2-Propanol	190	~100	0	100		
	160	53	47	53		
	145	38	71	29		
	130	17	88	12		
	145[b]	13	62	38		
2-Butanol	160	58	40		60	
	145	40	68		32	
	130	25	80		20	
2-Pentanol	160	65	8			92
	145	49	19			81
	130	46	30			70
	115	25	68			32

[a] The catalyst was reduced overnight at 300°C. See also footnote *a* in Table 1.

[b] Helium instead of hydrogen was used in the reaction.

Primary Alcohols

n-Butanol and neopentyl alcohol were passed over Pt–Cab-O-Sil and Ir–Cab-O-Sil catalysts and the results were compared with those obtained from Pd–Cab-O-Sil catalyst (*6*).

Yields of 94.7 and 83.3% of di-*n*-butyl ether were obtained with a conversion of 13.2 and 60% when *n*-butanol was passed over Ir–SiO_2 catalyst in the presence of hydrogen at 160 and 190°C, respectively (Table 4). Pd–Cab-O-Sil catalyst likewise gave high yields of ether. Pt–Cab-O-Sil catalyst under similar reaction conditions produced 20 to 28% ether; the remaining product was composed mainly of propane, a product of the reductive dehydroxymethylation of *n*-butanol.

Neopentyl alcohol, being sterically hindered, is more resistant to conversion. The main product of reaction at 160°C in the presence of Pt–SiO_2 was isobutane while Pd– and Ir–Cab-O-Sil catalysts produced dineopentyl ether, in selectivities of 73.4 and 57.1%, respectively. The remaining

TABLE 3

Effect of Contact Time upon the Conversion of 2-Propanol in the Presence of Rh–SiO_2[a]

Rate of hydrogen[b] (ml/min)	Temperature (°C)	Conversion (%)	Percentage alcohol converted to	
			Ether	Propane
59	190	75	11	89
24	190	96	0	100
24	160	21	67	33
12	160	41	15	85
12	130	15	53	47

[a] Catalyst reduced at 300°C for 10 min.

[b] Hydrogen to 2-propanol ratio 3/1.

TABLE 4

Reactions of *n*-Alkanols in the Presence of Hydrogen over Silica-Supported Catalysts

Catalyst[a]	Conversion (%)		Mole% of alcohol converted to					
			Ether		$C_{n-1}H_{2n}$		C_nH_{2n+2}	
	160°C	190°C	160°C	190°C	160°C	190°C	160°C	190°C
			n-Butanol					
					(Propane)		(*n*-Butane)	
Pd–SiO_2	14.2	25.8	91.9	85.7	2.1	10.8	6.0	3.5
Pt–SiO_2	11	30	20	27.6	70.0	62	10	10.4
Ir–SiO_2	13.2	60	94.7	83.3	1.5	10	3.8	6.7
			Neopentyl alcohol					
					(Isobutane)		(Isopentane)	
Pd–SiO_2	6.7	19.9	73.4	33.2	0	0	26.6	66.8
Pt–SiO_2	6	23	17	8.7	50	30.4	33	60.5
Ir–SiO_2	7	31	57.1	35.5	14.3	12.9	28.6	49.4[b]

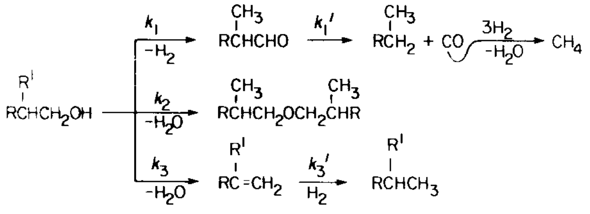
[a] Table 1, footnote *a*.

[b] 3.2% neopentane was also produced.

product in the presence of Pd was isopentane, while in the presence of Ir both isopentane, 28.6%, and isobutane, 14.3%, also were formed. Isopentane must have resulted from the dehydration of neopentyl alcohol, while isobutane was produced by dehydroxymethylation of the alcohol.

DISCUSSION OF RESULTS

Primary and secondary alcohols were passed over reduced transition metal oxide catalysts deposited on catalytically inactive silica (Cab-O-Sil) in the presence of a stream of hydrogen. Primary alcohols undergo two types of reactions: dehydrogenation, leading ultimately to dehydroxymethylation; and a dehydration reaction, which results in either inter- or intramolecular loss of a molecule of water. The rate at which each of these reactions occurs determines the final composition of the product.

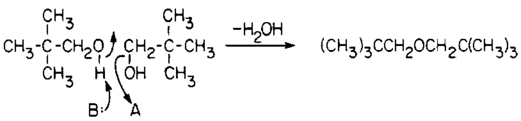


(R = CH_3, C_2H_5; R' = H, CH_3)

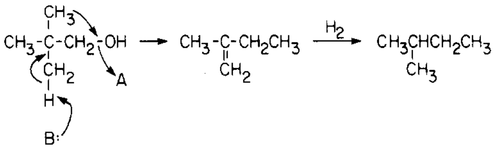
Using *n*-butanol as the alcohol and Pd–SiO_2 or Ir–SiO_2 as the catalyst, $k_2' \gg k_1 \sim k_3$. In the presence, however, of Pt–SiO_2 the relative rates of reactions are $k_1 \gg k_2 > k_3$. The relative rate of dehydrogenation (dehydroxymethylation) over Pt containing catalyst is much greater than that of the competitive reactions, while in the presence of Pd and Ir the rate of formation of ether is the predominant reaction.

Neopentyl alcohol acts about the same way as *n*-butanol, although the rate of conversion is smaller owing to steric effects. At 160°C the rate of reaction k_2 in the case of Pd and Ir is faster than that of k_3, and much faster than k_1. However, at 190°C intramolecular dehydration k_3 is the preferred reaction, even in the case of Pt–SiO$_2$ catalyst.

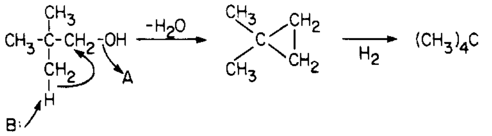
The production of ethers from primary alcohols, e.g., neopentyl alcohol, can best be explained by a cooperative action of intrinsic acidic and basic sites of the catalysts in the dehydration of the alcohol:



At higher temperatures, 190 instead of 160°C, the intramolecular dehydration leading to the eventual formation of isopentane is the preferred reaction and it can be explained by a similar cooperative mechanism:



The small amount of neopentane formed in the reaction of neopentyl alcohol over Ir–SiO$_2$ can be explained by an intermediate formation of 1,1-dimethylcyclopropane, which on hydrogenolysis affords neopentane, as has been observed with all the transition metal catalysts (*10*):



The formation of 1,1-dimethylcyclopropane from neopentyl alcohol over alumina has been reported (*11*).

Secondary alkanols produce ethers when passed over transition metals deposited on silica. At 160°C the yield of diisopropyl ether from 2-propanol ranges from 47 to 69%, with the highest yield occurring in the presence of Pt–SiO$_2$ catalyst. At 190°C the generation of alkanes is a competing reaction. Tables 2 and 3 give ample evidence that a substantial amount of the alkanes must have been produced from the hydrogenolysis of secondary dialkyl ethers which unlike di-*n*-alkyl ethers are susceptible to attack by hydrogen.

The increase in the conversion of 2-alkanols with the length of the alkyl group can be attributed to the polarity of the alcohols (*12*) and the polarity of the catalytic sites.

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