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AN ADSORBED PHASE SUBSTITUTION-ELIMINATION MECHANISM FOR CATALYTIC DEHYDRATION OF ALCOHOLS TO ETHERS AND TO OLEFINS OVER ALUMINA

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Mixtures of various aliphatic and alicyclic alcohols with phenol were submitted to catalytic dehydration over alumina in the temperature range of 160 to 300° in a flow system. The products were analysed by gas chromatography. Typical results of dehydration of methanol and t-butanol are listed in TABLES I and II, respectively. Similar results were obtained with other alcohols also.

TABLE I
Dehydration of Methanol

Temp	HLSV[a]	Reactants (moles)		Products			
		Methanol	Phenol	Dimethyl ether		Anisole	
				Moles	% Based on methanol	Moles	% Based on phenol
285	1	0.39	0.089	0.008	4	0.036	41
285	1	0.47	nil[b]	0.19	80	——	—

a. Hourly liquid space velocity, ie., volume of liquid per hour per unit volume of catalyst.

b. A neutral diluent, cyclohexane, was used to keep the number of moles passed per hour constant.

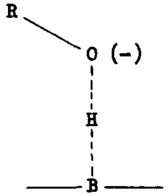
TABLE II

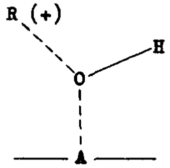
Dehydration of t-Butanol

Temp	HLSV[a]	Reactants (moles)		Product (Isobutylene)	
		t-Butanol	Phenol	Moles	% Based on t-Butanol
160	1	0.39	0.03	0.088	23
160	1	0.38	nil[b]	0.033	9

a & b. See footnots to TABLE I

It was found that dimethyl ether formation was suppressed and became negligible even under conditions where there is still appreciable concentration of alcohol molecules on the surface of the catalyst. (This fact, namely, that the phenol has not completely excluded the alcohol molecules from the surface of the catalyst, can be seen from the enhanced formation of olefins from higher alcohols, eg. t-butanol, in the presence of phenol at similar partial pressures of alcohol. Preliminary studies to understand the relative coverage of the surface by methanol and phenol also lead to the same conclusion). Under these conditions, dialkyl ether is not formed, but instead, phenyl alkyl ether is formed. These results rule out the possibility that ether is formed by the interaction of an alcohol molecule from the gas phase on an adsorbed alcohol molecule because, if this were the case, when phenol and methanol molecules from the gas phase are competing for adsorbed methanol molecules, dimethyl ether formation would have been easier than anisole formation due to the greater nucleophilicity of methanol compared to phenol. The possibility that anisole is formed by the interaction of an alcohol molecule from the gas phase with an adsorbed phenol molecule may be ruled out because this is equivalent to a nucleophilic attack by methanol on the aromatic ring which is unlikely. Thus it appears that catalytic ether formation takes place by the interaction of two types of adsorbed alcohol molecules. In line with the recent trend in the literature[1] to view alumina as composed of both nucleophilic and electrophilic sites on the surface, it is reasonable to assume that the adsorbed alcohol molecules exist as adsorbed carboniumions formed as a result of the interaction of the oxygen of the hydroxy group with surface nucleophile (acidic site) and adsorbed alkoxides formed by the interaction of the hydrogen of the hydroxy group with surface nucleophile (basic site). The two types of adsorbed species may be represented as shown below where B and A represent nucleophilic and electrophilic sites, respectively, on the surface.





A nucleophilic attack of the alkoxide type species on the positively polarised carbon leads to ether (cf. S_N2 reactions in homogeneous systems). Alternately, abstraction of a β -proton from the carbonium-ion by the alkoxide (or by a basic site on the surface as is currently considered) leads to olefin. Thus the catalyst, here, induces the necessary polarity in the reactant molecules in addition to fixing them in the proper orientation. The adsorbed phase is similar to a polar medium where both nucleophilic substitution and elimination are taking place at the same time and competing with each other.

When a mixture of phenol and an alcohol, say methanol, is passed over the catalyst, the phenol molecules preferentially get adsorbed on the nucleophilic sites and alcohol molecules on the electrophilic sites. Concentration of adsorbed alkoxide species under these conditions being low and concentration of phenoxide high, dialkyl ether formation is negligible, only phenyl alkyl ether is formed. Since the presence of phenol does not affect the concentration of adsorbed carboniumion-type species, olefin formation is not adversely affected. In fact, the presence of adsorbed phenoxide on the surface, in some manner facilitates the loss of proton from the carbonium ion leading to olefin as shown by the positive catalytic effect of phenol on olefin formation (see TABLE II).

Details of the mechanism including the stereochemistry of catalytic ether formation are at present being investigated.

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References

1. J. Herling and Herman Pines, Chem. and Ind., 1963 ,984 and references sited there.
See also, H. Pines and J. Manassen, Preprints of the Proceedings of the Third International Congress on Catalysis, Amsterdam, 1964, I, 53.