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Catalytic Conversion of Alcohols

XIV. Alkene Products from the Conversion of 3-Methyl-3-pentanol

We found (*1*) that the alkene distribution from the conversion of a number of alcohols with tungsten oxide closely resembled those several workers had reported for alumina (*2–4*). Included in this group of alcohols was 3-methyl-3-pentanol; there appeared to be excellent agreement between the alkene distribution we obtained with tungsten oxide catalysts (*1*) and that obtained by Knözinger *et al.* (*5*) with alumina. Unfortunately, further work with a number of catalysts caused us to realize that we had made an incorrect assignment for the *cis*- and the *trans*-3-methyl-2-pentene in the work with our tungsten (*1*) and yttrium (*6*) oxide catalysts. However, the more complete work emphasizes that alumina may be an exceptional catalyst for the conversion of this alcohol rather than a representative one.

The experimental procedures used for 3-methyl-3-pentene are the same as described in Ref. (*1*). The catalysts were prepared by air calcination of the metal "hydroxide" obtained by adding ammonium hydroxide to an aqueous solution of the metal (usually the nitrate). The alkene distribution was determined by gc using an OV-1 or an UC-W column at room temperature. *Trans*-3-methyl-2-pentene (Chem. Samp. Co.) was added to a portion of the liquid products from several of the catalysts, including aluminum, gallium, and tungsten oxides, to confirm the alkene identifications reported in this manuscript. Conversions were usually less than 20%; with a few oxides the flow was varied to show that the distributions did not change up to 20–40% conversion.

Our results in Table 1 for alumina agree with those reported by Knözinger and coworkers (*5*). The alkene distribution obtained with the gallia catalyst is very similar to the one obtained with alumina. However, the third member of Group IIIA, india, differs from alumina and gallia since it selectively produces the 1-alkene isomer.

The correct alkene distribution with tungsten oxide is quite different from the one obtained with alumina and is close to the equilibrium composition calculated from data in Ref. (*7*). As shown in Fig. 1, the alkene distribution obtained with the tungsten oxide catalyst is similar to those we obtained with 10 other metal oxide catalysts and all are near the equilibrium concentration over the temperature range we used. In fact, a plot comparing the *cis*-3-methyl-2-pentene/*trans*-3-methyl-2-pentene ratio we obtained experimentally to the one calculated from the data in Ref. (*7*) shows that these 11 metal oxide catalysts produce an equilibrium composition of the *cis* and *trans* isomers. However, the data in Fig. 1 shows that the amount of 2-ethyl-1-butene we obtain is approximately twice as great as the equilibrium composition calculated from Ref. (*7*) data.

In our earlier work with 2-methyl-2-butanol, a tertiary alcohol that is very similar to 3-methyl-3-pentanol, the amount of 2-methyl-1-butene formed did not depend on the catalyst but did increase with increasing reaction temperature (*8*). In general, the amount of the 1-alkene formed from 2-methyl-2-butanol in the temperature range 170 to 260°C was 40–55%; this is about twice the calculated equilibrium concentra-

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TABLE 1

Alkene Distribution Obtained from the Dehydration of 3-Methyl-3-pentanol with Metal Oxide Catalysts

	Temperature (°C)	Octene (%)			Reference
		1-	cis-2-	trans-2	
Al_2O_3	169	20	56	24	(*5*)
Al_2O_3	140	20	53	27	This work
	220	18	52	30	
	233	19	54	28	
Ga_2O_3	170	17	50	33	This work
	184	17	52	31	
	219	19	47	35	
	255	18	47	35	
In_2O_3	220	49	20	31	This work
WO_3	180	19	33	48	(*1*)
	214	20	31	49	
Y_2O_3	243	21	31	48	(*6*)

tion of about 23–29% for this temperature range. Ewell and Hardy (*9*) obtained an equilibrium composition of 23.2% 2-methyl-1-butene for isomerization of the alkene over alumina at 251°C; this is only slightly lower than the value of 28% calculated from data in Ref. (*7*).

The higher than equilibrium composition of the 1-alkene isomer from the dehydration of 2-methyl-2-butanol with many of the same catalysts as used in the present study with 3-methyl-3-pentanol should eliminate a subsequent isomerization of the gas-phase primary products. This would suggest that the greater than equilibrium amount of 2-ethyl-1-butene from 3-methyl-3-pentanol we obtained is valid. The results suggest that alumina, gallia, and india have a catalytic site that exerts a greater steric effect on the transition state to determine the alkene distribution than do the other oxides or that these three oxides allow desorption from the catalytic site before isomerization can occur as it apparently does with the other oxides.

It is clear that all alcohols will not show a similar selectivity trend within a series of metal oxide catalysts. The alkene selectivity with 2-methyl-2-butanol appears to be

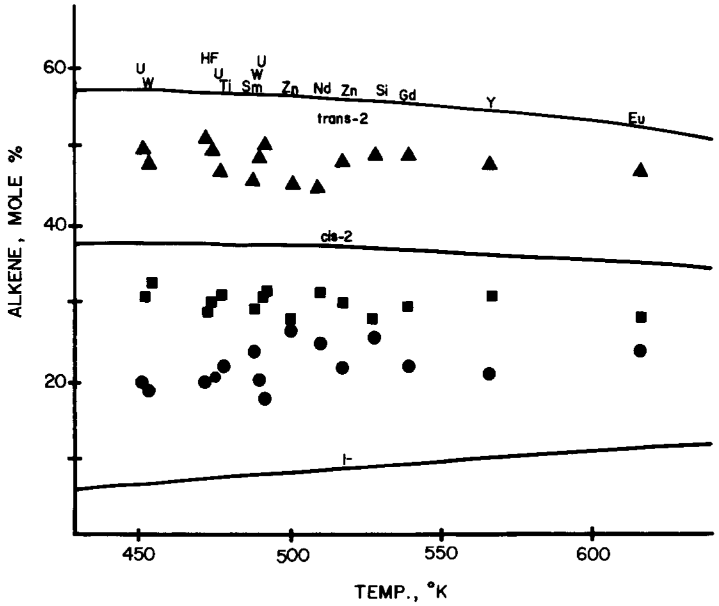

FIG. 1. Alkene distribution from the conversion of 3-methyl-3-pentanol with metal oxide catalysts. ▲, *trans*-3-Methyl-2-butene; ■, *cis*-3-methyl-2-butene; ●, 2-ethyl-1-butene; solid lines are the equilibrium values for these three isomers calculated from data in Ref. (*7*). The oxide catalyst used for each temperature is indicated by the chemical symbol for the metal at the top of the graph; i.e., at 450°K the two sets of alkene distributions were obtained using uranium and tungsten oxide catalysts.

nearly independent of the catalytic site but does not produce an equilibrium alkene composition. With 2-octanol the selectivity varies widely: a few oxides including alumina (*4*), tungstia (*1*), and gallia (*10*) produce a high *cis*-2-octene/*trans*-2-octene ratio and 30–45% of the 1-octene isomer while another group including thoria (*4*) selectively forms 1-octene. With 3-methyl-3-pentanol, Group IIIA metal oxides appear to be unique since they produce a distribution that is quite different from the nearly equilibrium distribution obtained with all the other metal oxides used in this study. The cyclic alcohol, 2-methylcyclohexanol, provides still another selectivity pattern (*11*, *12*).

As more of these selectivity patterns with alcohols with widely differing steric requirements become available for a series of metal oxide catalysts, it should be possible to make a better definition of the geometry of the catalytic site.

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REFERENCES

1. Davis, B. H., *J. Catal.* **55,** 158 (1978).
2. Pines, H., and Manassen, J., *Advan. Catal.* **16,** 49 (1966).
3. Knözinger, H., *Angew. Chem. Int. Ed.* **7,** 791 (1968).
4. Davis, B. H., *J. Org. Chem.* **37,** 1240 (1972).
5. Knözinger, H., Buhl, H., and Kochloefl, K., *J. Catal.* **24,** 57 (1972).
6. Davis, B. H., *J. Catal.* **52,** 176 (1978).
7. Kilpatrick, J. E., Prosen, E. J., Pitzer, J. S., and Rossini, F. D., *J. Res. Nat. Bur. Stand.* **36,** (1946).
8. Davis, B. H., *React. Kinet. Catal. Lett.* **11,** 1 (1979).
9. Ewell, R. H., and Hardy, P. E., *J. Amer. Chem. Soc.* **63,** 3460 (1941).
10. Davis, B. H., *J. Org. Chem.* **44,** 2142 (1979).
11. Kibby, C. L., Lande, S. S., and Hall, W. K., *J. Amer. Chem. Soc.* **94,** 214 (1972).
12. Davis, B. H., unpublished results.

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