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Catalytic Conversion of Alcohols. 8. Gallium Oxide as a Dehydration Catalyst.

Burtron H. Davis,* Steven Cook, and Robert W. Naylor

Potomac State College, Keyser, West Virginia 26726

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Gallia is a very selective dehydration catalyst for several primary, secondary, and tertiary acyclic alcohols. The alkene distribution from 2-ols with about 50% *cis*-2-, 30% 1-, and 20% *trans*-2-alkene resembles those obtained with alumina. For 2-methylcyclohexanols, the cis isomer is converted more rapidly than the trans isomer and a cis–trans isomerization of the alcohol does not occur. The alkenes from the cis and the trans isomers suggest that an anti elimination is a major reaction pathway in the conversion of 2-methylcyclohexanol. In general, gallia closely resembles alumina as an alcohol conversion catalyst.

Alumina is a widely studied alcohol dehydration catalyst and much of the work has been covered in recent reviews.[1–3] It is generally accepted that the elimination of water follows an anti mechanism; however, the elimination from 2-methylcyclohexanol may be more complicated.[4] A puzzling aspect of the reaction is the high cis/trans ratio for the alkene product from the dehydration of acyclic alcohols; a protonated alkene intermediate has been postulated to account for this.[1] Indium oxide, a member of the same family as aluminum oxide, is diametrically opposed to aluminum oxide in catalytic selectivity since it was much more selective for dehydrogenation and for the formation of 1-alkenes from 2-ols.[5]

Recently two studies have been concerned with the conversion of 2-propanol over various phase modifications of gallia. Bremer and Bogatzki[6] found that 50–80% of the conversion was dehydrogenation for most of the gallia catalysts they tested. Shilyaeva et al.[7] found the β modification about equally active for dehydration and dehydrogenation, the α phase showed an increased proportion of dehydration, and the δ phase only catalyzed dehydration.

The present results, in addition to adding more definition to the catalytic character of gallia, provide data to show how the catalytic selectivity and activity changes within a family in the periodic table.

Results

Gallia was a very selective dehydration catalyst. For the six acyclic secondary 2-ols listed in Table I, 3-pentanol and 4-octanol, and for cyclohexanol and the 2-methylcyclohexanols in Table II, >98% of the total conversion was dehydration to alkenes. Ether was not a significant product from the conversion of secondary alcohols. The dehydration selectivity did not change for the duration of a run or over the temperature range from 160 to 225 °C used with the above alcohols. The catalytic activity was also stable during the run and, except for 3-pentanol, the conversion declined by only 2–4% during the course of a run. The activity declined rapidly with the 3-pentanol reactant; it has not been determined whether this is due to a low concentration of impurity in the alcohol or to a reaction product peculiar to 3-pentanol. The activity of gallia was comparable to the activity of the transitional aluminas under similar reaction conditions and may be slightly higher if the conversion is expressed on the basis of unit surface area.[8]

To determine the amount of isomerization of the alkene products, we have previously used the technique of adding an alkene that is similar to the dehydration product.[8,9] In the present study, by adding 1- or 2-heptene to the 2-octanol charge, we ascertained that the octene dehydration products did not undergo isomerization after desorbing to the gas phase. Likewise, the conversion of a mixture of 1-octene and *trans*-2-methylcyclohexanol took place without isomerization of the added 1-octene. Consequently, the alkene dehydration products that we obtained are the primary gas-phase products.

The alkene distributions in Table I for the conversion of several 2-ols are for later times-on-stream and are representative of the entire run. The percentage yields of the products in the runs of Table I were constant to within ±2% during the runs. As with alumina, about 50% of the alkene fraction was the cis-2 isomer. The 1 isomer was present in a larger amount than the trans-2 isomer. An exception to this may be the products from 4,4-dimethyl-2-pentanol, where the trans-2 isomer was the major product; however there is some uncer-

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* Institute for Mining and Minerals Research, University of Kentucky, P.O. Box 13015, Lexington, Kentucky 40583

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Table I. The Alkene Distribution from the Conversion of Secondary Acyclic Alcohols over Gallium Oxide

charge	temp, °C	LHSV[a]	conversion,[b] mol %	alkenes, mol % 1-	*trans*-2-	*cis*-2-
2-butanol[c]	190	0.62		27	20	**53**
	200	0.62		24	20	**55**
2-pentanol	170	0.31	20–16	26	24	**51**
	185	0.62	30–24	26	23	**51**
	200	1.2	38–34	28	23	**49**
2-hexanol	185	0.62	29–25	46		**54**
2-octanol	178	0.62	20–18	30	19	51
	192	0.62	30	32	17	51
	222	4.5	30–25	32	17	51
4-methyl-2-pentanol[d]	185	0.62	30–26	29	71	
4,4-dimethyl-2-pentanol	180	0.62	38–35	36	49	15
3-pentanol	200	0.62	6–2	trace	41	59
4-octanol[e]	175	0.31	34–30		40	60
	187	0.62	44–41		39	61
	204	1.2	55–52		43	57

[a] LHSV, liquid hourly space velocity, cm^3 alcohol/cm^3 catalyst/h. [b] Conversion is for the range of the four to six samples collected during the run; alkene composition is the average during the run. [c] The conversion was in the 20–30% range but gaseous product decreased the accuracy of the mass balance. [d] Similar alkene distributions were obtained at 160 and 200 °C. [e] Alkenes were only analyzed for *cis*-3- plus *cis*-4-octene and for *trans*-3- plus *trans*-4-octene.

Table II. Products from the Conversion of 2-Methylcyclohexanols over Gallia

charge	temp, °C	LHSV	conv to alkene, mol %	alcohol composition[a] cis	trans	% alkene from[b] cis	trans	methylcyclohexene, mol % 3-	1-
cis	187	1.2	55	100	0.1	100	0	11	89
trans	188	0.31	37	0.1	100	0	100	54	46
trans	230	9.0	32					43	57
trans[c]	203	4.5	60	0.5	100	0	100	56	44
cis + trans[d]	184	2.4	31	34	66	96	4	16	84

[a] Composition of the alcohol fraction in the liquid products. [b] Calculated alkene fraction assuming the same selectivity as with the pure reactants. [c] a mixture containing 90 wt % 1-octene and 10% *trans*-2-methylcyclohexanol was passed over the catalyst; LHSV is given for the mixture; ~60% of the alcohol underwent conversion. [d] 53.1% cis isomer.

Table III. Conversion of Alcohol Mixtures over Gallium Oxide

reaction mixture	temp, °C	mole ratio alcohol/ 2-octanol in reactants	mole ratio (alkene/octene) formed
cyclohexanol/2-octanol	190	1.3	3.1–2.7
	210	1.3	2.1–2.7
4-methyl-2-pentanol/2-octanol	190	1.3	0.47–0.54
	210	1.3	0.53–0.60
2-methyl-2-butanol/2-octanol	190	1.8	13
	227	1.8	8.8–11

tainty about the identification of the GLC peaks on which the data in Table I for this alcohol are based.

The data in Table I show that the *cis/trans*-2-alkene ratio for the dehydration of 3-pentanol or 4-octanol is smaller than was obtained from the 2-ols. For both 3-pentanol and 4-octanol this ratio was in the range of 1.4–1.6; for both 2-pentanol and 2-octanol the ratio was in the range 2.1–3.0.

The data for the conversion of 2-methylcyclohexanol (Table II) show that the pure cis isomer was converted more rapidly than the trans isomer. Since the alcohol in the liquid product contained <0.1% of the other isomer, a cis–trans isomerization of the reactant did not occur. If it is assumed that cis–trans isomerization of the alcohol did not occur during the conversion of the mixture, we calculate that the cis alcohol was converted more rapidly during the conversion of a cis–trans mixture. The alkene fraction from the conversion of the pure cis alcohol was 88% 1-methylcyclohexene and the alkenes from the conversion of the mixture of cis plus trans alcohol contained 85% of the 1-methylcyclohexene isomer. Thus, the alkene products and the unconverted alcohol are consistent with a more rapid conversion of the cis alcohol in the mixture.

The molar ratios of alkenes obtained in the competitive conversion of a mixture of two alcohols are presented in Table III. With the mixture 4-methyl-2-pentanol/2-octanol about two molecules of 2-octanol were converted for each molecule of 4-methyl-2-pentanol. The surface coverage, θ, is related to the relative pressure, P/P_0, where P is the reactant pressure and P_0 is the vapor pressure at the temperature. At the reaction temperature the vapor pressure of 2-octanol is lower than for 4-methyl-2-pentanol. Thus, for the molar ratio for our alcohol mixture, 2-octanol could have a higher surface coverage and, hence, the observed higher conversion than 4-methyl-2-pentanol. The relative pressure, and the surface coverage, for cyclohexanol and 2-methyl-2-butanol should also be lower than for 2-octanol. However, both cyclohexanol and 2-methyl-2-butanol undergo a greater conversion than 2-octanol. Thus, the relative conversion of an alcohol in a mixture is more complicated than a simple competitive equilibrium adsorption mechanism.

Results for the conversion of three tertiary alcohols are presented in Table IV. The amount of 1-alkene from 3-methyl-3-pentanol is much lower than that obtained from the secondary 2-ol. Likewise, the cis/trans ratio (1.6) is about the same as obtained with 3-pentanol and much less than the 2.1–3.0 obtained from 2-pentanol or 2-octanol. In addition, 3-methyl-3-pentanol reacts slower than 2-methyl-2-butanol; the 3-methyl-3-pentanol requires about a 40 °C higher temperature for a conversion equal to the 2-methyl-2-butanol. With 2-methyl-2-butanol a larger amount of the more stable

Table IV. Products for the Conversion of Tertiary Alcohols over Gallium Oxide

charge	temp, °C	LHSV	conversion, mol %	alkene, mol % 1-		2-
2-methyl-2-butanol	118	0.62	18	38		62
	136	0.62	35	39		61
	152	2.4		43		57
	220		38	50		50
2,3-dimethyl-2-butanol	220		34	84		16
				1-	*trans*-2-	*cis*-2-
3-methyl-3-pentanol	170	0.62	34	17	33	50
	220	7.0	11	19	34	47

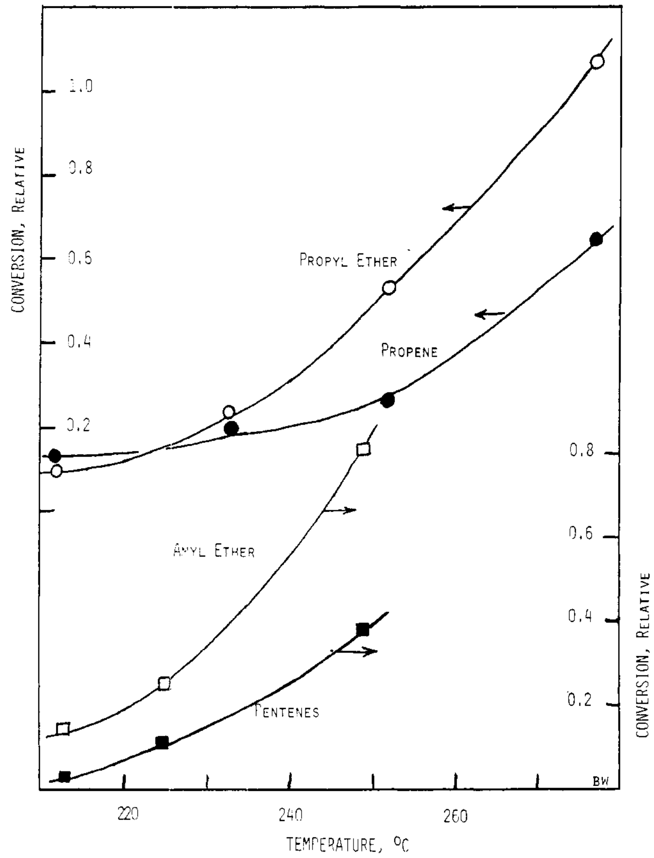

Figure 1. Products from the conversion of 1-propanol and 1-pentanol over gallium oxide at various reaction temperatures.

internal alkene was formed at the lower temperature. The amount of the terminal alkene increased with increasing temperature so that, at 220 °C, 50% of the alkene product was 2-methyl-1-butene. With 2,3-dimethyl-2-butanol more of the terminal alkene was formed (84%) than with 2-methyl-2-butanol (50%).

The conversion products, alkene and ether, for two primary alcohols are presented in Figure 1. The conversion at each temperature was adjusted to the highest flow at the highest reaction temperature so that we refer to a relative conversion in Figure 1. With gallia, just as with alumina, the primary alcohol forms ether as a dehydration product even though significant quantities of ether is not formed with either catalyst with secondary and tertiary alcohols. The maximum ether formation will fall at a temperature well above the 200–220 °C temperature for the maximum amount of ether formation over alumina.

The rate for four 2-ols (2-pentanol, 2- and 4-octanol, and 4-methyl-2-pentanol) was the same, within experimental error, and the Arrhenius plot yielded a temperature coefficient of 28 kcal/mol. For the cyclic secondary alcohols cyclohexanol and the mixture of *cis*- plus *trans*-2-methylcyclohexanol the apparent activation energy was in the 40–44 kcal/mol range. The temperature coefficient was 20 kcal/mol for the primary alcohols (ethanol, 1-propanol, and 1-pentanol). The reaction was considered to be zero order; we obtained a similar amount of product over gallia with 2-octanol at 0.5 and 1 atm.

Table V. Alkenes and Dehydration Selectivity for the Conversion of 2-Octanol over Group 3A Metal Oxide Catalysts

catalyst	dehydration (-ene)/(-ene + -one)	octene, mol % 1-	*trans*-2-	*cis*-2-
"acidic" alumina[a]	>98	40–45	5–10	50
"nonacidic" alumina[a]	>98	30–40	10–25	45–50
gallia	>98	30	20	50
india[b]	0.1–0.4[c]	90	8	2

[a] Data from ref 8. [b] Data from ref 5. [c] Varies with temperature and length of reaction time.

Discussion

The alkene selectivity from the conversion of 2-ols over gallia is very similar to that from alumina (Table V). *cis*-2-Alkene comprises about 50% of the alkene fraction from the conversion of 2-ols for both catalysts. The two catalysts differ in the ratio of the other two alkenes; more 1-alkene than *trans*-2-alkene is formed with both catalysts, but gallia is less selective for the 1 isomer than alumina was. The temperature coefficient for the alcohol conversion over gallia is similar to that obtained with both alumina[8] and india.[5] Knözinger et al.[10,11] and Krause[12] have observed a linear free-energy relationship (LFER) for the conversion of various alcohols of the general structure $RCHOHCH_3$ using alumina as a catalyst; we do not obtain this relationship with gallia.

Since the surface site density is not known, an absolute comparison of the rates of the three catalysts is not possible. For a given reactant flow per volume of catalyst, an equal conversion was obtained at approximately the same temperature with gallia and alumina, but india required about a 50 °C higher temperature. The surface area of the alumina was about four times that of gallia; this would imply that gallia was even more active than alumina.

Shilyaeva and Bekker[7] reported a different selectivity for the α, β, and δ gallium oxide phases. The phase transformations reported for gallia[13] indicate that our catalyst should be the β phase. The X-ray lines for our catalyst were very broad and weak, indicating that it was a material with a very small crystallite size. The two most intense peaks for the β and γ phases are at $2\theta = \sim 35$ and ~ 63.5; our catalyst had weak peaks at these positions. Hence, we believe our catalyst was the β modification.

Deuterium tracer studies and the alkenes from the dehydration of *trans*-2- and *cis*-2-methylcyclohexanol (86 and 22% of 3-methylcyclohexene, respectively) over alumina conform to the classical anti elimination mechanism.[1] A comparison of the alkene distributions from the conversion of the *cis*-2- and *trans*-2-methylcyclohexanol over gallia reveals that an anti elimination is a major reaction pathway. However, in comparison to alumina, gallia is either (a) not as demanding in the anti elimination pathway or (b) isomerization of the anti elimination product occurs prior to desorption of the alkene to the gas phase.

The selectivity does not change uniformly in going down group 3A, but undergoes an abrupt change between gallia and india. The change in selectivity appears to be related to the ability of india to activate the α C–H bond as well as the β C–H bonds. We proposed a mechanism with a common intermediate leading to both dehydrogenation and dehydration for the india catalyst.[5] In spite of minor variations, gallia very closely resembles alumina as a catalyst for the conversion of primary, secondary, and tertiary alcohols.

Experimental Section

Catalyst. The catalyst was prepared from gallium fluoride by dissolving the fluoride in distilled water and then precipitating the hydroxide by adding slightly more than the theoretical amount of ammonium hydroxide. The hydroxide was collected by filtration and washed with water. The solid was then dissolved in a slight excess of nitric acid and the hydroxide was again precipitated and washed. The precipitation procedure was repeated six times to ensure the removal of the fluoride ion. (The gift of a sample of gallium fluoride, rather than a preference for this method, determined the preparation procedure.) The catalyst had a nitrogen BET surface area of 50 m^2/g after heating at 500 °C in oxygen. Later we prepared another catalyst from gallium nitrate and did not observe a selectivity difference between the two for the conversion of 2-octanol.

Alcohols were purchased from Aldrich Chemical Co., Chemical Samples Co., Inc., or Fisher and were used without further purification.

Procedure. The alcohol was passed over the catalyst at atmospheric pressure unless indicated otherwise in the Results. The gallia gel was placed in the reactor and heated to 500 °C in an oxygen flow ~5 mL/min) and held at this temperature for 3 h. After cooling to the reaction temperature, a syringe pump was used to provide a constant plug-flow of reactant to a conventional fixed-bed reactor. Liquid samples were collected at intervals. The sample was analyzed for conversion to alkenes and ketone with a Carbowax 20M on acid washed Chromosorb. The alkene fraction was analyzed for individual isomers using a column selected from the group of Carbowax 20M, UC-W 98, or β,β'-oxydipropionitrile.

Depending on the liquid hourly space velocity (LHSV), we passed the reactant over the catalyst for 1–6 h and collected four to six samples for each reaction temperature. Rather than make corrections for the aging that is observed with any catalyst, we employed a standard regeneration between each run at a given flow rate and/or reaction temperature. After each run, the catalyst was cooled to near room temperature, an air flow (~5 mL/min) was started, and the temperature was increased to 250 °C, held at this temperature for 1 h before heating to 500 °C, and holding it at this temperature for 3–6 h.

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Registry No.—2-Butanol, 78-92-2; 2-pentanol, 6032-29-7; 2-hexanol, 626-93-7; 2-octanol, 123-96-6; 4-methyl-2-pentanol, 108-11-2; 4,4-dimethyl-2-pentanol, 6144-93-0; 3-pentanol, 584-02-1; 4-octanol, 589-62-8; 1-butene, 106-98-9; *trans*-2-butene, 624-64-6; *cis*-2-butene, 590-18-1; 1-pentene, 109-67-1; *trans*-2-pentene, 646-04-8; *cis*-2-pentene, 627-20-3; 1-hexene, 592-41-6; *trans*-2-hexene, 4050-45-7; *cis*-2-hexene, 7688-21-3; 1-octene, 111-66-0; *trans*-2-octene, 13389-42-9; *cis*-2-octene, 7642-04-8; 4-methyl-1-pentene, 691-37-2; *trans*-4-methyl-2-pentene, 674-76-0; *cis*-4-methyl-2-pentene, 691-38-3; 4,4-dimethyl-1-pentene, 762-62-9; *trans*-4,4-dimethyl-2-pentene, 690-08-4; *cis*-4,4-dimethyl-2-pentene, 762-63-0; *cis*-3-octene, 14850-22-7; *cis*-4-octene, 7642-15-1; *trans*-3-octene, 14919-01-8; *trans*-4-octene, 14850-23-8; gallium oxide, 12024-21-4; *cis*-2-methylcyclohexanol, 7443-70-1; *trans*-2-methylcyclohexanol, 7443-52-9; 3-methylcyclohexene, 591-48-0; 1-methylcyclohexene, 591-49-1; cyclohexanol, 108-93-0; 2-methyl-2-butanol, 75-85-4; 2,3-dimethyl-2-butanol, 594-60-5; 3-methyl-3-pentanol, 77-74-7; 2-methyl-1-butene, 563-46-2; 2-methyl-2-butene, 513-35-9; 2,3-dimethyl-1-butene, 563-78-0; 2,3-dimethyl-2-butene, 563-79-1; 3-methyl-1-pentene, 760-20-3; *trans*-3-methyl-2-pentene, 616-12-6; *cis*-3-methyl-2-pentene, 922-62-3; cyclohexene, 110-83-8.

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