Catalytic Conversion of Alcohols Part 10.—Influence of Pretreatment on the Selectivity of MgO and CaO

BY BURTRON H. DAVIS †

Potomac State College of West Virginia University, Keyser, West Virginia 26726, U.S.A.

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With both CaO and MgO catalysts, the hydrogen pretreated material is a selective dehydrogenation catalyst while the oxygen pretreated material has about the same activity for both dehydrogenation and dehydration. Initially the air (or oxygen) pretreated MgO sample produces an alkene distribution from 2-ols that resembles that obtained with alumina; as the reaction temperature is increased a similar alkene distribution, different from the equilibrium value, is obtained with both pretreatments. The three temperatures used with CaO yield an alkene distribution, with either pretreatment, that resembles the highest temperature run with MgO. Pure *cis-2*- or *trans-2*-methylcyclohexanol undergoes extensive *cis-trans* isomerization; the different alkene distributions from the two alcohols suggest that a *trans* elimination pathway contributes to the dehydration mechanism.

Group II metals form the most basic oxides of the group A elements that are not soluble in water. A knowledge of the activity and selectivity of these group IIA oxides is necessary if we are to obtain comprehensive ideas and theories for the catalytic action of metal oxides for the conversion of alcohols.

Studies with these oxides suggest that the number of basic sites depends on the calcination temperature; the maximum number appears to be present in a material calcined at 775-825 K.¹⁻³ These basic sites may determine the catalytic selectivity.⁴ Most studies of alcohol conversion over MgO and CaO indicate that both oxides are very selective dehydrogenation catalysts.⁴⁻¹² Only those materials that are contaminated with CO_2 (or carbonate) or which result from an incomplete decomposition of the carbonate appear to be active for alcohol dehydration.^{6,13} Propan-2-ol has been employed for the majority of the studies of alcohol conversion but it can only form one dehydration product. In a study with a higher carbon number alcohol, butan-2-ol, it was observed that, for the small amount of dehydration, the terminal alkene was greatly favoured.⁹ In another study, Canesson and Blanchard ⁴ reported that the selectivity for hex-1-ene from hexan-2-ol paralleled the base strength reported by Iisuka et al.³ Two recent studies have employed the microreactor technique (pulse method) to obtain the activity and selectivity for butan-2-ol conversion. Vinek et $al.^{14}$ found that the dehydrogenation selectivity depended strongly upon the storage time and calcination temperature; the increase in hydroxide layer and decreasing basicity with storage changed the selectivity from dehydrogenation into dehydration. Thomke ¹⁵ reported that the dehydration selectivity at 50 % total conversion, was 8 % for MgO and 70 % for CaO. The but-1-ene selectivity with MgO changed from ≈ 80 % at 673 K to 50 % at 773 K but with CaO the selectivity only varied from 20 to 30 %.

[†] Present address : Kentucky Centre for Energy Research Laboratory, University of Kentucky, P.O. Box 13015, Lexington, Kentucky 40583, U.S.A.

These limited studies suggest that group IIA metal oxides may resemble other selective α -olefin forming catalysts such as thoria.

Alumina has traditionally been viewed as a very selective dehydration catalyst.¹⁶ However, pretreatment in oxygen may impart a dehydrogenation activity that is at least as great as the dehydration activity.¹⁷ Even though the pretreatment may play a major role in determining the activity and selectivity, it has not received much attention for most of the metal oxide catalysts.

The present investigation defined the influence of the hydrogen or oxygen pretreatment on the dehydrogenation activity and the alkene selectivity of CaO and MgO. Hopefully, a unified picture of the catalytic selectivity will emerge as more oxides are studied.

EXPERIMENTAL

CATALYSTS

Magnesium oxide was suspended in distilled water and heated near the boiling point for 6 h. The solid was collected, dried at 390 K in air and then heated in air for 6 h at 1270 K. The CaO used for the runs with octan-2-ol [footnote (c), tables 1 and 2] was prepared by heating Fisher calcium hydroxide *in situ* in flowing oxygen or hydrogen to 825 K and holding it at this temperature in the flowing gas. The CaO used for the other runs was prepared by adding ammonium carbonate to a calcium nitrate solution. The resulting calcium carbonate was collected by filtration, dried at 390 K and then calcined in air at 875 K for four days.

PROCEDURE

A syringe pump was used to charge the reactant to a fixed bed glass reactor fitted with a thermowell. The liquid products, after passing through a water condenser, were collected at time intervals. The liquid was analysed for conversion using temperature programmed g.c. with a Carbowax 20M column. Alkenes were analysed using g.c. with the column appropriate for the particular alkene mixture : UC-W, Carbowax 20M or β , β' -oxydipropionitrile. *cis*- And *trans*-2-methylcyclohexanol content was determined by g.c. with a di-glycerol column.

Initially, the catalyst, in powder form, was pretreated in the reactor; thereafter, a standard regeneration was used prior to the next pretreatment in air, hydrogen or oxygen. The regeneration consisted of stopping the reactant flow and cooling the catalyst from the run temperature to near room temperature. A flow of air was passed over the catalyst while it was slowly heated (for 20-30 min) to 525 K and held at this temperature for ≈ 3 h. The temperature was then increased to 790-825 K and held at this temperature for 3-6 h. For an air pretreatment, the catalyst was then cooled to the reaction temperature in flowing air. For the other pretreatments the air flow was replaced by the pretreatment gas flow and the catalyst was heated at 790-825 K for 3-6 h. In all cases, the catalyst was cooled to the reaction temperature in the pretreatment gas flow.

RESULTS

The conversion data in fig. 1 for 4-methylpentan-2-ol over MgO clearly show the influence of pretreatment on the dehydration and dehydrogenation activity. The catalyst was about equally active for dehydration and dehydrogenation following an air pretreatment at 775 K [fig. 1(a)]. After completing the run represented in fig. 1(a), the catalyst was regenerated by the standard procedure and then pretreated with flowing hydrogen for 4 h. The sample now had about the same dehydration activity but the dehydrogenation activity was two to three times greater than that of the air pretreated sample [fig. 1(b)]. The decrease in dehydrogenation activity with time-on-stream for the air pretreated sample is not representative; in most cases the activity changed much more slowly (e.g., see the pentan-2-ol results in table 1). In comparing

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the data in table 1 it should be noted that the conversion range represents the high and low conversion for the 4-6 samples collected during the duration of the run so that there was little change in the activity during a run. Following the run for fig. 1(b), the sample was again given the standard air regeneration and air pretreatment; the dehydrogenation and dehydration activity of the catalyst repeated the original air pretreatment [compare fig. 1(a) and (c)].



FIG. 1.—Influence of pretreatment on the conversion of 4-methylpentan-2-ol to methylpentenes and 4-methylpentan-2-one over a magnesium oxide catalyst.

TABLE	1.—DEHYDRATION	SELECTIVITY	FOR	THE	CONVERSION	OF	ALCOHOLS	OVER	MAGNESIUM
AND CALCIUM OXIDE									

alcohol	pretreatment	LHSV ^a	T/K	length of run/min	conversion ^b range/mol %	dehydration ^b selectivity
				MgO		**************************************
pentan-2-ol	air	0.13	590	360	29-28	0.55-0.58
-		0.26	613	180	24-24	0.47-0.55
		0.51	633	105	25-22	0.35-0.38
	H_2	0.13	588	335	38-39	0.16-0.20
		0.26	608	160	39-40	0.15-0.17
		0.51	641	120	45-49	0.08-0.09
octan-2-ol	air	0.26	523	230	8-10	0.97-0.98
		0.26	578	380	15-18	0.88-0.90
		0.51	59 8	325	12-15	0.88-0.89
		0.51	618	240	16-23	0.68-0.86
		1.03	633	175	17-22	0.62-0.71
	H_2	0.26	588	365	26-27	0.29-0.31
		0.51	608	290	27-30	0.24-0.25
		1.99	633	70	23-24	0.15-0.17

alcohol	pretreatment	LHSV ^a	<i>T</i> /K	length of run/min	conversion ^b range/mol %	dehydration ^b selectivity
4-methyl-						
pentan-2-ol	air	0.13	587	270	—	0.58-0.73
		0.26	613	480	19-24	0.46-0.62
		0.51°	638	205	19-21	0.43-0.52
	H_2	0.13	589	375	43	0.29
		0.26	613	340	32-42	0.22-0.25
		0.51°	633	195	38-40	0.13-0.15
	air	0.51 ^c	633	130	18	0.60
(cis+trans)-	air	0.13	589	495	25-31	0.83-0.87
2-methylcyclo-	•	0.28	617	170	23-25	0.71-0.74
hexanol		0.51	633	295	16-22	0.62-0.63
	H_2	0.13	593	370	24-25	0.58-0.62
		0.26	613	415	41-48	0.20-0.26
		0.51	638	130	30-32	0.29-0.37
trans-2-methyl-	air	0.26	613	165	16-22	0.81-0.86
cyclohexanol	H_2	0.26	608	190	29-32	0.28-0.29
				CaO		
nentan_2_ol	air	0.13	603	295	- 22-35	0 54-0 55
pontan 2 or	uii	0.15	623	205	18-29	0.34-0.55
		0.20	643	130	18-32	0.37-0.57
octan-2-01	Ω_{a}^{d}	0.25	563	435	21-44	0.45-0.57
	H. e	0.25	563	305	12-16	0.11_0.14
	112 9ir	0.23	503	380	28-44	0.11-0.14
	64 11	0.15	613	310	20-44	0.36-0.62
		0.20	633	300	22-45	0.36-0.62
4-methyl- pentan-2-01	$H_2 f$	0.25	558	270	11-14	0.09-0.17
F	air	0.13	603	365	30-52	0.43-0.62
		0.61	633	90	27-42	0.35-0.74
	H.	0.26	591	305	10-29	0 07-0 14
	+-2	0.26	618	330	15-29	0.18-0.24
		0.51	643	245	18-25	0.17-0.21
(cis + trans)-	H.	0.13	603	360	28-33	0.52-0.66
2-methycyclo-		0.26	623	370	22-28	0 58-0 69
bexanol		0.51	643	175	11-24	0 55-0 63
trans-2-methyl- cyclohexanol	air	0.26	623	80	21-33	0.52-0.60
-,	H_{2}	0.26	623	85	11-24	0.33-0.56
<i>cis</i> -2-methyl- cyclohexanol	air	0.26	623	90	39-45	0.78-0.79

^a Liquid hourly space velocity (cm³ reactant per cm³ catalyst per h). ^b Values given are the extremes in conversion and selectivity for the 4-6 samples collected during the course of the run. ^c Runs with pretreatments of air, hydrogen and air (with regenerations between the runs) in succession. ^d Calcium hydroxide heated to 500 °C in flowing oxygen. ^e Sample given standard regeneration followed by hydrogen reduction. ^f Same as (d) except heated in flowing hydrogen.

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				4		alkene/mol %			
alcohol	pretreatment	LHSV	T/K	/min	/mol %	1-	trans-2-	cis-2-	
<u></u>	9 <u>- 19 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997</u>		М	gO	an <u>an an an a</u>				
pentan-2-ol	air	0.13	588	95	- 29	22	24	53	
-				205	32	26	25	49	
				280	30	24	31	45	
				360	30	23	34	43	
		0.26	613	180	24	22	32	46	
		0.51	633	105	22	22	35	43	
	H_2	0.13	588	335	38	16	55	29	
		0.26	608	160	40	24	43	33	
		0.51	643	120	45	29	34	37	
octan-2-ol	H_2	0.26	608	215	32	25	48	27	
				290	30	28	42	30	
			С	aO					
pentan-2-ol	air	0.13	603	195	- 25	27	37	36	
r				295	22	26	36	38	
		0.26	623	205	18	29	35	36	
		0.51	643	130	18	29	35	36	
octan-2-ol	O_2	0.13	563	435	23	34	31	35	
	H_2	0.13	563	305	13	34	32	34	

TABLE 2.—ALKENE SELECTIVITY FROM THE CONVERSION OF 2-OLS WITH CALCIUM AND MAGNES-IUM OXIDES

The selectivities for the conversion of pentan-2-ol and 4-methylpentan-2-ol over MgO are very similar for each temperature and pretreatment. Octan-2-ol and 2-methylcyclohexanol also have similar selectivities at each temperature and pretreatment; however, MgO appears to be more selective for the dehydration of these higher molecular weight alcohols than for the pentanols.

The CaO results in table 1 are similar to the corresponding runs using MgO and the dehydration selectivity for each alcohol corresponds closely to that obtained with MgO. However, the conversion varies over a much wider range during the course of a run showing that CaO ages more rapidly than does MgO. The two materials appear to have a similar initial activity when compared on an equal catalyst weight basis. The B.E.T. surface area of the catalyst was determined after use and storage for a month or more; it is unlikely that the area measured is the same as it would be if it was measured during use as a catalyst. The area, after evacuation at 473 K, was: MgO, 56 m² g⁻¹; CaO, 4.2 m² g⁻¹. This indicates that CaO, on an equal area basis, may be even more active than the MgO catalyst.

With MgO the dehydration selectivity decreased with increasing temperature for both pretreatments; this trend was not as clear-cut with CaO.

The alkene selectivity may also depend on the pretreatment. At 591 K, hydrogen pretreated MgO produced an alkene distribution that was constant with time and was essentially the equilibrium distribution (fig. 2). The air pretreated sample yielded an alkene distribution with *cis*-pent-2-ene as the major product; as the reaction progressed the alkene selectivity changed to produce more of the *trans*-2-isomer at the expense of

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FIG. 2.—Comparison of the alkene distribution from the conversion of pentan-2-ol over air and hydrogen pretreated magnesium oxide; ●, 1-pentene; ▲, trans-pent-2-ene; ■, cis-pent-2-ene [open symbols represent the equilibrium n-pentene composition calculated from data in ref. (26)].



FIG. 3.—Alkene composition from the conversion of pentan-2-ol over hydrogen and oxygen pretreated magnesium oxide catalyst [(______) represents the equilibrium value calculated using data from ref. (26); the open symbols are for the hydrogen pretreated sample; solid symbols are for the air pretreated sample].

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the *cis*-2-isomer. Initially, the alkene selectivity of MgO resembled that of alumina.¹⁸ Thus, the alkene selectivity of the air pretreated sample changed with time-on-stream even though the dehydration selectivity remained nearly constant with time. The alkene distribution changed with increasing temperature to approach an alkene composition that was the same for both pretreatments; this composition differs from the equilibrium value (fig. 3). The alkene distribution from pentan-2-ol was representative of the results obtained with MgO with the other acyclic 2-ols.

CaO yielded essentially the same alkene distribution with the hydrogen or the oxygen pretreated material with octan-2-ol and 4-methylpentan-2-ol. Octan-2-ol produced about equal amounts of the three alkenes allowed by β -elimination. The alkene distributions obtained with pentan-2-ol and 4-methylpentan-2-ol did not appear to change with temperature as was the case with MgO; the distribution with CaO was approximately the one that was obtained at the highest temperature used with the MgO catalyst.

Calcium and magnesium oxide catalysts were similar for the conversion of 2methylcyclohexanol. CaO may have been slightly more selective for dehydration than MgO was. With both catalysts the hydrogen pretreated material was 2-6 times more active for the *cis-trans* isomerization of the charged alcohol than the air pretreated sample (table 3). With the hydrogen pretreated samples, the amount of isomerized alcohol in the liquid product was as great as the total conversion by both dehydration and dehydrogenation. *trans*-2-Methylcyclohexanol conversion over the hydrogen or air pretreated MgO led to the same alkene composition; with CaO there was only a slight difference in the alkene compositions from the two pretreatments. The alkene composition from *trans*-2-methylcyclohexanol with both catalysts and both

						alcohol ⁴		methylcyclohexene		
isomer	treatment	<i>T</i> /K	LHSV	/min	/mol %	cis	trans	4- ^b	3-	1-
			Mg	0						
trans-2-	air H ₂	613 608	0.26 0.26	40 85 165 95 160 190	22 18 16 36 32 29	4.7 5.3 33 33 29	95.3 94.7 67 67 71	3	42 47 48 43 46 47	55 53 52 57 54 53
			Ca	0						
trans-2-	air	623	0.26	60 80	33 22	14 9.3	86 90.7	6.2 5.4	37 37	57 57
	H_2	623	0.26	35 85	24 21	32 22	68 78	6.7 6.3	43 42	51 52
cis-2-	air	618	0.26	50 95	45 39	87 93	13 7	1.8 2.2	23 24	75 74

TABLE 3.—PRODUCTS FROM THE	CONVERSION OF	PURE 2-MET	THYLCYCLOHEXANOL	ISOMERS	WITH					
CALCIUM AND MAGNESIUM OXIDE CATALYSTS										

^a Composition of the alcohol in the liquid reaction products; the alcohol reactant contained < 0.1 % of the other isomer. ^b May contain some methylcyclohexane.

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pretreatments differed significantly from that with the *cis*-alcohol over CaO. The alkene composition from the *cis*-alcohol over CaO is similar to that obtained with other oxides in this temperature range¹⁹ and is probably the equilibrium composition (considering only methylcyclohex-1- and -3-ene).

The kinetics for alcohol conversion with MgO 6,8,10,11 show an alcohol reaction order varying between zero and one. In most cases our data gave reasonable Arrhenius-type plots if the rate was assumed to be zero order in alcohol. However, the temperature coefficients calculated from these plots were only ≈ 10 kcal mol⁻¹. This low value could be accounted for by a rate with some order other than zero.

DISCUSSION

With both CaO and MgO, the hydrogen pretreated material was a selective dehydrogenation catalyst while the oxygen pretreated sample had about the same activity for both dehydrogenation and dehydration. The selectivity was imparted by the pretreatment and the catalyst could be changed from one selectivity to the other by the appropriate pretreatment. Hydrogen or oxygen pretreatment determines the selectivity for many catalysts²⁰ but in most cases we found a selectivity that was just opposite to that of CaO and MgO. For example, hydrogen pretreated alumina is a very selective dehydration catalyst but oxygen pretreated alumina is as active for dehydrogenation as for dehydration.¹⁷

The sites created by the pretreatment are catalytic. For example, a run with a mixture of *cis*- and *trans*-2-methylcyclohexanol using air pretreated MgO resulted in the conversion of 50 mmole over 6.3 g of MgO having a total surface area of 345 m^2 . Estimating the minimum dimension of the catalytic site as 10 Å^2 , a size only slightly greater than that of an oxide ion, enables one to calculate that a minimum of 10 molecules of alcohol were converted per site. Since the conversion remained nearly constant during the run it seems clear that sites are catalytic and not transient in nature.

The results from the conversion of *trans*-2-methylcyclohexanol suggest that dehydration and dehydrogenation may occur on different sites. The alkene fraction from the conversion of the *trans*-alcohol over both the air and the hydrogen pre-treated MgO at 613 K contained the same amount of methylcyclohex-3-ene. The total alcohol conversion was also similar. However, with the air pretreated sample 81-86 % of the conversion was dehydration while only 28-29 % of the total conversion was dehydration conversion was nearly equal to the amount of the *cis*-trans isomerization of the alcohol charge for both pretreatments, suggesting that the isomerization occurs on the same site that is active for dehydrogenation.

An oxygen species, O_2^- or OOH⁻, may serve as a site for dehydrogenation.²¹ Tench *et al.*²² observed that O⁻ on MgO abstracted the α -hydrogen from both ethanol and propan-2-ol. The air pretreated sample should have a higher concentration of oxygen species than the hydrogen pretreated sample and should be more selective for dehydrogenation. Since we observed the opposite effect, it appears that the oxygen ion is not responsible for dehydrogenation with CaO and MgO catalysts.

Derouane and Gieseke ²³ found that the paramagnetic centres formed by evacuation at 653 K were decreased by the adsorption of hydrogen at 293 K. Increasing the temperature to 443 K restored many of the paramagnetic centres as hydrogen was desorbed. These paramagnetic centres were active for H_2-D_2 exchange ²⁴ and dehydrogenation of alcohols could be viewed as a special H_2-D_2 exchange. Since hydrogen adsorption decreased with increasing temperature,^{23,25} we would expect alcohol dehydrogenation to likewise decrease; this is contrary to what was observed.

The alkene distribution from the acyclic alcohols suggests that the number and kind of dehydration sites change with temperature for MgO. At lower temperatures, an equilibrium distribution was obtained with the hydrogen pretreatment while the distribution from the air pretreated sample resembled that obtained with alumina. Thus, the hydrogen pretreated material adsorbs the alkene product more strongly so it has time to isomerize or the dehydration reaction occurs through a different intermediate on the two pretreated materials.

The different alkene distribution from pure *cis*- and pure *trans*-2-methylcyclohexanol rule out a mechanism with a common intermediate and is consistent with an *anti* elimination mechanism. However, the 50 % methylcyclohex-3-ene from *trans*-2-methylcyclohexanol suggests a contribution from a *syn* elimination or an isomerization of the alkene during formation or as a secondary reaction.

In summary, the hydrogen or air (oxygen) pretreatment determined the dehydration selectivity. The selectivity is imparted by the pretreatment and can be altered by the next pretreatment. The ability to change from one selectivity to another suggests that the range of selecticities reported by earlier workers probably resulted from the pretreatment. It will require more work to decide which of the variety of paramagnetic sites, if any, determine the selectivity.

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