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Catalytic Properties of Attrition Ground Silica

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In studies conducted by the Federal Bureau of Mines, high-surface-area silica catalysts prepared by attrition milling demonstrated activities similar to conventional silica catalysts. Attrition-milled silica possessed the highest activity of the catalysts tested for *n*-hexane cracking but a lower activity for ethanol dehydration. Attrition milling may provide an alternate method of preparing high-specific-surface catalysts.

NOMENCLATURE

F	total gas flow, $cm^3\ sec^{-1}$
k	reaction rate constant, $cm^3\ sec^{-1}\ g^{-1}$
W	catalyst weight, g
x	fraction hexane converted

INTRODUCTION

Solid materials can be easily ground to small sizes having high surface areas using an attrition mill developed by the Bureau of Mines (*1*). Specific surfaces of 50 to 100 m^2/g can be obtained in reasonable milling times under proper conditions for a wide variety of materials. The mill is designed to grind by the intense agitation of a grinding medium slurry containing the powders being ground. This type of equipment is presently being used commercially to prepare fine powders for paper coatings and paint pigments.

Silica was selected to demonstrate the catalytic properties of attrition-milled materials because it is commonly used as a catalyst and a catalyst support. In addition, it had previously been used for other attrition milling studies (*2*). This report describes the use of three materials for the cracking of *n*-hexane and the dehydration of ethanol. These diverse reactions have been previously investigated by others using metallic oxide catalysts (*3,4*).

EXPERIMENTAL METHODS

Materials

The *n*-hexane and ethanol reactions employed in this study were >99% pure and the nitrogen carrier gas was high-purity, dry grade. The properties of the five catalyst materials employed are given in Table 1. The first two were attrition milled using minus 14- plus 28-mesh Ottawa sand as milling medium, and the second two represent commercial materials. The last (S5) is unmilled silica from which the first two were prepared. The material used to produce S1 was a minus 400-mesh, 99+% silica flour (Ottawa Sand Corp., Ottawa, IL). Catalyst S2 is produced from the same raw material that had been heated for 2 hr at 1500°C to convert a substantial portion of the quartz to cristobalite.

The attrition mill consisted of a cylindrical cage-like rotor mounted concentrically in a similarly shaped stator. Both stator and rotor were contained in a cylindrical chamber. The rotor operated at 1400 to 1600 rpm and was driven by a 1-hp motor. The mill was charged with 360 g silica flour, 1100 g Ottawa sand, and 1700 cc water. The rate of size reduction of the attrition milled silica is shown in Fig. 1. Milled powders were leached in concentrated HCl to remove iron contami-

TABLE 1
CATALYST PROPERTIES AND ANALYSES

	Catalyst				
	S1[a]	S2[a]	S3	S4	S5
Crystal form	α-quartz	α-quartz/ α-cristobalite mixture	Amorphous (silica gel)	Amorphous (diatomaceous earth)	α-quartz
Surface area (m^2/g)	51.8	53.8	725	75	~0.2
Chemical analysis (wt%: Fe)	0.08	0.11	nd[b]	nd	0.15
Spectrographic analysis (wt%)					
0.1–1.0	—	—	—	Al, Fe	—
0.01–0.10	Al, Ca, Na	Al, Ca, Na	Al, Cu, Ti	Ca, Cr, K, Mg, Na, Ni, Ti, V	Al, Ca, Na
0.001–0.01	Cr, Mg, Mn, Ni, V	Cr, Mg, Mn, Ni, V	Fe, Na	B, Cu, Li, Mn, Sn	Cr, Mg, Mn, Ni, V
0.0001–0.001	Cu	Cu	—	—	Cu
<0.0001	Sn, Ti	Sn, Ti	Mg	—	Sn, Ti

[a] Attrition milled.

[b] nd = not determined.

nation from the mill, washed, dried, and passed through a 6-mesh screen.

Catalyst S3 was a commercial silica gel consisting of minus 28- plus 48-mesh particles. Catalyst S4 was a commercial catalyst support prepared from diatomaceous earth. This amorphous silica material contained numerous fragmentary diatoms and sponge spicules. It was received as 1/8-in. extrusions and ground to minus 14- plus 48-mesh sizes for testing.

Equipment and Procedures

Catalytic activity data were obtained by chemical reaction measurements. A 2.54-cm diameter Vycor[1] glass tube, heated by a 750-W split jacket tubular electric furnace, was employed. Catalyst bed temperatures were measured by a type J thermocouple. Heating was controlled manually with a variable transformer. The 15-cc catalyst charges were held in the center of the reactor by 0.35-cm glass spheres. Dry nitrogen carrier gas was passed through a fritted glass disc and a sparger containing reactant liquid at 25°C. The saturated gas stream flowed continually to the catalyst bed.

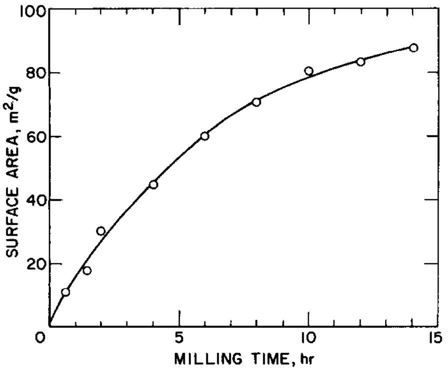

FIG. 1. Effect of attrition milling time on size reduction of silica powder.

During the *n*-hexane cracking experiments, the nitrogen flow to the sparger was held constant at 100 cc/min (measured at 25°C and 1 atm), while the saturated gas contained the hexane at a partial pressure of 0.2 atm. The catalysts were initially subjected to nitrogen treatment for approximately 30 min at 550°C prior to testing. Product gases were analyzed after 10 min of reactant gas flow using a gas chromatograph with 1/8-in. diameter by 5-ft long column of 3% SE-30 on minus 100- plus 120-mesh Varaport 30. The column temperature was maintained at 0°C, nitrogen

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[1] Reference to brand or trade names is for identification only and does not imply endorsement by the Bureau of Mines.

carrier gas held constant at 20 cc/min, and detection was carried out by flame ionization. Conversion data for hexane cracking were considered meaningful only between 5 and 40% of *n*-hexane conversion. Data below 5% were rejected because of analytical inaccuracies and above 40% to avoid errors in the measurement of intrinsic catalytic activity and catalyst deactivation due to coking caused by heat and mass transport effects and overcracking.

In the ethanol dehydration experiments, the nitrogen flow to the sparger was varied between 25 and 120 cc/min, and the saturated gas contained ethanol at a partial pressure of 0.079 atm. The chromatographic column used to detect the reaction products was 10% dinonyl phthalate on minus 80- plus 100-mesh Chromosorb W packed in a 1/8-in. diam × 10-ft column. The column temperature was maintained at 100°C. No appreciable catalyst deactivation was observed after 10 min in the ethanol dehydration tests; therefore, several operating conditions were investigated with the same catalyst sample. The catalytic activity was rechecked periodically.

Ammonia adsorption measurements were made with a controlled atmosphere thermogravimetric analyzer.[2] Approximately 50 mg of catalyst sample was heated at a rate of 10°C/min to 500°C, held for 30 min, and weighed continuously. Ammonia was then introduced at 250 standard cc/min, and the pressure was maintained by a vacuum pump at 76 Torr. During treatment, the samples were cooled at 2°C/min and continuously weighed. Sorption–desorption cycles were repeated to insure that equilibrium conditions were achieved.

DISCUSSION OF RESULTS

Hexane Cracking

Empty reactor tests with each reactant showed no detectable conversion at the conditions used. Results of the hexane cracking experiments with the silica catalysts were correlated by using a conventional reaction rate model. A simplified first-order reaction rate constant was calculated for each test run in a manner similar to a previous study of hexane cracking with zeolite catalysts (*3*). At a given temperature, the reaction rate constant, k, is described as

$$k = \left(\frac{F}{W}\right) \ln \left[1/(1-x)\right], \qquad (1)$$

where F (cm^3/sec), is the total gas flow of both nitrogen and organic vapor, W the catalyst weight (g), and x the fraction hexane converted. Rate constant, k, was calculated on a weight basis in this paper rather than on a volume basis as in the reference because of the wide variation found in the catalyst charge bulk densities.

Figure 2 presents an Arrhenius plot of the observed rate constants with temperature. "Apparent" activation energies calculated from the slopes of the lines in Fig. 2 range from 26 to 36 kcal/mole. These values compare favorably with, and are probably not significantly different from, 30 kcal/mole reported in the literature (*3*).

A comparison of conversions at the same nominal conditions is made in Table 2. Although attrition milled catalyst, S1,

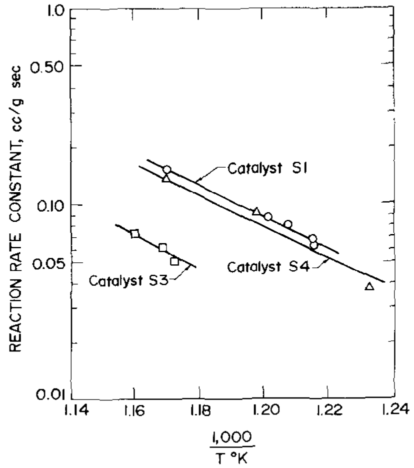

FIG. 2. Effect of temperature on *n*-hexane cracking activity.

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[2] Tem-Pres (Carborundum Corp.) Model TG-716 and Cahn Model RG electrobalance.

TABLE 2

Comparison of n-Hexane Cracking Reaction over Silica Catalysts[a]

	Units	Catalyst		
		S1	S3	S4
Catalyst charge				
Vol	cc	15	15	15
Wt	g	6.86	9.90	8.00
Temp	°C	582	580	580
Conversion	%	16.5	8.0	17.7
Rate constant, *k*	cc/g-sec	0.157	0.051	0.145

[a] Nitrogen flow rate: 100 cc/min (25°C and 1 atm).

had a slightly lower conversion than commercial catalyst S4, its observed rate constant was higher because the weight of the catalyst was less. Both S1 and S4 were considerably more active than the silica gel, S3.

Relative activities for S1, S3, and S4 are compared in Table 3, wherein attrition-milled S1 was observed to be the most active on both weight and surface area basis. The relative activities on a weight basis were calculated from the ratio of each catalyst's reaction rate constant at a fixed temperature to the rate constant for catalyst S1. Similar calculations were made on the surface area basis.

Product compositions from *n*-hexane cracking did not vary significantly among the silica catalysts. Typical product distributions from cracking over S1 and S4 are presented in Table 4. The product spectrum indicates a predominance of two-carbon atom compounds and a C_2/C_4 mole ratio of approximately 10. For simple one carbon–carbon bond splitting with *n*-hexane, there should be as many four-carbon fragments as there are two-carbon fragments. Products from S1 and S4 indicate that simultaneous scission of two carbon–carbon bonds occurs with some hexane molecules or that recracking of four-carbon fragments takes place. A previous study (*5*) of cracking hexene-1 over silica at 500°C also showed a high C_2/C_4 ratio.

TABLE 3

Calculated Relative Activities for Hexane Cracking

	Catalyst		
	S1	S3	S4
Relative activity			
Wt basis	100	32	93
Surface area basis	100	2	64

TABLE 4

Typical Product Distribution from Hexane Cracking

Product spectrum (mole% of total converted product)	Catalyst:	S1	S4
	Temp (°C):	558	550
	Conversion (%):	10.5	8.0
Methane		18.3	16.2
Ethane		10.7	12.6
Ethylene		33.3	30.1
Propane		12.6	14.0
Propylene		20.9	22.7
Butanes		0.5	1.0
Butenes		3.7	3.4
Pentanes		Tr	Tr
Isohexanes		Tr	Tr

Ethanol Dehydration

In the conversion of ethanol over the silica catalysts, the principal reaction products were ethylene, water, and diethyl ether. Although previous studies (*4*,*6*) indicated that dehydrogenation reactions also occurred, no substantial quantities of acetaldehyde or other dehydrogenation products were detected in this investigation. The lack of dehydrogenation activity was probably due to the lower temperatures employed.

Figures 3 through 6 present the effect of temperature on the dehydration reaction for S1, S2, S3, and S4. In these experiments, the gas flow was constant at 100 cc (STP)/min with an initial ethanol pressure of 70 Torr. Catalysts S1 and S2 produced little ether in all cases, but S3 and S4 produced mostly diethyl ether at the lower

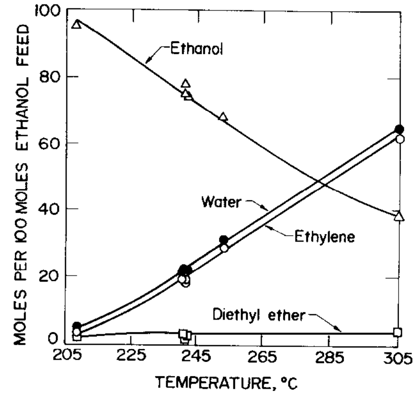

Fig. 3. Effect of temperature on ethanol dehydration using catalyst S1.

temperatures and had a temperature maximum for ether formation. These data suggest that the major reaction for S1 and S2 is

$$C_2H_5OH \rightleftarrows C_2H_4 + H_2O. \quad (2)$$

The major reaction at lower temperatures for S3 and S4 appears to be

$$2C_2H_5OH \rightleftarrows C_2H_5OC_2H_5 + H_2O, \quad (3)$$

and the temperature maximum for ether formation indicates a secondary decomposition of ether to olefin, as follows:

$$C_2H_5OC_2H_5 \rightleftarrows 2C_2H_4 + H_2O. \quad (4)$$

The dependence of ethanol dehydration on contact time with S1 is shown in Fig. 7. Ether formation did not increase appreciably with long contact times.

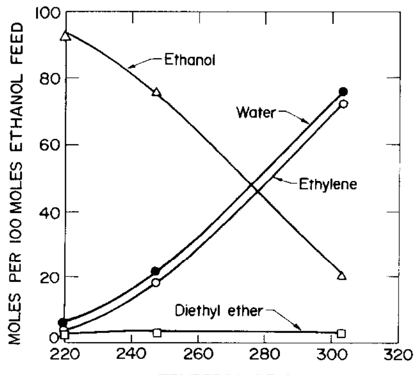

Fig. 4. Effect of temperature on ethanol dehydration using catalyst S2.

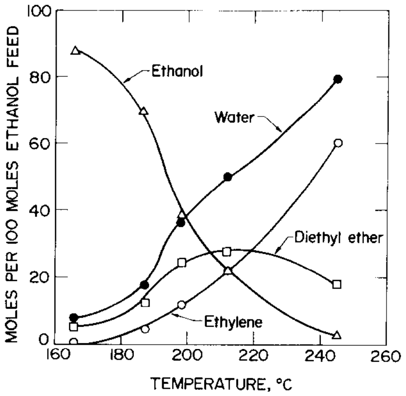

Fig. 5. Effect of temperature on ethanol dehydration using catalyst S3.

Several tests were conducted with S5 in order to better understand the unusual selectivities of S1 and S2. Results from tests with S5 are compared with results from S1 in Table 5. These data indicate that S5 is inactive at conditions that produce appreciable dehydration with the other catalyst materials and that approximately 100°C higher temperature is needed for S5 to produce the same conversion as S1. By comparing the data in Table 5 with Figs. 4 through 6, it is seen that S5 produced more diethyl ether than S1 and S2; however, ether production was much lower than with S3 and S4 at the same total conversion. This suggests that either minor impurities or the crystal structures of S1, S2, and S5 contribute to the low activity for ether production.

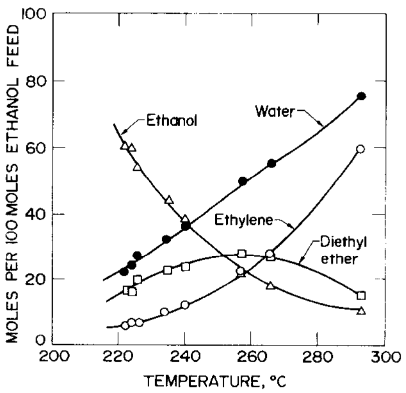

Fig. 6. Effect of temperature on ethanol dehydration using catalyst S4.

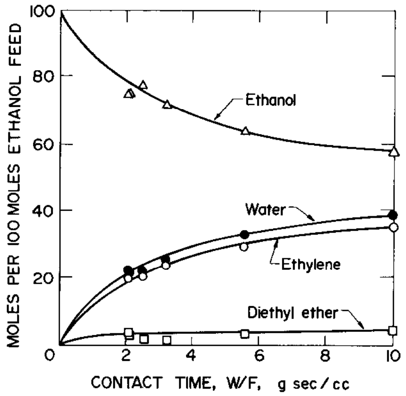

FIG. 7. Effect of contact time on ethanol dehydration using catalyst S1 (241°C).

On a total conversion basis, S3 had the highest activity for ethanol dehydration and S1 and S2, the lowest activities. This may be seen in Table 6 by comparing the total conversion achieved at similar operating conditions.

Ammonia Adsorption

Results on the quantity of ammonia adsorbed by the catalysts are presented in Table 7. This provides additional information on the nature of catalyst surfaces. Ammonia adsorption at 200 to 400°C was very high for S1 and S2. Previous studies (*7*) indicated that ammonia adsorption in this temperature range is on "strong" acid sites at the high temperature and "medium" acid sites at the lower temperature. The strength of the sites is determined by the ability of the surface to absorb ammonia at higher temperatures, which is correlatable with capacity to catalyze certain types of reactions. Cracking of hydrocarbons is generally accepted to proceed primarily by a carbonium ion mechanism that is induced by acidic sites on the catalyst surface (*8*).

TABLE 5

EFFECT OF ATTRITION MILLING ON ETHANOL DEHYDRATION[a]

	Catalyst S1		Catalyst S5	
Temp (°C):	240	305	230	416
Catalyst charge				
Vol (cc)	15	15	15	15
Wt (g)	8.05	6.39	11.83	11.83
Conversion (%)	21.5	63.1	0.0	68.7
Product (moles/100 moles ethanol feed)				
Ethylene	19.7	59.8	—	55.1
Diethyl ether	1.0	1.7	—	6.7
Ethanol	78.5	36.9	100	31.3
Water	20.7	61.5	—	61.8

[a] 109 cc/min gas (92.1% N_2, 7.9% ethanol).

TABLE 6

COMPARISON OF ETHANOL DEHYDRATION REACTIONS OVER SILICA CATALYSTS[a]

	Catalyst			
	S1	S2	S3	S4
Charge				
Vol (cc)	15	15	15	15
Wt (g)	6.39	8.68	10.34	7.70
Temp (°C)	241	247	245	240
Conversion (%)	25.9	24.3	97.4	61.0
Product (moles/100 moles ethanol feed)				
Ethylene	19.1	18.4	61.1	13.0
Diethyl ether	3.5	3.1	17.9	24.0
Ethanol	74.1	75.7	2.6	39.0
Water	22.6	21.5	79.0	37.0

[a] 109 cc/min gas (92.1% N_2, 7.9% ethanol).

TABLE 7

AMMONIA ADSORPTION CAPACITY OF SILICA CATALYSTS[a]

	Catalyst			
Temp (°C)	S1	S2	S3	S4
50	9.85	6.27	1.57	9.02
100	7.48	4.44	0.64	6.60
200	5.76	3.40	0.43	4.16
300	3.73	2.34	0.32	2.44
400	2.03	1.17	0.20	0.69
450	1.00	0.78	0.11	0.33

[a] 76 Torr pressure (mequiv $NH_3 \times 10^3$ sorbed/m^2 catalyst surface).

CONCLUSIONS

The research work described herein has demonstrated that attrition milling is a promising method of producing high-surface-area catalysts from materials that are not otherwise available in suitable forms. In both reactions tested in the present study, new surfaces created by attrition milling were catalytically active. Catalysts of attrition milled crystalline α-quartz and a mixture with α-cristobalite were similar in catalytic activity to conventional silica catalysts. In fact, the milled quartz catalyst had the highest hexane cracking activity of those tested. The observed enhanced cracking activity shown by the attrition-milled silica catalyst could be due to a difference in the level of surface impurities and/or a difference in crystal structure at the surface.

Ammonia adsorption measurements also indicated that the quartz surface had a relatively high degree of acid strength. Although acidity and cracking activity were correlated in past studies, such a correlation was not successful here.

Ethanol dehydration activity was low for the attrition-milled catalysts, probably due to different active sites being required for dehydration. Previous studies indicated that aluminosilicate "acid" sites were not effective for dehydration (*9*). All of the crystalline silica catalysts appeared to have a low activity for ether production from ethanol, yet the attrition-ground materials had relatively good activity for ethylene formation.

Most metal oxide dehydration catalysts favor ether formation at lower temperatures and ethylene formation at higher temperatures. Both thoria and tungsten oxide catalysts have been notable exceptions (*6*). Both behave similarly to the attrition-ground silica materials, favoring ethylene production and producing little ether. No generally accepted explanation exists for the behavior of thoria and tungsten oxide. The distribution of reaction products in ethanol dehydration displayed by the crystalline silicas compared with silica gel and the diatomaceous material appears to be due to minor impurities or the crystalline structure.

Attrition milling may offer an alternate to conventional methods of catalyst manufacture. Other areas where attrition milling may have potential would include the preparation of doped catalysts. It is often desired to dope solid catalyst material with trace quantities of another solid to alter catalytic characteristics. Doping is generally carried out at high temperatures at which high-specific-surface structures would normally be destroyed. With attrition-milled materials, however, the doping could be carried out prior to milling.

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