used as first proposed by Oliensis in 1936 (*1*), or other liquids may be employed whose solvent power differentiates between the relative heterogeneity of such bituminous materials. Solvents such as tetrahydronaphthalene, decahydronaphthalene, and cyclohexane should be of interest in this connection.

The positive spots obtained with furfural and aniline, and particularly with pyridine and nitrobenzene (materials of high solvent power for asphalts), indicate that, while in general for the same class of solvents the solvent power varies frequently with the surface tension of the solvent, there may be a vast difference in the reaction upon asphalt of solvents of equal surface tension but of different chemical types.

Acknowledgment

The authors gratefully acknowledge constructive criticism of this work by E. F. Kelley, U. S. Public Roads Administration, F. V. Reagel of the Missouri State Highway Department, and especially by G. L. Oliensis of the Barber Asphalt Corporation.

Literature Cited

(1) Oliensis, G. L., *Proc. Am. Soc. Testing Materials*, 33, II (1933); 36, II (1936).

(2) Oliensis, G. L., *Proc. Montana Natl. Bituminous Conf.*, 1939, 193, 204.

(3) Winterkorn, H. F., and Eckert, G. W., *Assoc. Asphalt Paving Tech., Proc. Tech. Sessions*, 11, 207–57 (1940).

Vapor-Phase Esterification of Benzoic Acid with Ethyl Alcohol

Effect of Oxides on Catalytic Activity of Silicon Carbide and Alundum

ARTHUR A. VERNON[1] AND BERTRAM M. BROWN[1]
Rhode Island State College, Kingston, R. I.

The vapor-phase esterification of benzoic acid with ethyl alcohol was investigated using, as catalyst, twelve difficultly reducible oxides suspended on Alundum and on silicon carbide. Comparison with previously published results showed that the catalyst mass activity varies with the carrier for the same oxide and is related partly to the way in which the oxide adheres to the carrier.

The best catalyst found was titanium oxide on Alundum at 370° C. A life test on this catalyst mass actually showed an increase in activity with time of use. The best catalyst from the point of view of extrapolated values was magnesium oxide on silicon carbide at 450° C. The relation between conversion and side reactions is emphasized.

THE first paper of this series[2] reported the results of an investigation on the esterification of benzoic acid with ethyl alcohol, using as catalysts difficultly reducible oxides on silica gel. This paper gives the results of further work using silicon carbide and Alundum as carriers.

Experimental

MATERIALS. U. S. P. benzoic acid was used as in the previous work while ethyl alcohol was distilled twice from calcium oxide and once from sodium. The titanium tetrachloride and the salts were C. P. grade; the tungstic oxide was technical; the manganous nitrate was a 50 per cent solution of C. P. grade.

The Alundum was 4–8 mesh material furnished by the Norton Company and the silicon carbide was given by The Carborundum Company. The latter was crystal size No. 6.

TABLE I. CATALYTIC EFFECT OF CARRIERS

	Silicon Carbide			Alundum		
Temp., ° C.	Space velocity of acid	% acid to ester	% acid to side reactions	Space velocity of acid	% acid to ester	% acid to side reactions
410	298	20	..	282	2	16
430	308	21	1	289	3	12
450	316	21	1	298	2	12
430	308	18	2	289	2	12
430	154	20	2	145	8	9
430	77	30	11	72	11	23

TABLE II. CATALYTIC EFFECT OF ZIRCONIUM AND ALUMINUM OXIDES WITH CARRIERS

Zirconium Oxide				Aluminum Oxide			
Temp., ° C.	Space velocity of acid	% acid to ester	% acid to side reactions	Temp., ° C.	Space velocity of acid	% acid to ester	% acid to side reactions
				Silicon Carbide			
410	286	12	2	410	286	43	5
430	295	17	1	430	295	49	5
450	304	18	2	450	304	49	11
450	304	18	3	430	295	49	5
450	152	20	3	430	148	51	9
450	76	31	11	430	74	58	22
				Alundum			
410	285	78	5	390	274	77	12
430	292	79	10	410	282	78	14
450	302	78	12	430	290	66	24
430	292	75	12	410	282	74	17
430	146	75	15	410	141	81	12
430	73	76	15	410	70	81	13

---

[1] Present address, Northeastern University, Boston, Mass.

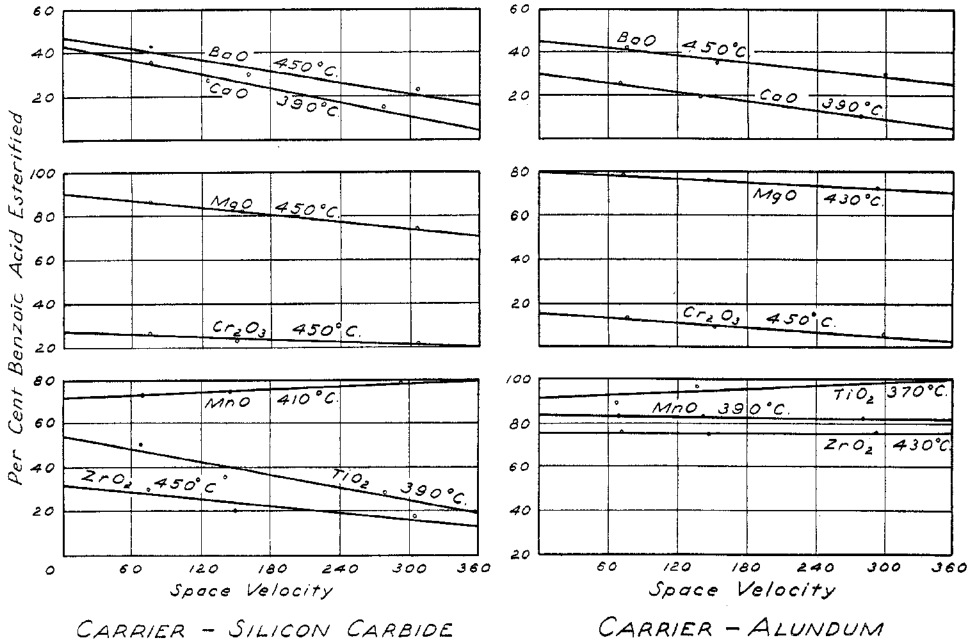

FIGURE 1. VARIATION OF ESTERIFICATION WITH SPACE VELOCITY

PREPARATION OF CATALYSTS. Titanium hydroxide was precipitated on the carrier by hydrolysis of titanium tetrachloride. The Mn_3O_4 catalyst mass was prepared by soaking the carrier in the 50 per cent solution, adding ammonium hydroxide, filtering, and igniting. The tungstic oxide mass was prepared by converting the technical oxide to ammonium tungstate and precipitating the oxide on the carrier with hydrochloric acid. All other catalyst masses were prepared as previously reported[2].

APPARATUS AND PROCEDURE. The apparatus was the same one used in the earlier work, and the experiments were performed under the same conditions. A small proportion of the excess ethyl alcohol was oxidized to acetaldehyde in all the runs, but this was the only alcohol reaction observed other than the esterification.

Results

In the tables space velocity is expressed in liters of vapor per hour per liter of catalyst at the reaction temperature. The reaction mixture was always composed of 5 moles of ethyl alcohol per mole of benzoic acid. Table I shows the catalytic effect of silicon carbide and Alundum; Table II gives typical results for zirconium and aluminum oxides on silicon carbide and Alundum. Table III includes data for optimum temperatures for each catalyst mass and percentage conversions at three different space velocities. These space velocities represent the limits of flow obtainable with accuracy, and the variations in different tests are due to the fact that it was difficult to reproduce rates exactly.

The best catalyst found in the experiments was titanium oxide on Alundum. A 6-hour run was made with this catalyst mass at 370° C. and an acid space velocity of 276. At the start 85 per cent of the acid was converted to ester and 7 per cent was used in side reactions. At the end of 4.5 hours the side reactions had decreased to zero and the acid conversion had risen to 99 per cent. It continued unchanged during the rest of the run.

A comparison with data from the previous paper[2] shows that the catalytic activity of the carriers decreases in the order silica gel, silicon carbide, Alundum. However, in con-

TABLE III. EFFECT OF TEMPERATURE AND SPACE VELOCITY ON CONVERSION

	Silicon Carbide				Alundum			
Oxide	Optimum temp., ° C.	Space velocity of acid	% acid to ester	% acid to side reactions	Optimum temp., ° C.	Space velocity of acid	% acid to ester	% acid to side reactions
ZrO_2	450	304	18	3	430	292	75	12
		152	20	3		146	75	15
		76	31	11		73	76	15
ZnO	450	304	11	4	430	290	8	6
		152	12	5		145	11	4
		76	17	7		72	13	26
MgO	450	304	74	..	430	292	73	5
		152	82	..		146	77	5
		76	86	..		73	78	7
Al_2O_3	430	295	49	5	410	282	74	17
		148	51	9		141	81	12
		74	58	22		70	81	13
Cr_2O_3	450	304	21	..	450	298	5	3
		152	23	4		149	9	9
		76	26	7		75	13	9
CaO	390	278	16	32	390	274	10	42
		139	23	17		137	19	39
		70	37	18		68	24	41
BaO	450	304	23	17	450	298	28	15
		152	29	19		149	34	21
		76	43	31		75	42	38
SrO	450	304	17	9	410	282	7	29
		152	24	10		141	12	28
		76	46	12		71	24	27
BeO	410	286	5	4	450	298	2	12
		143	8	10		149	4	13
		72	14	10		75	13	43
Mn_3O_4	410	287	79	9	390	278	82	11
		143	75	16		139	83	11
		72	74	19		70	83	11
TiO_2	390	278	28	2	370	270	98	..
		139	36	..		135	97	..
		70	49	2		68	88	3
WO_3	390	282	3	9	390	282	0	10
		141	4	12		141	2	12
		70	5	12		71	5	21

---

[2] IND. ENG. CHEM., 32, 534–6 (1940).

trast with silica gel, the other two carriers cause much less carbonization.

The same oxide suspended on the different carriers shows different catalytic properties. Much of the variation here might be attributed to the difference in the amount of oxide which adheres to the surface of the carrier as well as to the variation in surface area afforded for the deposition of the oxide. Magnesium oxide adheres much better to the silicon carbide than to the Alundum or silica gel. It is therefore not surprising to note that the oxide on the carbide is more efficient than on silica gel or Alundum. With those oxides which give poor results on all three carriers, the results are generally higher with the silica carrier. With those oxides which gave good results on all three carriers, the results were generally lower with the silica gel. It is thus evident that the primary factors are the oxide and how well they adhere rather than the activity of the carrier.

Figure 1 shows plots of per cent acid converted to ester against space velocity for some of the better catalyst masses. Manganous oxide on silicon carbide and titanium dioxide on Alundum give a decreasing yield with decrease in space velocity, and an increase in side reactions occurs at the same time. In the life test with titanium dioxide on Alundum the amount of acid esterified increased as the side reactions decreased, thus indicating that the side reactions are very sensitive to catalyst surface. The best catalyst mass from the point of view of extrapolated values was magnesium oxide on silicon carbide. This gave about 90 per cent conversion at 450° C. and zero space velocity. It should be noted that the extrapolated values assume a constant amount of side reaction over all the range. At low space velocities, however, the side reactions may increase faster than the esterification.

Acknowledgment

The authors are grateful to Northeastern University for assistance in the clerical and calculation work.

Carbonaceous Zeolites from Bituminous Coal

S. J. BRODERICK AND DALE BOGARD
Southern Experiment Station, U. S. Bureau of Mines, Tuscaloosa, Ala.

Bituminous coals from Alabama, Indiana, Kentucky, Virginia, and West Virginia have been used in the preparation of carbonaceous hydrogen exchangers by treating with sulfur trioxide at 150° C. The working capacities are from 9500 to 12,800 grains of calcium and magnesium per cubic foot of exchanger.

A study of the physical properties and chemical constitution of the coals revealed no definite characteristic or property upon which exchange capacity is dependent. Narrow particle-size range (−28 to +35) material was used in manufacturing the exchanger and in determining the working capacities.

CARBONACEOUS zeolites have successfully passed the development stage and are now available commercially. The properties of this new material, which is nonsiliceous, of high exchange capacity, rugged, and capable of acting as a hydrogen exchanger, have placed it in a unique field. It found immediate favor in boiler-feed-water conditioning, where the nonsiliceous property is much desired and where control of the acidity of the water is important (*1, 18, 19*).

A previous paper (*3*) dealt with the making of carbonaceous zeolites from Alabama coal refuse and good grades of coal. The method used for exchange activation consisted of digestion of the coal in concentrated sulfuric acid at 100° C. (212° F.) for 3 hours (*15*). The exchange capacity obtained by this treatment was somewhat low, and the early work was limited to Alabama coals. The present investigation was undertaken in cooperation with the University of Alabama and is an extension of the previous report, but an improved method of activation that gave higher exchange capacity is used. Seventeen samples of coal from different fields in five states were used in the study. Physical and chemical analyses of these coals have been completed by the Petrographic Section of the Coal Division of the Bureau of Mines. An attempt was made to correlate the exchange capacity of these coals with the physical and chemical characteristics in order to classify coals according to their suitability as raw materials for carbonaceous exchangers.

Sulfuric acid as an activating agent had certain limitations: (I) reactions of activation were carried out at 100° C. or less; (II) the granulated coal swelled and caked so that the mixture could not be stirred; and (III) the resulting exchange capacity was low, owing perhaps to (I) and (II). Sulfur trioxide (*17*), however, offered a means of activation superior to sulfuric acid; when this was used, these objections were removed.

Apparatus

The design of the apparatus is shown in Figure 1:

It is adapted to the use of sulfur trioxide gas, which is made from commercial sulfur dioxide and oxygen. The tanks containing these gases are shown at the extreme left; after passing through the respective flowmeters, they come in contact with each other in the glass tube leading to the preheater furnace, where the mixed gases pass through a glass tube 1 inch in diameter filled with broken porcelain to facilitate heating to the desired tempera-