

Induction of Catalytic Activity by Neutron Irradiation of Silica and Silica-Alumina

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Induction of catalytic activity, for double bond isomerization of butene-1, in silica by neutron irradiation is demonstrated beyond statistical doubt for a total dosage of $\sim 10^{20}$ nvt. A 1.5- to 3-fold increase of activity occurs, for this dosage level, on catalytically active silica-alumina. The observations are consistent with the assumption that atomic displacements are responsible for the effects.

INTRODUCTION

In previous work (1) it was shown that a statistically significant enhancement of catalytic activity toward double bond isomerization of an olefin, hexene-1, was obtained on pure porous silica, as a result of its irradiation with a total neutron flux of $\sim 10^{19}$ nvt.* Kohn and Taylor have demonstrated (2) an induction of H_2 - D_2 -exchange activity in silica by both X-ray and neutron irradiation. However, Lucchesi, *et al.*, have recently reported (3) a decrease in the activity of silica-alumina for butene-1 isomerization after exposure to neutrons. In the present work we have extended the previous study (1) of the effects of neutron irradiation of these catalysts on double bond isomerization of butene-1 to a tenfold greater dosage of neutrons, i.e. $\sim 10^{20}$ nvt. The purpose has been to raise the effect of irradiation beyond the realm of statistical interpretation. The purity of the materials was designed to eliminate possible ambiguities due to effects involving such impurities, including their possible chemical transmutation.

EXPERIMENTAL

The pure silica was produced from an acidic alcoholic solution of ethyl silicate.

* Neutrons per square centimeter: n = neutron density, neutrons/cm³; v = average neutron velocity, cm/sec; t = time, seconds.

After gelling with NH_4OH , the material was water-washed, dried with steam at 130°C, and finally calcined for 16 hr at 540°C. The final product contained <10 ppm Al_2O_3 , 5 ppm Ni, 10 ppm Fe, 9 ppm Cu, and 10 ppm V.

The silica-alumina contained 10.3% Al_2O_3 . It was prepared by gelling, with NH_4OH , a mixture of ethyl silicate and aluminum chloride. The hydrogel was aged for 16 hr at 43°C before being washed free of chloride, dried at 130°C, and calcined for 10 hr at 540°C. Impurities were: Ni, 5 ppm; Fe, 100 ppm; Cu, 9 ppm; and V, 10 ppm.

These materials were irradiated in the facilities of the Industrial Reactor Laboratories, Inc. The oxide powders were placed in aluminum thimbles, calcined at 525°C for 16 hr under oxygen, and cooled in a desiccator. The thimbles were sealed by lead "stoppers," and pressed into place using a small pressure from a hydraulic press. Both oxides were irradiated simultaneously, present in the same reactor positions. A measure for the flux of neutrons was obtained by the resultant activation of cobalt wires placed immediately beneath the thimbles. The total flux was thus estimated to be $\sim 10^{20}$ nvt. Catalytic measurements were made approximately 6 months after completion of the neutron exposure, at which time the radioactivity

amounted to less than 0.25 mr/hr measured at contact with the sample-containing vials.

The catalytic activities of the irradiated and control catalysts were measured at atmospheric pressure in a flow microreactor which could accommodate 0.2 to 0.5 g of catalyst. The molar flow rate of butene-1 was measured using a capillary and differential manometer. Analyses were obtained by diverting portions of the effluent gas stream through a chromatographic column by means of a helium carrier stream. The chromatographic column consisted of 35 wt % of a *n*-propyl sulfone/dimethyl sulfolane mixture (73/27 by volume) on firebrick. The column length was 10 ft which gave excellent separation of butene-1, *cis*-butene-2, and *trans*-butene-2 at room temperature.

Each catalyst sample was pretreated at 370°C in a flow of air for 1 hr with subsequent cooling to the lowest reaction temperature in flowing helium. This relatively mild temperature was used to prevent annealing of defects. However, with the silica-alumina catalysts, no apparent difference was found in the activities measured after a pretreatment at 370°C or 540°C. In no case was the activity measured at a temperature which was above that of the pretreatment.

The surface areas of the solids were measured by a conventional BET volumetric procedure.

RESULTS

The observed conversion and product-isomer data for the catalysts are listed in Table 1 along with calculated rate con-

TABLE 1
ISOMERIZATION OF BUTENE-1 BY SILICA AND SILICA-ALUMINA

Catalyst	Weight (g)	Temperature (°C)	Molar flow (mmoles/min)	Butene-1 (mole %)	<i>Cis/trans</i>	k, (mmoles)/(min)(g)
SiO ₂ , unirradiated	0.191	371	1.23	99.86	1.14	0.0087
			1.23	99.81	2.40	0.0120
SiO ₂ , irradiated	0.201	288	2.46	97.34	1.00	0.236
			1.23	95.14	1.07	0.258
			0.533	89.95	1.04	0.261
		316	2.46	96.86	1.03	0.298
			1.24	94.09	1.04	0.329
			0.533	87.18	1.03	0.343
		343	0.492	84.54	1.00	0.392
			371	1.23	92.53	1.41
	0.496	78.50	1.09	0.578		
SiO ₂ /Al ₂ O ₃ , unirradiated (1st aliquot)	0.211	38	1.34	99.57	1.39	0.0273
		93	1.34	94.86	1.22	0.335
			1.34	94.62	1.08	0.351
		149	1.34	61.50	0.96	3.09
SiO ₂ /Al ₂ O ₃ , unirradiated (2nd aliquot)	0.245	66	1.23	98.39	1.36	0.0813
		93	1.23	92.06	1.48	0.406
		121	1.23	77.27	1.03	1.29
SiO ₂ /Al ₂ O ₃ , irradiated (1st aliquot)	0.208	38	1.34	98.19	1.21	0.118
		93	1.34	89.86	1.18	0.690
				89.42	1.92	0.721
		149	1.34	52.4	0.76	4.17
SiO ₂ /Al ₂ O ₃ , irradiated (2nd aliquot)	0.195	38	1.23	98.75	1.02	0.0790
		66	1.23	96.24	1.02	0.242
		93	1.23	88.05	1.02	0.802
		121	1.23	69.30	0.90	2.31

stants for the conversion of the butene-1.

The rate constants were derived by assuming a first order reaction. They are defined by

$$k = (f_m/w) \ln (B/B_0)$$

where f_m is the total molar flow rate of reactant and products, w is the weight of catalyst, and B_0 and B are the concentrations of reactant charged and remaining

after contact, respectively, in any convenient relative units.

Figure 1 illustrates measured rate constants for the silica catalysts presented in the form of an Arrhenius relationship. The irradiated silica has been raised to an activity of at least one and one-half orders of magnitude above that of the control catalyst. This represents a conservative estimate inasmuch as the conversions

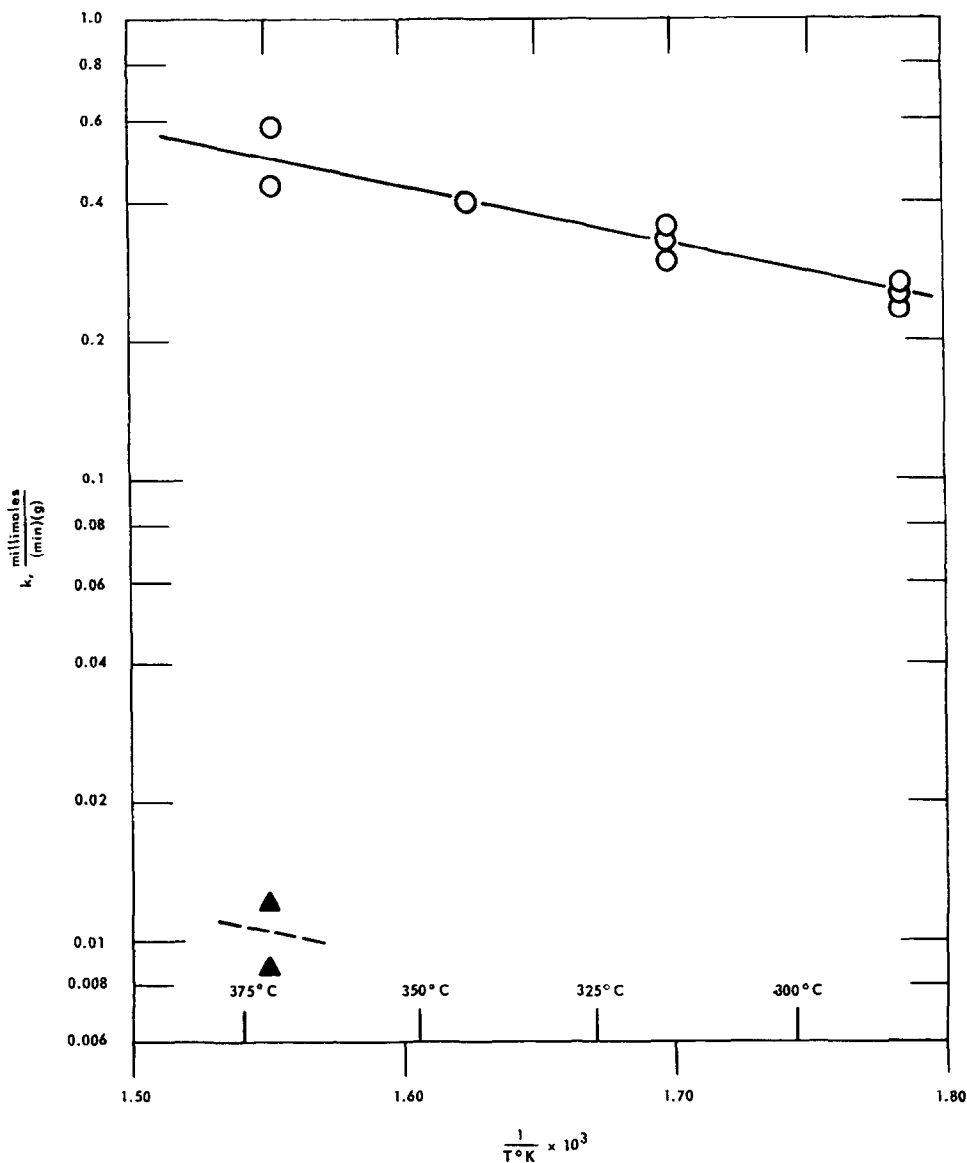


FIG. 1. Butene-1 isomerization over silica; ○, irradiated; ▲, unirradiated.

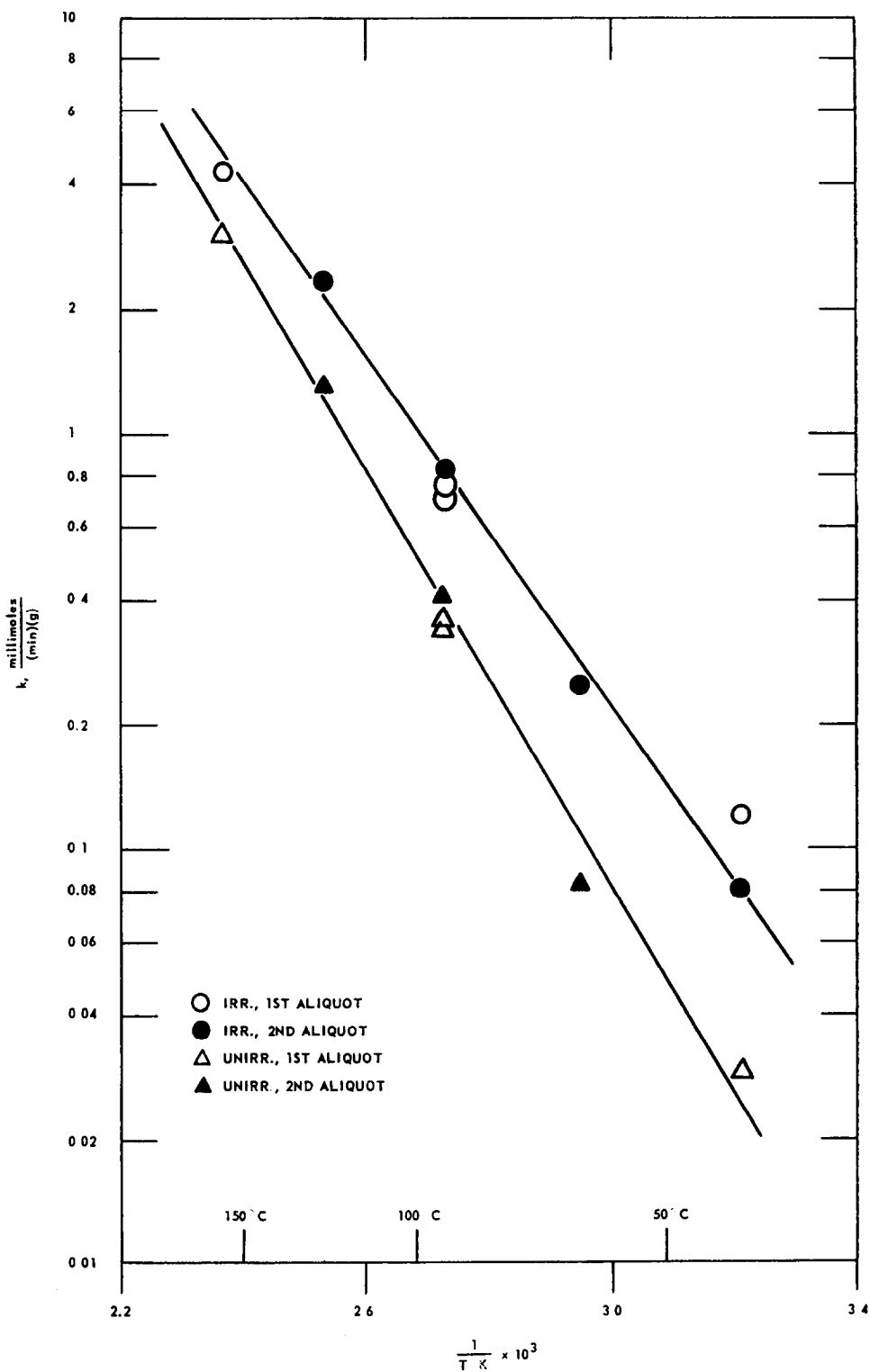


Fig. 2. Butene-1 isomerization over silica-alumina.

measured for the control catalyst were small and approached in magnitude results obtained in "blank" experiments, i.e. thermal contacts without catalyst in the contact space. The activation energy calculated from the slope is 5.7 kcal/mole.

Figure 2 similarly presents the data obtained with the silica-alumina catalysts. Although the effect of the irradiation is smaller than that for silica it still corresponds to a 1.5- to 3-fold activation. In order to define the effect of irradiation with more certainty, two aliquot portions of each of the catalysts were used. The observed temperature dependence would calculate to activation energies for the isomerization of butene-1 over the unirradiated silica-alumina of 11.4 kcal/mole, and of 9.7 kcal/mole for the irradiated catalyst.

The product selectivity shown by the catalysts can be characterized by the ratio *cis*-butene-2/*trans*-butene-2 found in Table 1. The values fall in the range of ~ 0.75 to ~ 1.5 ; a majority of the values lie between 1 and 1.2. With increasing conversion of the butene-1, the *cis/trans* ratio declines in a manner apparently independent of the catalyst, neutron irradiation, and the temperature used to measure the conversion. Only at conversion levels $>25\%$ does the *trans*-butene-2 predominate.

A gross effect of the irradiation was noticed in the changes in surface areas. The measured BET areas are given in Table 2. The reduction resulting from neu-

on a surface area basis would, of course, show an even greater effect of irradiation.

DISCUSSION

Previous studies (1-4) have involved total neutron dosages ranging between 10^{15} and 10^{18} nvt. Prior evidence of the activation of silica for olefin double-bond isomerization (1), at a dosage level of 10^{18} - 10^{19} nvt, had to rely partly on a statistical test for significant effects. At the higher dosage level of this study, such activation appears to be demonstrated beyond statistical doubt.

It had been estimated (1) that 10^{19} neutrons/cm² could result in a fraction of dislocated atoms approaching the order of magnitude of a per cent of the normal lattice sites. Indeed, Wittels and Sherrill (5) have shown that at this level of irradiation measurable changes of bulk properties, such as the density, begin to appear. The changes in the surface area of both silica and silica-alumina which have occurred in this study are consistent with these previous estimates and observations.

The enhancement of the already high activity of silica-alumina for double bond isomerization is in direct contrast to the observations reported by Lucchesi *et al.* (4), who noted a decrease of activity for the same reaction. It must be noted that their total irradiation dose was about one order of magnitude smaller than ours and that their catalyst undoubtedly differed in method of preparation from ours. Because a large inherent activity exists in silica-alumina, due to the presence of a second component in the silicate-structure, it is possible that irradiation may, in addition to the creation of active sites in the silica matrix, affect already existing sites. The superposition of both phenomena could lead to a net deactivation, followed by net activation at higher dosage levels. The second consideration (a significant difference in starting materials) is suggested by the nature of the isomer distribution of the products of Lucchesi *et al.* as compared to ours.

In our study the initial *cis*-butene-2/

TABLE 2
SURFACE AREAS

Catalyst	Surface area (m ² /g)
Silica, unirradiated	395
Silica, irradiated	354
Silica-alumina, unirradiated	274
Silica-alumina, irradiated	218

tron bombardment is large; $\sim 10\%$ for silica and $\sim 20\%$ for silica-alumina. Because of this reduction, activities placed

trans-butene-2 ratio at low conversion was found to be ~ 1.5 and to undergo a decrease at higher conversion; this change was independent of the irradiation. Similar values of ~ 1.2 were observed by Brouwer (6) to characterize the selectivity of conventional unirradiated silica-alumina (Ketjen MS3-A fluid catalyst). Haag and Pines (7) also found a *cis/trans* ratio of ~ 1.7 for the initial conversion over an unidentified silica-alumina. However, Lucchesi *et al.* used a pelleted silica-alumina (Davison, 13% alumina) catalyst; they also found an independence of the *cis/trans* ratio from the radiation dosage, but their initial ratios were as high as ~ 6.5 .

Thus the differences in the initial isomer ratio appear to depend upon the nature of the starting catalyst composition. The similarity of the isomer ratio for non-activated and for radiation-activated ma-

terial in all cases suggests that the active centers created are not dissimilar in their mode of catalytic action.

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