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The Catalytic Activity of Silica Gel

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We have investigated the isomerization at 100 and 200°C in hydrogen carrier of 1-hexene, 2-methyl-1-pentene, and 2-ethyl-1-butene on various silica gels activated in oxygen at 500°C and then hydrogen at 400°C. Davison gels 59 and 70 isomerize 1-hexene rather slowly, but the other two olefins, several hundred times more rapidly. A gel made by the hydrolysis of purified ethyl orthosilicate exhibits only about $\frac{1}{30}$th the activity of Davison 59. However, dosed with $Al(NO_3)_3$ to $Al/Si = 0.0002$, it is more than 100 times as active as Davison 59. Dosed with $(NH_4)_2SO_4$, it is about as active as Davison 59 but this dosed gel activated to only 400°C in oxygen is seven times as active. The isomerization of 1-hexene on these catalysts gives somewhat more *trans*- than *cis*-2-hexene. Only very small amounts of skeletal isomerization occur.

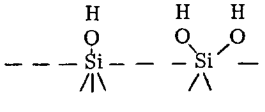
The site density was measured by poisoning by ammonia. The turnover number for isomerization of 1-hexene was several hundred times greater for the sites on the Al^{3+}-dosed gels than for those on Davison 59.

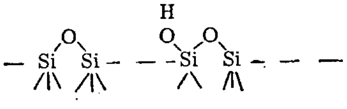
Many reactions reported to be catalyzed by silica gel probably occur at impurity sites, most likely Al^{3+}.

INTRODUCTION

It is often desirable to disperse the ingredient which is catalytically active in a heterogeneous catalytic reaction upon a support (*1*) and, in many cases, upon a support which itself has as little catalytic activity as possible. Silica gel is a relatively inactive support which has the advantages of being available in forms of high area in a number of differing textures and of resisting sintering. It is one of the most employed of the "inert" supports, but there is considerable question as to just how catalytically inert it is.

Silica gel consists of an agglomeration of primary particles of amorphous silica of a diameter of the order of magnitude of 10 nm (100 Å) (*2*). The porosity of the gel is like that of a loosely cemented gravel bed. After evacuation at about 150°C to remove hydrogen-bonded water, the gel is covered with silanol (≡SiOH) groups, about 5 per nm². Upon heating above 150–200°C, silanol groups condense to form strained surface siloxane groups and water and only about 2 silanol groups per nm² remain at 500°C (*2*). Thus, one might expect to find the following surface species at the surface of silica gel although not all, perhaps, under the same conditions of pretreatment.





Surface silanol groups are weakly acidic with pK_a's which are probably in the vicinity of 9–10 (*3*). One would hardly expect pure silica to function as a catalyst in a reaction known to require rather strong acids. Nor would one expect the surface groups shown above to provide elementary processes which could lead to the catalytic hydrogenation or isomerization of olefins nor, indeed, to many reactions of any nature. Nevertheless, scattered throughout the literature are a number of reports of silica gel as a heterogeneous catalyst (*4*).

Gallaway and Murray (*5*) observed silica gel to cause isomerization of 2,2,4-trimethyl-1-pentene to 2,2,4-trimethyl-2-pentene at 25°C (or, whatever temperature the gel reached as a result of the heat of adsorption). 1-Hexene did not react under the same conditions. Walling (*6*) suggested that this isomerization resulted from impurity of mineral acid in the gel. However, washing the gel with aqueous base has been reported not much to reduce similar isomerizations (*7*). Isomerization of unbranched olefins has been recorded at higher temperatures on silica gel, for example, of 1-butene to 2-butenes at 200°C (*8*).

Hunter and Brogden (*9*) observed double bond isomerizaton of limonene at 100–150°C and also disproportionation to cymene and menthenes. They suggested that there might be some alumina impurity in their silica gel and that such impurity might be the origin of the catalytic activity. Rudakov and Shestaeva (*10*) provided evidence for a catalytic effect of small quantities of alumina. A gel made by hydrolysis of silicon tetrachloride was inactive for the skeletal isomerization of α-pinene, but incorporation of only 0.13 mole % aluminum (in total Si + Al) gave substantial activity.

One of us (*11*) observed that pure silica gel from the hydrolysis of ethyl silicate was nearly inactive for the isomerization of 1-hexene at 200°C but that addition of 0.002 mole % aluminum imparted detectable activity. This led to other observations in this laboratory. A commercial silica gel, Davison Grade 70, catalyzed the conversion of 2-propanol + 2-butanone to propanone + 2-butanol at 120°C, but pure gel was inactive at 175°C (*12*); 2-methyl-1-butanol was unaffected by pure gel at 190°C, but even 0.02% aluminum imparted detectable dehydration activity (*13*).

Since a truly inert support would be particularly useful in the study of heterogeneous catalytic reactions of hydrocarbons, we have further examined the behavior of olefins on pure silica gel, on silica gel containing small quantities of surface alumina, and on pure gel dosed with ammonium sulfate. The last material derives from the work of Shibata, Kiyoura, and Hayashi (*14*), who found that pure gel, which was inactive for the depolymerization of paraldehyde at 26°C, became active after impregnation with ammonium sulfate and heating to 400°C owing, they suggested, to formation of adsorbed ammonium bisulfate.

EXPERIMENTAL

Olefins from the Chemical Samples Co., Columbus, OH, were distilled from potassium and stored under nitrogen (1-hexene) or at −78°C. By gas chromatography, 1-hexene and 2-ethyl-1-butene each contained about 0.1% of other olefins. 2-Methyl-1-pentene contained a total of about 1% of other olefins and 2-methylpentane. Prepurified hydrogen was passed through a thimble of 75% palladium–25% silver as it entered the apparatus and commercial grade oxygen, through Linde Molecular Sieve 5A.

The wide pore silica gel employed was Davison Grade 59 or, in earlier experiments, Grade 70. The two are very similar. The manufacturers analysis reports 0.10 percent Al_2O_3, 0.01% Fe_2O_3, 0.02% TiO_2, 0.07% CaO, 0.06% Na_2O and 0.03% ZrO. The nominal pore diameter is 14 nm. The gel was crushed and sieved to 40–60 mesh in carefully cleaned sieves reserved for use with silica gels. Commercial gels were soaked in ten successive portions of 0.1 *M* hydrochloric acid, then in ten batches of doubly distilled water, and dried at 145°C in an oven.

Gels 7, 8, and 9 were prepared by mixing 400 cc of ethyl orthosilicate which had been fractionally distilled with 250 cc of absolute ethyl alcohol and about 170 cc of doubly distilled water which was 0.05 or 0.12 *M* in nitric acid. After about 1 hr, aqueous ammonia (prepared from doubly distilled water and gaseous ammonia) of about the same molarity as that of the nitric acid employed was added in slight excess, and the material allowed to gel in flat polyethylene vessels to give a slab about 1 cm thick. After being cut into cubes of 1 cm edge, the gel was soaked in polyethylene vessels in 16–19 changes of doubly distilled water and then dried for several months over calcium chloride. A sample of gel 7 of finer mesh than those used in our experiments was kindly analyzed by C. J. Perry of the Universal Oil Products Company for content in aluminum by atomic absorption spectroscopy. He found 0.0072% by weight of Al_2O_3. Whether the analytical sample had become contaminated vs the samples used in our catalytic runs or whether the Al^{3+} in gel 7 was of a buried type is not clear.

Nitrogen physisorption isotherms were measured on the gels using an Aminco Adsorptomat. The gels were activated as described later, transferred to a sample tube, and evacuated at 200°C overnight before runs. The surface areas in m^2/g, average pore diameters in nm from the desorption branch of the isotherm, and porosity in cc/g were: Davison Grade 70: 265, 13.2, 1.08; Gel 7: 650, 4.0, 0.66; Gel 8: 641, 2.2, 0.36; Gel 9: 669, 2.6, 0.40. A few experiments were run on Davison Grade 950 silica gel, the reported physical properties of which are essentially identical to those of Gel 8 above.

Gel 12 was prepared from Gel 7 to contain 0.012 mole % Al.* Gel 7 was impregnated with a volume of water which contained the desired amount of aluminum nitrate and then dried at 140°C.

A flow reactor with Teflon needle valves was used. The hydrogen passed through a bed of 40–60 mesh Filtros-FS140, the pores of which were filled with deaerated olefin (*15*). The bed was thermostatted at that temperature which made the ratio (partial pressure of hydrogen)/(partial pressure of olefin) = 3. The hydrogen–olefin vapor then passed through the catalyst held between Pyrex glass wool plugs in the vertical arm of a U-tube. Thence, the gas passed through a trap cooled in Dry Ice to collect samples, through a rotameter, and when desired through a soap film flowmeter.

In most experiments, 1.0–1.5 g of silica gel was heated in flowing oxygen to 500°C at 2°C/min, held for 4 hr, evacuated while cooling to 400°C, flushed with hydrogen for 4 hr, and cooled in flowing hydrogen to reaction temperature. The oxygen treatment was designed to burn off any adsorbed organic matter and, for the pure gel, to eliminate unhydrolyzed ethoxy groups. The hydrogen treatment at 400°C was designed to eliminate any adsorbed oxygen and to simulate conventional treatment of silica-supported catalysts. Hydrogen was used as a carrier gas by analogy with hydrogenation studies of olefins on silica-supported catalysts. After the catalyst had reached reaction temperature, deaerated olefin was introduced into the saturator, and, after some minutes to allow the system to come to a steady state, collection of a product sample was started. Unless otherwise stated, the olefin flow rate was about 3.3 millimole g^{-1} hr^{-1}, and the hydrogen flow rate was three times larger.

Analyses were performed on a 5-m column of 7.5% dimethylsulfolane on Anakrom C22a (firebrick) at 25°C using hydrogen flame detection. Where the most detailed analyses were needed, in particular, to separate *cis*-3- and *trans*-2-hexene, a 15-m column at 0°C was used. Where appropriate, conversions were corrected for the content of impurity in the feed olefin.

Runs at 200°C in an empty tube activated in the standard fashion gave negligible conversions of 1-hexene, but untreated Pyrex wool about (0.12 g) similarly pretreated gave 5.6% isomerization and 2.4% hydrogenation at a total flow rate of 5 mmole of 1-hexene/hr. If the Pyrex wool was first treated with a mixture of 1 vol of concentrated nitric acid to 10 of sulfuric acid at about 85°C, washed with water, and heated in air overnight at 560°C, the isomerization was 0.23% and the hydrogenation, 0.13%. MacDonald and Hayes have reported rather similar results of pretreatment for the catalytic activity of glass wool in the oxidation of carbon monoxide (*16*). About 0.12 g of Pyrex wool so treated was used to contain the samples of silica

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* Throughout this paper, mole % Al is taken to signify mole % of Al in Al + Si.

gel in our experiments, and corrections were made to the observed conversions from the data above. At 100°C, conversions on the treated Pyrex wool were negligible. Similar effects of treatment but slightly smaller conversions were observed on Amersil fused silica wool.

The commercial silica gels gave substantial conversions. The rate of deactivation of Davison Grade 70 for the isomerization of 1-hexene was measured at 200°C. At 0.5 hr, the conversion was 35%, and it was constant at 30% from 1.5 to 8 hr. At 100°C, activity appeared to decline somewhat more rapidly. Selectivities were unaffected by deactivation. Catalysts were periodically reactivated by repetition of the original activation.

A number of runs with 1-hexene at varying flow rates were made on Davison 59 at 200°C and analyzed on the 15-m chromatographic column so as to determine initial selectivities. Total conversions varied from 54% on fresh catalyst at the standard flow rate to 2%.

Measurement of the rates of isomerization of trisubstituted ethylenes required large space velocities. On Davis 70 at 100°C, 2-methyl-1-pentene was 35% isomerized at a flow rate of 101 mmole g^{-1} hr^{-1} with 2-methyl-2-pentene being the only product detected. 2-Ethyl-1-butene appeared to isomerize several times more rapidly to give *trans*- and *cis*-2-methyl-2-pentene in a ratio of 1.8 (in *cis*-, the methyl groups are *trans*). Rate ratios could not be measured by feeding equimolar mixtures of 1-hexene and either tri-substituted ethylene. At measureable conversions of hexene, the methylpentenes were near equilibrium. However, the added olefin reduced the fractional isomerization of 1-hexene by a factor of about 10.

In a few experiments, Davison 70 and 59 were activated merely by heating in hydrogen. Activation at 303°C and 400°C gave gels of somewhat lower catalytic activity but of the same general catalytic properties.

The pure gels were much less active. At 200°C, for example, conversions of 1-hexene were: gel 7, 1.5%; gel 8, 1.6%; and gel 9, 4.7%. Selectivities to the various isomeric olefins were about the same as on Davison 70.

Gel 12 (gel 7 + 0.012 mole % Al^{3+}) was very active. At 100°C, even at a flow rate of 71, the residual 1-hexene amounted only to 14.1% (equilibrium, 2–3%). The yield of detectable methylpentenes at this flow rate was about 0.1%. On the other hand, activity for hydrogenation was undetectable even at the standard flow rate at 200°C.

The effect of the addition of small amounts of basic nitrogen compounds was examined. They were injected through a septum which was added just ahead of the catalyst. The injection of 0.04 cc/g of pyridine on Davison 70 almost completely eliminated activity for isomerization of 1-hexene at 200°C. Evacuation at 300°C overnight restored only about 0.1 of the activity. Injection of 0.005 cc/g onto a gel containing 0.006 mole % Al^{3+} also essentially completely eliminated activity at 200°C. This quantity of pyridine corresponds to 1 molecule/7 nm^2. However, the same amount of pyridine only reduced the activity for isomerization of 2-methyl-1 pentene to about one-third of the initial.

The effect of ammonia in smaller quantity on the isomerization of 1-hexene at 100°C was examined. It was established that all ammonia was adsorbed at least initially. Injection of 0.047 cc/g onto Davison 70 reduced conversion from 3.8 to 1.5%. On the simplest basis, then, complete loss of activity would correspond to 0.078 cc/g or 2×10^{18} molecules/g. This corresponds to 140 nm^2 per molecule of ammonia.

After injection of 0.047 cc/g onto gel 12, the conversion was 54.2%, after another 0.047 cc/g, 18.4%. Complete loss in activity would correspond to 200 nm^2 per molecule of ammonia.

A sample of pure gel 7 was impregnated with 0.1 mmole of ammonium sulfate/g and activated as usual, except that the temperature of oxygen treatment was only 400°C. 1-Hexene was passed over the gel under standard conditions at 100°C. After 45 min, the conversion was 39.3%. Activity declined with time and was 26% at 7 hr, and the gel became brown in contrast to all other cases. In a similar experiment with the usual activation (oxygen at 500°C), the initial conversion was only 6.5%. In both experiments, selectivities to the hexene isomers were little different from Grade 70, and hydrogenation was not detectable. Trace amounts of methylpentenes appeared to be formed but at concentrations too low for reliable measurement. Detectable skeletal isomerization proceeded at a rate no greater than 0.0005 that of double bond migration.

DISCUSSION

Davison Grade 59 silica gel and its very similar antecedent gel, Davison 70, are wide pore gels (pore radius about 7 nm) with large specific pore volumes. These gels have been frequently used as catalyst supports during the past few years because their textural characteristics would tend to give less severe mass transport effects than those of narrow pore gels like Davison 950.

Table 1 provides some rough values for rates of isomerization of olefins in hydrogen carrier at 100°C on Davison 59 or 70 activated in oxygen at 500°C and then in hydrogen at 400°C. The partial pressures of olefin and hydrogen were ¼ and ¾ atm, respectively.

TABLE 1
RATES OF ISOMERIZATION ON SILICA GELS AT 100°C

Gel	Rate of isomerization [mmole hr^{-1} (g catalyst)$^{-1}$]	Turnover No. [sec^{-1}]
Isomerization of 1-hexene		
59 or 70	0.2	0.01–0.02[a]
pure	0.006	
pure + 0.012% Al	60	3[a], 8[b]
pure + $(NH_4)_2SO_4$		
act at 400°C	1.4	
act at 500°C	0.2	
Isomerization of 2-methyl-1-pentene		
59 or 70	~50	~4[a,c]
Isomerization of 2-ethyl-1-butene		
pure	0.6	

[a] Number of sites from ammonia poisoning.

[b] Number of sites assuming each added Al^{3+} is a site.

[c] Not very meaningful since not all sites are poisoned by ammonia.

Although some of the rates are rather crude estimates, they serve to indicate the general level of catalytic activity. We have assumed that Davison 70 and 59 are equivalent catalytically, but this was not tested in all of the reactions above. The activity for the isomerization of 1-hexene on Davison 70 was about eight-fold greater at 200°C than at 100°C.

Table 2 gives the composition of the initial hexene product of the isomerization of 1-hexene on Davison 59 as determined by extrapolation to zero conversion. Some 3-hexene is an initial product unlike the case for isomerization on alumina at 250°C (*17*). The initial ratio, *cis*-2-hexene/*trans*-2-hexene, is larger than the reported experimental equilibrium ratio. The decline in apparent selectivity to *cis* which we observed at higher conversions supports this conclusion. In addition to 2- and 3-hexenes, the initial product contains 0.2% of detectable methylpentenes. Skeletal isomerization is probably several fold higher because 2-methylpentenes were obscured by hexenes in our gas chromatographic analysis. The initial product also contained 0.5–1.5% hexane, but this value is of low accuracy because of the blank on Pyrex wool. Davison 950 behaved similarly but gave much more hydrogenation, over fifty times more at the same flow rate.

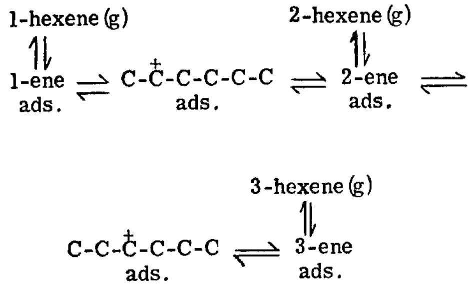
As shown in Table 1, trisubstituted olefins isomerize 200 or more times faster than 1-hexene. This accords with the view that

TABLE 2
COMPOSITION OF HEXENES FROM THE ISOMERIZATION OF 1-HEXENE ON DAVISON 59 AT ZERO CONVERSION AT 200°C

	cis-2-hexene	*trans*-2-hexene	*cis*-3-hexene	*trans*-3-hexene
Davison 59	40	54	1	5
Equilibrium[a]	21	53	26	

[a] From Ref. 18.

the isomerizations proceed via a carbonium ion-like mechanism (*17*), since the trisubstituted olefins can form a tertiary carbonium ion. The isomerization of 1-hexene can then be represented:



The rate 2-hexene(ads) → 2-hexene(g) must be fast vs 2-hexene(ads) → $C{-}C{-}\overset{+}{C}{-}C{-}C{-}C$ but not tremendously so, since some 3-hexene is an initial product.

A pure gel made from purified ethyl orthosilicate gave much lower rates of olefin isomerization as shown in Table 1. The rate listed at 100°C is that at 200°C corrected on the assumption that the ratio of rates at 200°C and 100°C is the same as for Davison 70. We do not know whether the observed activity of the pure gel represents the intrinsic activity of silica gel or the effect of residual impurity. As mentioned in the introduction, similar differences in activity between Davison 70 and pure gel appear in the catalysis of the alcohol–ketone interchange reaction.

Thus, standard commerical gels exhibit substantial catalytic activity for olefin isomerization at 200°C. Activity at 100°C might often be significant vs that of a catalytic ingredient supported on the gel. At room temperatures, activity would probably be negligible for most purposes, but reactions involving trisubstituted olefins might be confused by the activity of the support. The use of pure gel would almost always eliminate complications.

There have been two suggestions as to the impurities which might impart 'excess' activity to silica gel: surface Al^{3+} and surface mineral acid. We studied a pure gel impregnated with aluminum nitrate, dried, and activated. The ratio Al/Si was 0.00012 and, presumably, the Al^{3+} was all or largely on the surface. As shown in Table 1, the gel was very active, about 10^4 times more active than the pure gels and about 300 times more active than Davison 70. Even at 60°C at the standard flow rate, 79% of 1-hexene was isomerized. Somewhat erratic activities were obtained in scanning experiments with gels of much lower content in Al^{3+} but, considering the traces of Al^{3+} involved in their preparation, this is not surprising. However, gels in which Al/Si was 0.00001 were clearly rather active. The selectivities for isomeric products in the isomerization of 1-hexene were essentially the same as for Davison 59, but the very high activity of these gels did not permit comparison at the same temperature.

As reported in Table 1, a pure gel impregnated with ammonium sulfate is a catalyst for the isomerization of 1-hexene after it has been activated. The selectivities for *cis*- and *trans*-2-hexene on this gel are nearly the same as those on Davison 59. The gel is rather active after activation at 400°C but much less so after activation at 500°C. Our preparation of this catalyst duplicated that of Shibata, Kiyoura, and Hayachi (*14*), who suggested that the active catalyst was NH_4HSO_4 formed during the activation process. However, the active catalyst might be adsorbed H_2SO_4 or the surface species $\equiv Si{=}O{=}SO_3H$, molecular analogies to which are known (*19*). We doubt that sulfuric acid or the like was responsible for the catalytic activity of the commercial gels which we studied. Protracted extraction by 0.1 *M* hydrochloric acid should have eliminated sulfate. It is, however, conceivable if unlikely that the gels contained traces of encapsulated sulfuric acid which migrated to the surface during activation.

Pyridine added at 1 molecule/7 nm^2 completely poisons the isomerization of 1-hexene on Davison 70 at 200°C. From the effect of dosing with ammonia on this isomerization at 100°C, the area per site is crudely about 1 site/140 nm^2 for Davison 70 and 1 site/200 nm^2 for the Al^{3+}-dosed gel. These values are lower limits, since we do not know that the ammonia was adsorbed completely selectively at the catalytic sites. From its Al^{3+} content, there is one $Al^{3+}/540\ nm^2$ for the Al^{3+}-dosed gel, which is in fair agreement with the value derived from ammonia poisoning.

Turnover numbers for Davison 70 derived from the site density measured by ammonia poisoning are shown in Table 1. If the activity of Davison 70 results from Al^{3+} impurity, the environments of Al^{3+} on Davison 70 and the Al^{3+}-dosed gel are different, since the turnover number is much greater on the latter catalyst. Per site, the Al^{3+}-dosed gels are very active indeed. This may be the result of isolation and a lower degree of incorporation of the Al^{3+} into the silica structure in the impregnated pure gel. Such a proposal has been made by Bourne, Cannings, and Pitkethly (*20*) with respect to adsorption of benzene and the dealkylation of *t*-butylbenzene at about 200°C on Al^{3+}-dosed silica gels containing about 0.4 mole % Al^{3+} made by cogelling and by impregnation. Since they observed that a commercial silica gel which contained 0.04 mole % Al was inactive for the dealkylation, a buried type of Al^{3+} must also exist. Similar variation in the type of Al^{3+} appears in studies of the adsorption of triethylamine and in the uv absorption spectrum of certain organic molecules (*21*).

There is substantial evidence that the isomerization of olefins on conventional silica–alumina catalysts occurs not at the Al^{3+} site but on a low polymeric material which forms at this site (*22*). Our data do not establish whether such polymer is involved on the commercial gels or on the pure gel dosed with very low contents of Al^{3+}. The gels do deactivate with use, but the rate of deactivation of Davison 70 is rather low.

Davison 59, 70, and particularly 950 gave small amounts of hydrogenation, but the rate of hydrogenation on the greatly more active Al^{3+}-dosed pure gel was negligible even at 200°C at the standard flow rate. We suspect that the hydrogenation activity of the commercial gels may result from traces of transition metals, most probably iron.

A rather large number of catalytic reactions have been reported to occur on silica gels (*4*), and in most cases, even the most recent, the authors of the reports have not considered the possible role of impurities. We strongly suspect that most of the reported reactions will turn out to depend upon impurities in the silica gel.

REFERENCES

1. DOWDEN, D. A., "I. Chem. E. Symposium Series No. 27," p. 18. Inst. Chem. Engrs., London, 1968.

2. OKKERSE, C., *in* "Physical and Chemical Aspects of Adsorbents and Catalysts" (B. G. Linsen, Ed.), Chap. 5. Academic Press, London, 1970.

3. BURWELL, R. L., JR., PEARSON, R. G., HALLER, G. L., TJOK, P. B., AND CHOCK, S. P., *Inorg. Chem.* **4,** 1123 (1965).

4. For a detailed survey, see: WEST, P. B., Doctoral Dissertation, Northwestern University, 1973.

5. GALLAWAY, W. S., AND MURRAY, M. J., *J. Amer. Soc.* **70,** 2584 (1948).

6. WALLING, C., *J. Amer. Chem. Soc.* **72,** 1164 (1950).

7. LANDA, S., AND MARKOVEC, L., *Coll. Czech. Chem. Commun.* **29,** 2309 (1964).

8. ZHARKOVA, V. R., AND MOLDAVSKII, B. L., *Zhur. Obshchei Khim* **17,** 1268 (1947).

9. HUNTER, G. L. K., AND BROGDEN, W. B., JR., *J. Org. Chem.* **28,** 1679 (1963).

10. RUDAKOV, G. A., AND SHESTAEVA, M. M., *J. Gen. Chem. USSR* **29,** 2030 (1959).

11. HALLER, G. L., Doctoral Dissertation, Appendix V, Northwestern University, 1966.

12. PATTERSON, W. R., AND BURWELL, R. L., JR., *J. Amer. Chem. Soc.* **93,** 833 (1971).

13. KOBYLINSKI, T. P., AND PINES, H., *J. Catal.* **17,** 384 (1970).

14. SHIBATA, K., KIYOURA, T., AND HAYASHI, Y., *J. Res. Inst. Catal. Hokkaido Univ.* **19,** 29 (1971).

15. BURWELL, R. L., JR., HALLER, G. L., TAYLOR, K. C., AND READ, J. F., *Advan. Catal.* **20,** 1 (1969).

16. MACDONALD, R. W., AND HAYES, K. E., *J. Chem. Soc. Chem. Comm.* **1972,** 1030.

17. MAUREL, R., GUISNET, M., AND PEROT, G., *J. Chim. Phys. Physicochim. Biol.* **68,** 573 (1971).

18. MAUREL, R., GUISNET, M., AND BOVE, L., *Bull. Soc. Chim. France* **1969,** 1975.

19. SCHMIDT, M., AND SCHMIDBAUR, H., *Chem. Ber.* **94,** 2446 (1961).

20. Bourne, K. H., Cannings, F. R., and Pitkethly, R. C., *J. Phys. Chem.* **75**, 220 (1971).
21. Zubareva, N. A., Kiselev, A. V., Lygin, V. I., *Kinet. Katal.* **12**, 720 (1971); Ash, S. G., Kiselev, A. V., and Kuznetsov, B. V., *Trans. Faraday Soc.* **67**, 3118 (1971).
22. Finch, J. N., and Clark, A., *J. Catal.* **13**, 147 (1969); Hightower, J. W., and Hall, W. K., *J. Amer. Chem. Soc.* **89**, 778 (1967).