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Effect of Ultrasonic Waves on the Catalytic Activity of Silica Gel

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It has been found that silica gel, prepared in the presence of ultrasonic waves (90 kHz), is more active as a catalyst in the decomposition of hydrogen peroxide (0.3 wt % aqueous solution) than silica gel prepared with only the usual stirring techniques. The reaction studies carried out at 37, 44, 54 and 63°C in a batch reactor showed that both the activation energy and the frequency factor were higher for the insonated gel than the uninsonated gel. The increase in activation energy and the catalytic activity has been explained in terms of the compensation effect. Surface area, pore volume, and pore-size distributions were also measured. The existing kinetic data on the catalytic decomposition of hydrogen peroxide (using various catalysts) has been correlated in terms of the "isokinetic temperature" and a "characteristic frequency factor." This correlation enables the kinetic parameters of a new catalyst (for H_2O_2 decomposition) to be determined with a minimum of experimental work.

INTRODUCTION

The effect of ultrasonics in the field of cleaning and chemical reactions is well known (*1–4*). In these phenomena, it is considered that cavitation, and to a lesser extent, ultrasonically produced mixing play a major role. However, the effect of ultrasonics on the activity of catalysts has been examined only recently. The information reported in the literature (*5–20*) is too scant to afford a clear picture of the subject. The literature indicates that several different techniques have been employed to study the effect of ultrasonics on the activity of a catalyst. For example, the work done by Li Wen-Chou, Mal'tsev, and Kobozev (*5–7*, *9*) shows the complexity of the effect of insonation on catalysts. They observed that for powdered, unsupported palladium and platinum-black catalysts, the effect of insonation on the catalytic activity varied depending upon the frequency of sound waves, method of preparation of the catalysts, the concentration of reactants used for the preparation of catalysts, the blanketing (inert) atmosphere during insonation, and the reaction used to check the activity of the catalyst. The effect of ultrasonics on catalytic activity has been studied in three different ways: (1) insonation of the catalyst during the preparation stage, (2) insonation of the already prepared catalyst, and (3) insonation of the reaction mixture (including the catalyst).

Insonation of the Catalyst During the Preparation Stage

In this method the insonation takes place during the formation and preparation of the catalyst and as the ultrasonic waves produce cavitation and mixing phenomena at the microlevel, it is conceivable that they might affect the catalyst particle size, crystal structure, pore size, crystallite size and the pore-size distribution. For example, Slaczka (*8*) studied the effect of

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insonation on the preparation of nickel and cobalt oxalates. He reported that insonation (25 kHz) reduced the praticle diameter of nickel oxalate from 15.4 to 7.2 μ and of cobalt oxalate from 13.3 to 1.7 μ. He also found that the porosity of nickel oxalate was reduced from 69.0 to 42.2% and of cobalt oxalate from 83.1 to 55.5%. Though the porosity decreased in both the cases, the activity for hydrogenating benzene to cyclohexane increased by 87% for the nickel catalyst obtained from the reduction (with H_2) of nickel oxalate and 14% for the cobalt catalyst obtained from the reduction of cobalt oxalate.

It is interesting to note that whereas Slaczka observed that particle diameters of nickel and cobalt catalyst decreased with insonation, Li Wen-Chou, Mal'tsev and Kobozev (*5*) reported an increase in the particle size of platinum-black catalyst from 85 to 106 Å. However, their insonation frequency was much higher (3000 kHz). They also reported an increase in surface area from 11.7 to 19.0 m^2/g. Furthermore, it was found also that the change in the activity of platinum black depended greatly on the blanketing atmosphere present during the catalyst preparation.

A literature search was made for the catalysts studied with insonation during the preparation stage. The results are reported in Table 1.

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TABLE 1

INSONATION OF THE CATALYST DURING THE PREPARATION STAGE

No.	Catalysts studied	Reactions used	Insonation variables	Reference
1	Copper and nickel-metal powder	Hydrogenation of oils	Frequency: 300–1000 kHz	Tyutyunnikov, and Novitskaya, Ref. (*22*)
2	Platinum black and palladium-black powder	1. Decomposition of hydrogen peroxide 2. Oxidation of ethanol 3. Hydrogenation of 1-hexene	Frequency: 20–3000 kHz Intensity: 14.6 W/cm^2 (Different blanketing atmospheres of nitrogen, oxygen and air were used during insonation)	Li Wen-Chou, Mal'tsev, and Kobozev, Ref. (*5*, *6*)
3	Platinum supported on silica or alumina gel	1. Decomposition of hydrogen peroxide 2. Hydrogenation of 1-hexane	Frequency: 548–3000 kHz Intensity: 5.4–14.6 W/cm^2	Li Wen-Chou, Mal'tsev, and Kobozev, Ref. (*9*)
4	Alumina gel	Adsorption of ethylene, butane, and propane	Frequency: 20–550 kHz Intensity: 1 and 3 W/cm^2	Paryichak, Mal'tsev, and Kobozev, Ref. (*10*)
5	Nickel and cobalt-metal powder	Hydrogenation of benzene	Frequency: 25 kHz Intensity: 0.3 W/cm^2	Slaczka, Ref. (*8*)
6	Manganese dioxide	Decomposition of hydrogen peroxide	Frequency: 25 kHz Power: 600 W (Insonation carried out while the manganese dioxide was being prepared electrolytically)	Kowalska, Kowalski, and Slaczka, Ref. (*11*)
7	Platinum-black powder	Decomposition of hydrogen peroxide	Frequency: 21 kHz Power: 4.5 W/ml (Concentration of chloroplatinic acid used for catalyst preparation varied from 0.05 to 0.5 wt % platinum.)	Wawrzyczek, Ref. (*12*) and Li Wen-Chou, Mal'tsev, and Kobozev, Ref (*7*)

lyst during preparation may be considered analogous to the insonation of a solution during crystallization. For example, Kapustin (*21*) observed that insonating the solution during crystallization alters the grain size of crystals and produces fine-structured crystals. He examined thirty different substances and concluded that crystals produced with insonation had smaller grain size than the crystals prepared without insonation.

Insonation of the Already Prepared Catalyst

In this case, the insonation is carried out while the catalyst particles are suspended in a liquid medium. This method has been found useful in regenerating spent catalysts. It appears that ultrasonically produced cavitation helps to remove the deposits on the spent catalyst and to regenerate its activity. Graves, Steiner, and Hirdler (*15*) used this method to regenerate the spent brass catalyst (Cat. S-305), used in the production of acetone from isopropyl alcohol, by immersing it in a bath containing about 50 wt % solution of sulfuric acid, nitric acid and sodium dichromate in water and insonating it from 18 to 22 kHz and 6 to 20 W/in^2 intensity. The activity of the ultrasonically regenerated catalyst was 83% compared to the activity of the fresh catalyst, whereas the activity was only 63% if conventional chemical treatment alone was used.

Mertes (*14*) studied the effect of insonation on titanium-trichloride catalyst particles suspended in an inert liquid such as isooctane. The frequency of insonation ranged from 20 to 500 kHz and intensity from 4 to 20 W/cm^2. This catalyst is effective in the polymerization of propylene. Mertes was able to reduce the catalyst particle-size range from 15 to 40 μ to 0.1–5.0 μ. The ultrasonic treatment and the reduction in catalyst particle-size range resulted in the production of a more crystalline polymer with a more uniform molecular weight distribution than in the case of the catalyst without the ultrasonic treatment.

A literature search was made for the catalysts studied in this manner. The results are reported in Table 2.

Insonation of the Reaction Mixture (Including the Catalyst)

In this case the reaction mixture containing both the catalyst and the reactants is insonated (*17–20*). Insonation done in this manner could affect both the catalyst and the reactants. Wiener and Young (*20*)

TABLE 2
Insonation of the Already Prepared Catalyst

No.	Catalysts studied	Reactions used	Insonation variables	Reference
1	Nickel–magnesium oxide mixed catalyst from formates and oxalates	Hydrogenation of cyclohexene	Frequency: 800 kHz Duration: 5–10 min	Langenbeck, Hansdreyer, and Nehring, Ref. (*13*)
2	Titanium trichloride with aluminum alkyl activator	Olefin polymerization	Frequency: 20–500 kHz Intensity: 4–20 W/cm^2	Mertes, Ref. (*14*)
3	Brass catalyst (S-305)	Acetone from isopropyl alcohol	Frequency: 20 kHz Intensity: 6–20 W/in^2	Graves, Steiner, and Hirdler, Ref. (*15*)
4	Catalyst containing mixture of CaO, MnO, CuO, PtO and PdO supported on magnesium and calcium compounds and hydrated aluminum silicate	Purification of internal combustion engine exhaust gas	Intensity: 20–100 W/cm^2	Berger, Ref. (*16*)

studied the effect of stationary sound waves on the decomposition of formic acid, the decomposition of ammonia, and the hydrogenation of ethylene using nickel filament as catalyst. The reaction was carried out in the filament temperature range of 120–190°C. With this type of ultrasonic treatment, the decomposition rate of formic acid increased by about 50%, that of ammonia by about 15%, while hydrogenation of ethylene remained unaffected. The increase in reaction rate was attributed to an increase in mass transfer due to insonation.

Nikolaev and Askadskii (*17*) used this method in studying the effect of insonation (20 kHz) on the decomposition rate of 0.1 *M* hydrogen peroxide with silica-gel catalyst. The increase in the rate of decomposition was attributed to an increased breaking of the silica-gel particles. According to these authors, the sound waves did not change the concentration of hydrogen peroxide without the catalyst.

A literature search was made for the catalysts studied in this manner. The results are reported in Table 3.

Of the methods suggested for studying the effect of insonation, the application of sound waves during the preparation stage of the catalyst appears to be most fruitful. Since the insonation process is carried out during the formation stage, it might have an effect on crystal structure (*21*), particle size (*5*), surface area (*5*, *8*) and porosity (*8*). To a large extent this hypothesis is confirmed by the observations of Li Wen-Chou, Mal'tsev and Kobozev (*5*) who observed that the platinum and palladium-black catalysts showed an increase in activity when insonated during preparation. On the other hand, these catalysts showed no increase in activity when insonated after preparation. This might be, as they point out, due to the stability of lattice structure after formation. It is felt that insonation of the reaction mixture will not have much effect on the catalyst.

In the present investigation, the effect of ultrasonics on the physical characteristics and catalytic activity of silica gel was studied. The gel and insonated gel were compared using the decomposition of 0.3 wt % hydrogen peroxide (in water).

EXPERIMENTAL METHODS

The kinetic studies were carried out in a batch reactor using silica-gel catalyst (prepared with and without insonation). Surface area, pore volume and pore-size distributions were measured. A microscopic examination of the catalysts was also made.

TABLE 3
INSONATION OF THE REACTION MIXTURE (INCLUDING THE CATALYST)

No.	Catalysts studied	Reactions used	Insonation variables	Reference
1	Ammonium molybdate, silica gel and free acid ($P_2O_5 \cdot 24MoO_3 \cdot xH_2O$)	Decomposition of hydrogen peroxide	Frequency: 20 kHz	Nikolaev and Askadskii, Ref. (*17*)
2	Manganese dioxide gels and suspensions	Decomposition of hydrogen peroxide	Frequency: 875 kHz	Greguss and Greguss, Ref. (*18*)
3	Platinum, nickel or iron wires coupled to a transducer	Catalytic formation of ammonia and sulfur trioxide, fat hardening and several other processes	Frequency: 0.5–300 kHz	Aero Projects Inc., Ref. (*19*)
4	Nickel filament	1. Hydrogenation of ethylene 2. Decomposition of formic acid 3. Decomposition of ammonia	Frequency: 13.5 kHz Intensity: 0.05 W/cm² (stationary sound waves)	Wiener and Young, Ref. (*20*)

Gel Preparation

The apparatus for preparation of the silica-gel catalyst with and without insonation essentially consisted of a glass vessel for the preparation of the gel, the equipment for the generation of ultrasonics, and the equipment for the washing and drying of the gel.

The preparation of gel and insonated gel was carried out in a flat-bottomed cylindrical glass-vessel reactor 5.5 cm in diameter and 20.5 cm long which was immersed in the ultrasonic tank. The tank was filled with water and the reactor-vessel bottom was always maintained 0.5 cm above the bottom of the ultrasonic tank. The ultrasonic equipment consisted of a generator (model No. G40C1-PO) and a tank (model No. T-40C1), both manufactured by Ultrasonic Industries, Plainview, N. J. The generator was capable of producing ultrasonic waves at 90 kHz at an average output of 80 W. The tank dimensions were $5\frac{3}{4} \times 5\frac{1}{2} \times 4$ in. (length × width × depth), and the transducer was located at the bottom of the tank.

The preparation of silica gel was carried out by the method proposed by Walton (*23*). Since hydrogen peroxide decomposition is quite sensitive to impurities, pure sodium meta-silicate ($Na_2SiO_3 \cdot 9H_2O$) was used instead of water glass. The sodium meta-silicate (certified, number S-408) was supplied by Fischer Scientific Company. This contained only 0.0012% metallic impurities and the total impurity content was only 0.0092%. One-hundred ml of 2.03 N sulfuric acid was initially stirred in the glass-vessel reactor at 550 rpm for 3 min. To it, 100 ml of 11.02 wt % sodium meta-silicate solution was added very rapidly. Stirring was continued for 5 min after the addition of sodium meta-silicate solution. The gelation indicated by the appearance of a white, turbid, viscous mixture occurred within 3 min of addition of sodium meta-silicate solution. In the case of insonated silica gel, the same procedure was followed as described above, except that after the addition of sodium *meta*-silicate solution, the mixture in the glass-vessel reactor was insonated for 30 min.

After the initial gelation procedure both gel and insonated gel were treated exactly the same way. Ten batches of each gel were prepared according to the above procedure. They were mixed together and allowed to set for 113 hr. After setting the gel was washed free of sodium silicate with distilled water. The washing was continued until the effluent gave a yellow color (neutral reaction) with thymol blue (*23*).

The washed gel was filtered and first dried slowly at 66°C for 54 hr and then dried to a constant weight at 120°C. Initially the gel was dried at a low temperature because rapid drying at high temperatures produced opaque, white powdery gel. The dried gel was crushed in a mortar, sieved, and the fraction in the size range of −20 +25 mesh (0.0328–0.0278 in.) separated. This fraction was again dried to constant weight and kept in a desiccator.

Kinetic Studies

The decomposition of hydrogen peroxide was selected mainly because the analytical technique and reaction procedure are simple and there are no side reactions (*5, 6, 9, 11, 12, 17, 18, 24, 25*). The experimental technique is the same as that suggested by Keating and Rozner (*24*). The decomposition of 0.3% aqueous hydrogen peroxide solution with about 0.5 g of −20 +25 mesh silica-gel catalyst was carried out at temperatures of 37, 44, 54, and 63°C. For each temperature a duplicate run was also carried out simultaneously in a different reactor to check the consistency of the results. As glass is also active in decomposing hydrogen peroxide, blank runs (without any silica-gel catalyst) were carried out at each temperature for each reaction vessel.

The hydrogen peroxide was obtained from Baker and Adamson (Grade 1802). It was a 30 wt % solution in deionized water without any stabilizer or organic matter. The solution was diluted to 0.3 wt % with triply distilled water (*28*).

A 1000-ml round-bottomed, three-necked Pyrex vessel, painted black to prevent the admission of light, was used as a batch reactor for the kinetic studies. This vessel was immersed in a constant temperature bath whose temperature was controlled with a simple on–off controller. A thermometer was placed through one neck of the reaction flask. The temperature in the reaction vessel was always within ±0.2°C of the desired temperature. The glass stirrer in the center neck was passed through a water-jacketed condenser in order to prevent any water vapor escaping from the reactor. The stirring speed, measured stroboscopically, was maintained constant at 435 ± 15 rpm. The third neck was closed with a ground stopcock and was used to introduce the catalyst as well as for taking samples.

Reaction Procedure

The cleaning of all glassware was necessary to prevent any surface contaminants enhancing the hydrogen decomposition reaction. The cleaning procedure suggested by Keating and Rozner (*24*) was used. All the glassware contacting hydrogen peroxide was soaked in a 35 wt % sulfuric acid followed by a rinse of triply distilled water and then was dried at 66°C.

The reaction vessel initially contained 500 ml of 0.3 wt % hydrogen peroxide. It was placed in the constant temperature bath and was allowed to reach the desired reaction temperature. Then 0.5 ± 0.002 g of -20 $+25$ mesh catalyst was added and immediately 10 ml of reactant sample pipetted out for analysis. The concentration of this sample was taken as the initial concentration. For blank runs without the catalyst, the first sample was taken as soon as the constant reaction temperature was reached in the reactor. The concentration of hydrogen peroxide in the sample was found by titrating 10 ml of reactant (to which 10 ml of 6 N sulfuric acid had been added) against 0.07 N potassium permanganate. At low temperatures, the hydrogen peroxide decomposition rate was very low. Hence the reaction was allowed to continue for a fairly long time (for example, at 37°C the reaction was followed for 40 hr) to get significant decomposition. On the other hand at 63°C the reaction was followed for only 10 hr.

Experimental Difficulties

The two major difficulties encountered during the experimentation were in the preparation of silica gel and in the decomposition of hydrogen peroxide.

Silica Gel Preparation

Even a slight change in the concentration of solutions varied the gelation time greatly. In the preliminary experiments various concentrations were tried to obtain a reasonable gelation time. The concentrations were selected such that the gelation time was not too long. As has been indicated earlier, the gelation time eventually selected was about three min.

Initially, the gel was allowed only 4 hr of setting time after gelation. As the yield was low, a separate batch was prepared for every kinetic experiment. It was found that the activity of each batch was not reproducible. Also, large volumes of solutions could not be used as it reduced the efficiency of insonation. Higher concentrations of sodium meta-silicate solutions could not be used as its maximum solubility (in water) was only 15 wt % at 20°C (*42*). Plank (*43*) has reported that at short setting times even a slight change in process variables affects the physical properties of the final dry gel; whereas for long setting times there were no such effects. Therefore, ten batches of each gel were prepared separately, mixed together and then allowed to set for 113 hr. This method enabled the preparation of a large batch of catalyst which was sufficient for all kinetic runs. Also, consistent results were obtained during experimentation.

In addition to gelation time, the drying technique was also important in the preparation of clean, transparent, dry gel. If the drying was too rapid, the final gel was opaque, white and powdery. After some trials, it was found that initial drying at 66°C for 54 hr and then at 120°C to a constant weight, gave the best results.

Decomposition of Hydrogen Peroxide

It was found that the decomposition of hydrogen peroxide was quite sensitive to impurities. Utmost care was necessary to keep the glassware clean.

An attempt was made to carry out the reaction in an open-conical flask as suggested by Keating and Rozner (*24*), but the blank runs at 44 and 37°C showed an increase in concentration of hydrogen peroxide with time instead of a decrease as expected. This was found to be due to evaporation of water vapor. Keating and Rozner may not have noticed this, as it is possible that the Corning glass vessel used by them may have been more active in decomposing hydrogen peroxide which masked the increase in concentration due to evaporation. Hence to prevent evaporation of water vapor, a three-necked flask with a condenser was used to carry out the decomposition reaction.

Measurement of Surface Area, Pore Volume and Pore-Size Distribution

The Perkin-Elmer model 212-D Sorptometer was used for measuring the surface area, pore volume and pore-size distribution of the catalysts. The gases used were high-purity nitrogen and helium supplied by Canadian Liquid Air. The adsorption measurements were carried out at liquid nitrogen temperature (—196°C) which was measured using a saturation pressure manometer filled with purified nitrogen.

RESULTS

The decomposition of hydrogen peroxide followed first order kinetics as reported by other workers (*24, 26, 27*). A typical first order plot for the decomposition reaction at 63°C is shown in Fig. 1. The rate constants were calculated by fitting the kinetic data using the method of least squares. The measured first order reaction rate constants of uninsonated and insonated gels were corrected at each temperature for the activity of the respective glass vessel. The correction was carried out as follows:

$$k_C = k - k_B, \qquad (1)$$

where k_C is the corrected rate constant for the catalyst, hr^{-1}, k_B is the rate constant for the reaction without the catalyst, hr^{-1}, and k is the rate constant for the reaction with catalyst, hr^{-1}.

The corrections were different for the two reaction vessels as their activities were different. The arithmetic mean for the corrected rate constants of the two reaction vessels was taken at each temperature and reported as the average corrected rate constants in Table 4.

The activation energy, E, and the frequency factor, A, were calculated for the average corrected rate constants. The accuracy of analysis at 37°C might not be reliable because the hydrogen peroxide decomposition rate was extremely low and required long time intervals between two readings to get an appreciable conversion. Therefore, the Arrhenius parameters have been calculated without the 37°C rate-constant values and are shown in Table 4.

The surface area and apparent pore volume were measured using a Perkin-Elmer model 212-D Sorptometer. The calculations were done according to procedures suggested in Perkin-Elmer catalogues 990-9550 and 990-9351. The surface areas of uninsonated and insonated gel were 337 ± 10 and 274 ± 10 m^2/g, respectively.

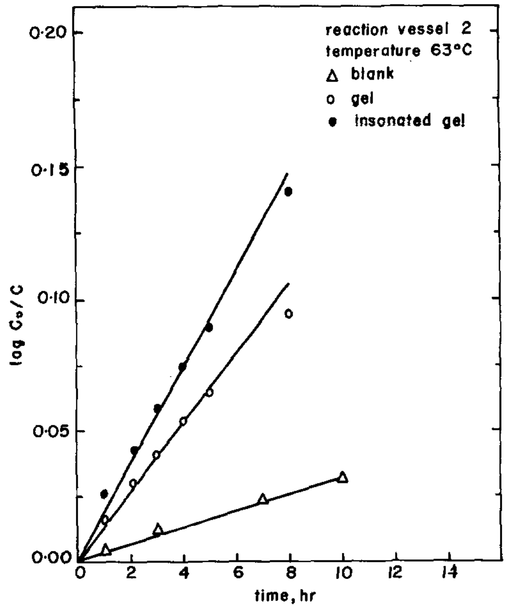

FIG. 1. Decomposition of hydrogen peroxide on gel and insonated gel.

TABLE 4

Average Corrected Rate Constants[a] and Arrhenius Parameters[a] for the Decomposition of Hydrogen Peroxide

Temperature (°C)	Average corrected rate constants				
	Blank ($hr^{-1} \times 10^4$)	Rate constant, $hr^{-1}\ g^{-1}$-(cat) $\times 10^4$		Rate constant, $hr^{-1}\ m^{-2} \times 10^4$	
		Uninsonated gel	Insonated gel	Uninsonated gel	Insonated gel
37	2.97 ± 0.40	29.5 ± 4.2	29.9 ± 4.4	0.089 ± 0.014	0.109 ± 0.016
44	7.74 ± 0.33	52.7 ± 4.1	48.1 ± 4.4	0.156 ± 0.012	0.175 ± 0.016
54	18.51 ± 0.53	127.0 ± 4.0	158.4 ± 0.6	0.377 ± 0.012	0.578 ± 0.002
63	60.00 ± 10.00	364.0 ± 25.0	597.0 ± 39.0	1.08 ± 0.070	2.18 ± 0.140

Arrhenius parameters	Blank	Uninsonated gel	Insonated gel
E, kcals	23.2 ± 1.7	21.5 ± 0.1	28.0 ± 0.4
log A (A in $hr^{-1}\ g^{-1}$ cat)	12.9 ± 1.1	12.5 ± 0.04	17.0 ± 0.2

[a] The deviations shown are the differences of the average values from those of reaction vessel 1 and 2.

The measured apparent pore volume was corrected for the nitrogen adsorbed on the unfilled pores. The plot of corrected pore volume against pore diameter is shown in Fig. 2. The corrected pore volume at any particular diameter is the total pore volume of all pores less than that diameter. The corrected pore volume of all pores less than 260 Å diameter was 1.130 ml/g for uninsonated gel and 0.792 ml/g for insonated gel. Pore-size distribution was measured only up to 260 Å diameter because higher relative pressure ratios of nitrogen were difficult to maintain in the sorptometer.

The slope ($\Delta v_p/\Delta r_p$) of the pore volume against the pore-radius curve at any particular pore radius gives the relative frequency of occurrence of that pore size (*29*). The slopes obtained by the numerical differentiation of the pore volume-pore radius data were plotted against pore radius in Fig. 3. This curve gives the relative frequency of occurrence of different pore sizes and also a comparative idea of pore structure of uninsonated and insonated gel. Apparently insonation has evened out the distribution of pore sizes between 30 and 130 Å in radius.

Microscopic studies of samples of uninsonated and insonated gels were also made. The photomicrographs of both samples with 4 hr setting time and with 113 hr setting time are shown in Fig. 4.

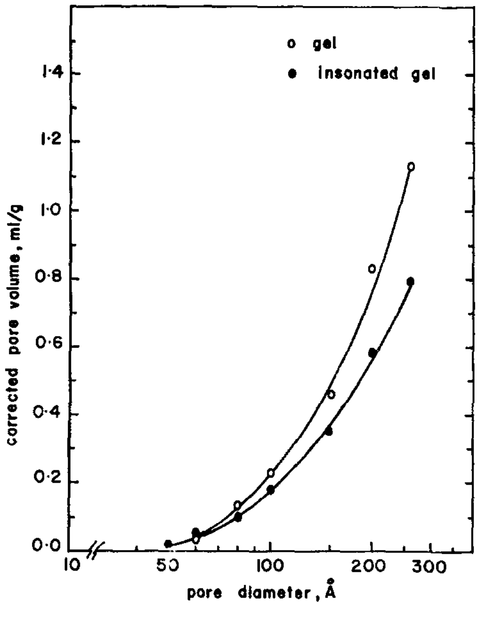

Fig. 2. Corrected pore volume of gel and insonated gel.

Discussion

It is seen from Table 4 that the activation energies of the decomposition of hy-

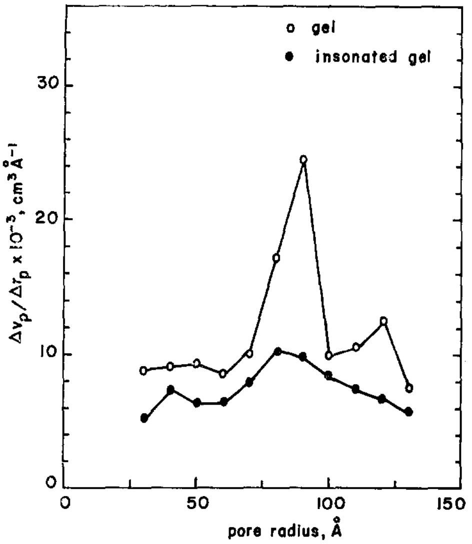

FIG. 3. Pore-size distribution of gel and insonated gel.

drogen peroxide with silica gel and insonated silica gel are significantly different; as are the absolute activities (k_C). Assuming that the reactions follow the Arrhenius law:

$$k_C = A \cdot \exp(-E/RT) \qquad (2)$$

the energies of activation, (E), are as follows:

Case	Catalyst	E (kcal)
1	None	23.2
2	Uninsonated gel	21.5
3	Insonated gel	28.0

Normally one would expect a catalyzed reaction to have a lower activation energy than an uncatalyzed one. For example, Walas (30) gives the following values for the decomposition of hydrogen peroxide with different catalysts:

Catalyst	E (kcal)
None	18.0
Iodide ion	13.5
Colloidal platinum	11.7
Liver catalase	5.5

Since insonated gel is more active as a catalyst than uninsonated gel (for reaction temperatures above ca. 47°C) one would expect activation energies to fall in the order of:

$$E_1 > E_2 > E_3 \qquad (3)$$

instead of the observed order of

$$E_3 > E_1 > E_2. \qquad (4)$$

Evidently the silica-gel catalyst has been affected by insonation in such a way that both the catalytic activity as well as the activation energy have increased. The reason is that the value of the activation energy alone does not permit a complete evaluation of the activity of a catalyst since the frequency factor A is also catalyst dependent. This type of behavior, where both A and E seem to be linked together so that A increases as E increases, has been called the "Compensation Effect" by Cremer (*31*) and the "Theta Effect" by Schwab (*32*). It was first noticed by Constable (*34*) when studying the dehydrogenation of ethanol over copper catalysts. Catalysts prepared at different temperatures showed different values of E, but high values of E were accompanied by high values of A. Cremer (*31*) reported similar results on a detailed investigation of the decomposition of formic acid over magnesite pretreated at various temperatures. Other examples have been reported in the literature (*26*, *31*, *33*, *35*).

The compensation effect, as Cremer (*31*) pointed out, might be due to the formation of active centers of different activation energies, change in the concentration of surface impurities and the apparent compensation effect due to diffusional resistance. In the case of uninsonated and insonated gels, the pore-diffusional resistance was negligible as the Arrhenius plot (Fig. 5) gave a straight line fit (*36*). Furthermore, if pore-diffusional resistance is significant then the increase in the rate constant will be less at higher temperatures than at lower temperatures (*37*). The mass-transfer resistance from the bulk of the liquid to the outside surface of both the catalysts was also negligible as the activation energies were high (in the case of mass-transfer control E values are usually in the range 2–2.5 kcals (*37*)). The impurities in the unin-

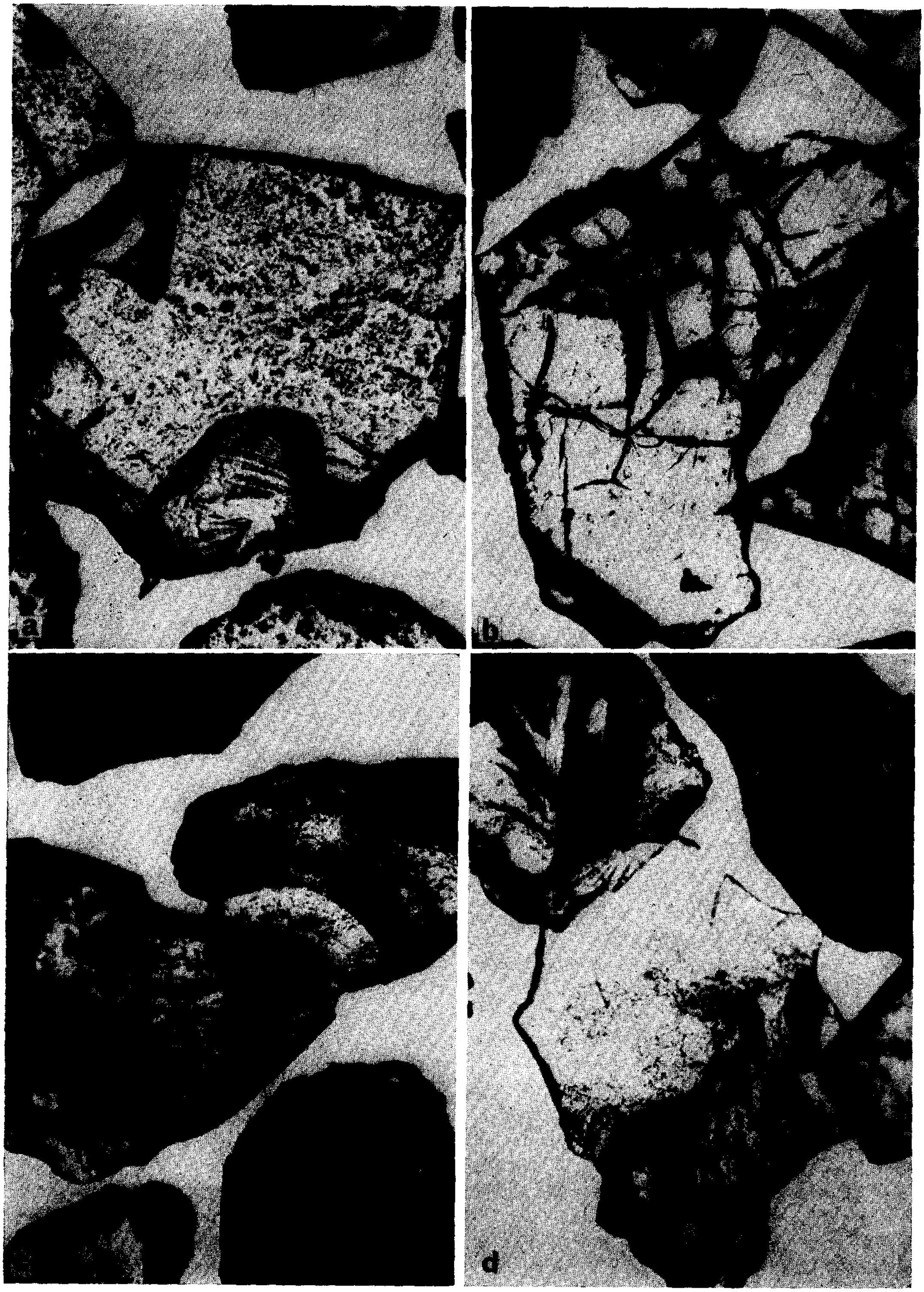

FIG. 4. Photomicrographs of gel and insonated gel (X50): (a) Uninsonated gel with 4 hr setting time (X50); (b) Insonated gel with 4 hr setting time (X50); (c) Uninsonated gel with 113 hr setting time (X50); (d) Insonated gel with 113 hr setting time (X50).

sonated and insonated gels were of the same kind as the same reactants were used for the preparation of both the gels. Therefore, the possibility of an apparent compensation effect can be discounted.

Apparently then the insonation has produced a catalyst surface with activated centers having higher energies of activation and higher frequency factors than the active centers in the uninsonated gel. Cremer (*31*) suggests that the increased catalyst preparation temperature changed the catalyst surface through a sintering effect in the formic acid-magnesite case. In the present case, however, one may postulate that insonation during catalyst preparation has produced unusual stresses and some collapse of the ordinary porous gel structure, thus forming new types of active centers by producing cracks in the gel. Pore-volume measurements and surface-area measurements tend to confirm this postulation. One would expect that both pore volume and surface area could decrease if the gel were to collapse on itself, and this is shown by experimental measurement as follows:

	Pore volume (ml/g)	Surface area (m^2/g)
Uninsonated gel	1.130	337
Insonated gel	0.792	274

Further supporting evidence may be gleaned from photomicrographs (Fig. 4) of uninsonated and insonated silica-gel catalysts showing unusual surface cracks in the case of the insonated gel.

Mikovsky and Weisz (*38*) have noticed similar behavior while studying the effect of neutron irradiation on the catalytic activity of silica and silica-alumina for double-bond isomerization of butene-1. They observed that irradiation decreased the silica surface area from 395 to 354 m/^{2}g and silica-alumina surface area from 274 to 218 m^2/g. They explained their results by assuming that atomic displacements are responsible for these decreases in surface area. They found that the irradiated catalysts also had higher activity. Taylor (*39*) has pointed out that reduction in surface area with irradiation seems to be the rule with metals as well as nonmetals such as carbon, silica, silica-alumina and titania.

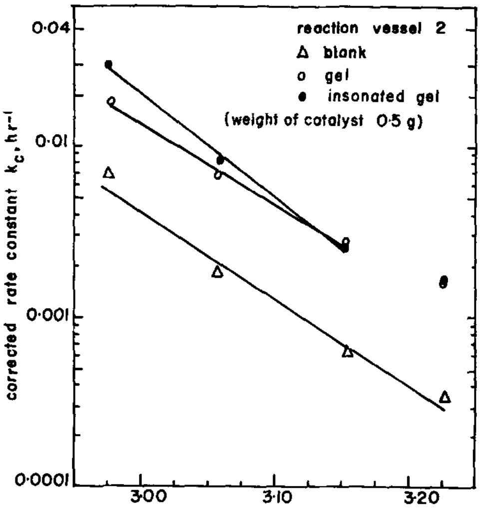

FIG. 5. Arrhenius plot for decomposition of hydrogen peroxide.

Correlation

In cases where a compensation effect occurs it has been found (*31*, *40*) that the relation between A and E can be represented by the equation

$$\log A = mE + \log k', \qquad (5)$$

where m and k' are constants. Fig. 6 shows a plot of log A vs E for the available data on the hydrogen peroxide decomposition. It may be seen that Eq. (5) is obeyed and that the two data point obtained in this work correlate well with other investigators' determinations (*26*, *33*). It is quite remarkable that data obtained on such divergent catalysts seem to fit Eq. (5) so well.

It can be shown that if a compensation effect described by Eq. (5) is present, there must be some characteristic temperature T_s at which all the rates are equal. This temperature has been called the "isokinetic temperature" by Boudart (*41*). It has been shown by Bond (*40*) that the slope in (Eq. 5) can be expressed as

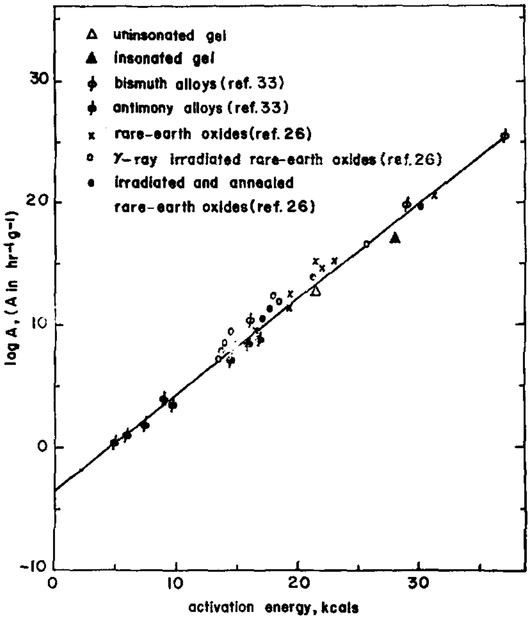

FIG. 6. Compensation effect for the decomposition of hydrogen peroxide on various catalysts.

$$m = 1/(2.303\, RT_s), \qquad (6)$$

where R is the gas constant.

Substituting the above value of m in Eq. (5) and simplifying the equation thus obtained, yields:

$$A = k' \exp(E/RT_s). \qquad (7)$$

Further substitution of the value of A from Eq. (7) into Eq. 2 yields

$$k_C = k' \exp\left[-\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_s}\right)\right], \qquad (8)$$

where k' and T_s are characteristic constants for a given reaction. A similar equation has been derived by Boudart (*41*). Knowing the values of m and $\log k'$ from the plot of Eq. (5), both T_s and k' can be evaluated. Or, T_s can also be evaluated from the plot of $\log k_C$ vs $1/T$. This is the point where the Arrhenius lines for different catalysts intersect. The values of m and $\log k'$ were evaluated from the data of Fig. 5 using the least square method. The values obtained were

$$m = 0.7791 \text{ (kcal)}^{-1} \text{ (g. mole)}$$
$$\log k' = -3.096 \ (k' \text{ in hr}^{-1}\text{ g}^{-1})$$

In the present case T_s was evaluated from the plot of $\log k_C$ vs $1/T$ (Fig. 5) and was found to be equal to 320°K. A close examination of the data of Fig. 5 shows that 33 points plotted on the graph correspond to quite diverse catalysts used in the study of the decomposition of hydrogen peroxide. It would be logical to assume that this compensation effect will apply if some other catalyst is used for the study of hydrogen peroxide decomposition. That is, no matter what the catalyst studied with this reaction, the values of characteristic constants k' and T_s will already be known from Fig. 5.

Therefore, in order to study a new catalyst for this reaction, only one pair of k_C and T values needs to be experimentally determined. Then these values of k_C and T can be substituted in Eq. (8) to determine E (and hence A from Eq. (5). This reduces the amount of experimental work needed to specify the kinetics of a new catalyst.

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