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Catalytic Vapor-Phase Hydration of Propylene on the Metal Sulfate–Silica Gel Catalyst

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The vapor-phase hydration of propylene was carried out over metal sulfate–silica gel catalysts under various conditions. It was found that the catalytic activity obeys a simple rule. Namely, the catalyst containing a sulfate of trivalent metal was the most active and the catalyst containing a sulfate of bivalent metal followed this, while the catalyst containing a sulfate of univalent metal showed no activity. Further, the catalytic activity was found to decrease in the order of Fe > Al > Cr > Cu > Zn > Co > Cd > Ni > Mn > Mg > K, Na. Thus, it was shown that nearly the same order as that of the decreasing hydrogen ion concentration in the hydrolysis holds for the catalytic activity.

From the results described above, it was considered that the catalyst would be acidic and the surface acidity would be related closely to the catalytic activity. Results of the acidity measurement showed that the catalysts are actually acidic and supported the view described above. From the results of acidity measurements and X-ray diffraction studies, it was presumed that the observed acidity would result from an interaction between silica gel and sulfate.

To relate the catalytic activity with the surface acidity, a rate equation $r = k_1 p_{H_2O} p_{C_3H_6} - k_2 p_{iso\text{-}C_3H_7OH}$ was derived. From the proportionality between the acidity of $1.5 \geq H_0 \geq -3.0$ and the rate constant, it was concluded that acids existing in this region would contribute to the catalytic activity.

INTRODUCTION

The hydration of olefin to produce alcohol is one of the important petrochemical reactions. This reaction proceeds both in a vapor phase and in a liquid phase in the presence of a suitable catalyst, and from long ago, the liquid-phase process is employed in industrial alcohol manufacture. However, the vapor-phase process is considered to be more favorable than the liquid-phase process because of several disadvantages in the latter process, e.g., corrosion by the sulfuric acid catalyst.

Much research has been carried out to find adequate catalysts for the vapor-phase hydration process (*1–3*). From a survey of this work, the present author pointed out the existence of an intimate relation between the catalytic activity and the surface acidity (*4*). There was much qualitative experimental evidence to support this relation. However, little information concerning a quantitative relation between the activity and the acidity was available.

Considering the circumstances described above, the author has attempted to study the vapor-phase hydration of propylene. A series of catalyst composed of silica gel and metal sulfate have been prepared, and the catalytic activity has been measured unde various experimental conditions. By applying a rate equation to the experimenta results, rate constants have been determined to compare them with the surface acidity.

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EXPERIMENTAL

Catalysts. The names, components, and compositions of the catalysts employed in the present research are given in Table 1. These catalysts were prepared in the following manner: Commercial granules of silica gel of 1–2.5 mm size were immersed in an aqueous solution of a given concentration of a desired metal sulfate and the mixture was heated and evaporated to dryness on a water bath. Then, the resultant granular material was dried in an oven at 130–150°C for 6 hr, after which it was cooled and stored in a desiccator.

TABLE 1
NAMES, COMPONENTS, AND COMPOSITIONS OF CATALYSTS

Catalyst	Components: Silica gel and	Composition, sulfate/SiO_2 (by weight)
Al-I	Aluminum sulfate	1/14
Al-II		2/14
Al-III		4/14
Al-IV		7/14
Fe-I	Ferric sulfate	1/14
Fe-II		2/14
Fe-III		3/14
Fe-IV		4/14
Cr-I	Chromium sulfate	1/14
Cr-II		2/14
Cr-III		4/14
Cr-IV		7/14
Cu-II	Copper sulfate	2/14
Zn-II	Zinc sulfate	2/14
Zn-III		4/14
Co-II	Cobalt sulfate	2/14
Cd-II	Cadmium sulfate	2/14
Ni-II	Nickel sulfate	2/14
Mn-II	Manganese sulfate	2/14
Mn-III		4/14
Mg-II	Magnesium sulfate	2/14
K-II	Potassium sulfate	2/14
Na-II	Sodium sulfate	2/14

Activity tests under ordinary pressure. In the measurement of the catalytic activity under ordinary pressure, a conventional flow-type reactor having a 5-ml catalyst bed was used and the following conditions were adopted: the reaction temperature was 110–200°C, the mole ratio of propylene to water in the feed vapor was $\frac{1}{2}$, the mole ratio of inert gas (mainly ethane and propane) to propylene was 0.091, and the space velocity *SV* was 3.0×10^3 hr^{-1}.

Prior to the activity measurement the following pretreatment for the catalyst bed was carried out: The temperature of the catalyst bed was raised to about 150°C, then hydrogen was passed through the bed for 2–3 hr, after which water was introduced from an injector into the reactor and the temperature was adjusted to a desired value.

The measurement was started after a steady condensation of the exit vapor into the separator was recognized. At first, the feed of hydrogen was stopped and propylene was introduced into the reactor. Then, after a short time to establish a steady state, liquid products were collected. The products were analyzed by gas chromatography. In this analysis, the flow rate of carrier gas (hydrogen) was 75 ml/min and the temperature was 92° ± 0.5°C. The gas chromatographic column of 2-m length was packed with Cellite powder (C-22, 60–80 mesh) containing 60% of polyethyleneglycol-400.

Activity tests under 5 kg/cm² pressure. Catalytic activities under the pressure of 5 kg/cm^2 were measured with the apparatus shown in Fig. 1. Two series of experiments were carried out. In one series, the reaction temperature was varied between 140° and 180°C, and mixed vapor having the composition of $C_3H_6/H_2O = 0.65$ (mole ratio) was fed at the space velocity of 8×10^3 hr^{-1}. In the other series, the temperature, the composition of the feed vapor and the space velocity was 150–200°C, 0.95 (mole ratio), and 6×10^3 hr^{-1}, respectively.

Besides the usual activity tests described above, kinetic experiments were also carried out under 5 kg/cm^2 gauge pressure. In these experiments, the stabilized Al-II catalyst which had been exposed under the reaction condition at 250°C for 2 hr was used. Four series of experiments where the respective composition of the feed vapor (C_3H_6/H_2O, mole ratio) was 0.67, 0.84, 0.97, and 1.19 were carried out. In each series, the alcohol content in the exit vapor was measured at

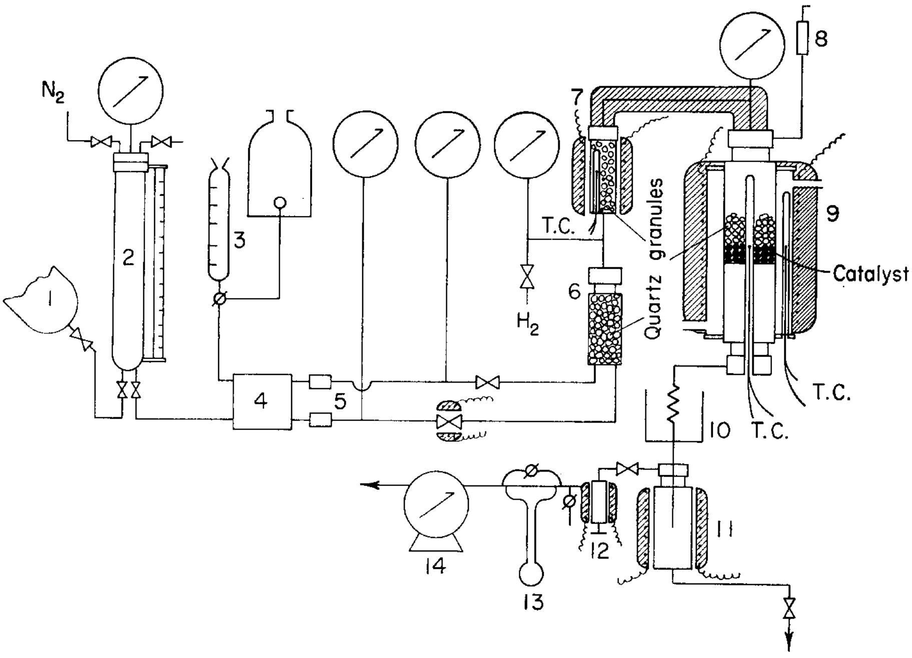

FIG. 1. Apparatus for activity tests under high pressures. 1, propylene cylinder; 2, propylene reservoir; 3, water reservoir; 4, pump; 5, check valve; 6, mixer; 7, preheater; 8, relief valve; 9, reactor; 10, condenser; 11, separator; 12, control valve; 13, gas flow meter; 14, wet test meter.

various values of the reciprocal space velocity ranging from 2.4×10^{-5} to 1.9×10^{-4} hr.

Acidity measurements. At first, qualitative acidity tests were carried out. Into 10 ml of purified benzene containing about 0.7 g of granular sample catalyst several drops of an indicator solution were added and the color of the adsorbed indicator was observed. In this manner, two series of experiments were carried out. In one series, samples A, i.e., the catalysts which had been exposed to the air moisture for several hours, was used. In the other series, samples B, i.e., the catalysts which had been subjected to heating at 120°C for 2 hr after the same treatment as for the samples A, were used. In both series, the following indicators were used: phenylazonaphthylamine ($pK_a = 4.0$), *p*-dimethylaminoazobenzene ($pK_a = 3.3$), benzeneazodiphenylamine ($pK_a = 1.5$), dicinnamalacetone ($pK_a = -3.0$), benzalacetophenone ($pK_a = -5.6$), and anthraquinone ($pK_a = -8.2$).

Next, the surface acidity was measured quantitatively with essentially the same method as that of Benesi (*5*). The same indicators as above were used. However, only sample B served for the measurement.

X-Ray diffraction. Powder X-ray diffraction patterns of the Al-I, Al-II, Al-III, Al-IV and some reference materials such as aluminum sulfate octadecahydrate were obtained with an X-ray diffractometer. The Cu $K\alpha$ radiation filtered by Ni was used.

RESULTS

Catalytic activities. Catalytic activities which were measured under ordinary pressure are given in Fig. 2. In this figure the activities of catalysts having a given composition, that is sulfate/silica gel = 1/7 (by wt), are shown as a function of the reaction temperature. It can be seen that the decreasing order of the catalytic activity is Fe > Al > Cr > Cu > Zn > Co > Cd > Ni > Mn > Mg > K, Na. Apparently, the catalyst containing a sulfate of metal of a higher valency has a higher activity, and the catalyst containing a sulfate of univalent metal is inactive.

Effects of the composition of the catalyst

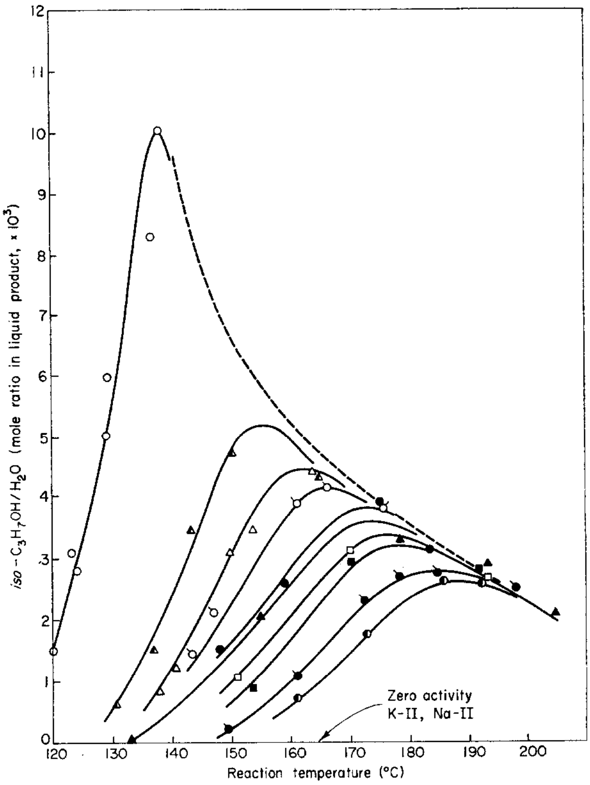

FIG. 2. Catalytic activities of various catalysts under the atmospheric pressure and at various temperatures: ○, Fe-II; ▲, Al-II; △, Cr-II; ○, Cu-II; ●, Zn-II; ▲, Co-II; □, Cd-II; ■, Ni-II; ●, Mn-II; ◐, Mg-II.

upon the catalytic activity were also measured under ordinary pressure, and the results are given in Fig. 3. It can be seen that the increase in the content of sulfate in the catalyst resulted in an increase in the catalytic activity.

Catalytic activities which were measured under 5 kg/cm^2 gauge pressure are given in Fig. 4. The figure shows that the decreasing order of the catalytic activity obtained under pressure is analogous to the order obtained under ordinary pressure. Namely, the decreasing order of the catalytic activity was Al > Zn > Mn, and the catalytic activity of the Al catalyst increased with the increase in the sulfate content in the catalyst.

The gas chromatographic analysis of the liquid product obtained in the activity test under 5 kg/cm^2 gauge pressure showed that, in addition to the main product, i.e., isopropanol, by-products such as acetone, *n*-propanol and an oily material were produced. However, the contents of *n*-propanol was such an order of magnitude as might be negligible in comparison with the content of isopropanol. For instance, in cases where the Al-III catalyst was used, the mole ratio of acetone to isopropanol was always less than 0.055.

Kinetic data. Results of the kinetic run are given in Fig. 5(a). In this figure, the mole fraction of isopropanol in the exit vapor is given as a function of the reciprocal space velocity. It can be pointed out that the curves in this figure have the same initial slope. This fact shows that the initial rate of reaction has a constant value irrespective of the composition of the feed vapor.

Surface acidities. Results of the qualitative acidity tests are summarized in Table 2. As can be seen in this table, all catalysts were acidic against the indicators of high pK_a values. However, the number of catalysts keeping an acidic character diminished with the decrease in the pK_a value. At first, the K-II catalyst became basic at $pK_a = 1.5$. Next, at $pK_a = -3.0$, the Zn-III (A) and the Mn-III (A) became basic. Then, at $pK_a = -5.6$, all of the Al (A) catalysts became basic, whereas the Zn-III (B), the Mn-III (B), and all of the Al (B) catalysts remained in an acidic state at this pK_a value. At last, at $pK_a = -8.2$, all catalysts became basic irrespective of the pretreatment.

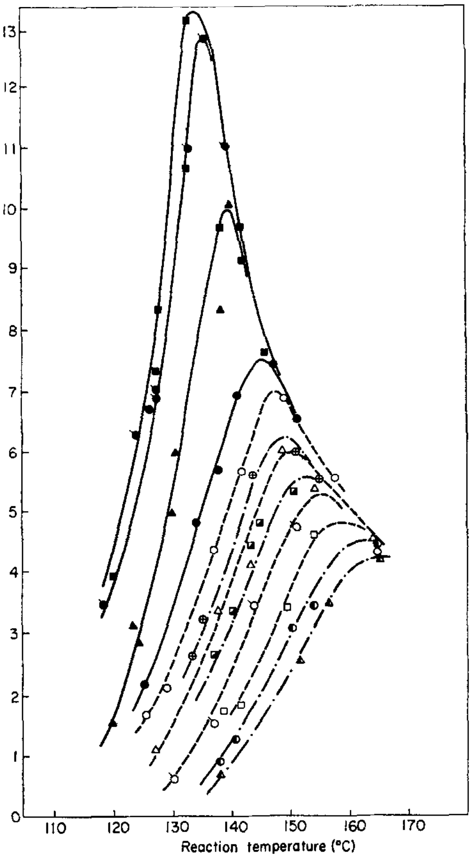

FIG. 3. Effects of the composition of catalysts on the catalytic activity under the atmospheric pressure and at various temperatures: ■, Fe-IV; ◕, Fe-III; ▲, Fe-II; ●, Fe-I; ---○---, Al-IV; ---△---, Al-III; ---◔---, Al-II; ---□---, Al-I; -··-⊕-··-, Cr-IV; -··-◪-··-, Cr-III; -··-◐-··-, Cr-II; -··-◭-··-, Cr-I.

Results of the quantitative determination of the surface acidity are given in Fig. 6, where the abscissa H_0 represents Hammett's acidity function and the ordinate represents

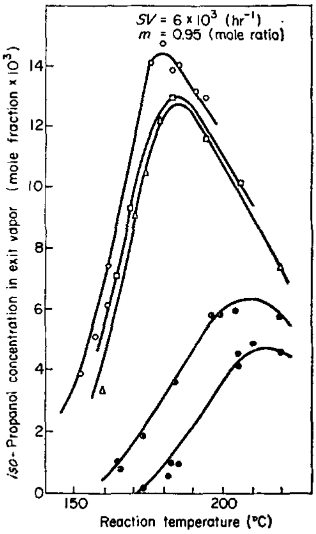

FIG. 4. Catalytic activities of various catalysts under 5 kg/cm² gauge pressure and at various temperatures: ○, Al-III; □, Al-II; △, Al-I; ◐, Zn-III; ●, Mn-III.

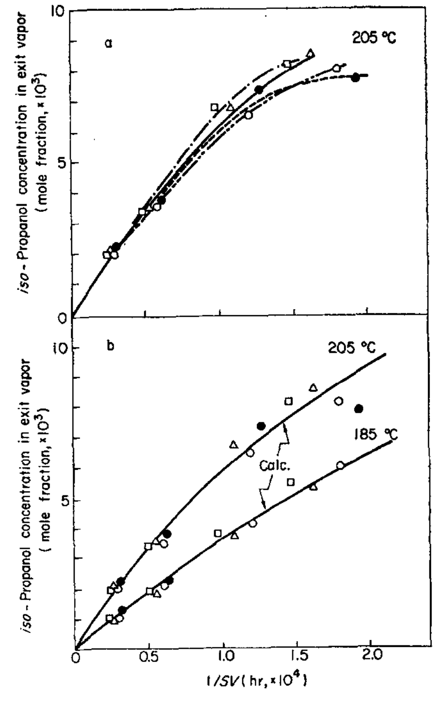

FIG. 5. (a) Kinetic data obtained under 5 kg/cm² gauge pressure. (b) Comparison of the calculated rates with the experimental data: □, $m = 1.19$; △, $m = 0.97$; ○, $m = 0.84$; ●, $m = 0.67$.

TABLE 2
RESULTS OF ACIDITY TESTS

Sample		pK_a					
		4.0	3.3	1.5	−3.0	−5.6	−8.2
Al-I	A	acidic	acidic	acidic	acidic	basic	basic
	B	acidic	acidic	acidic	acidic	acidic	basic
Al-II	A	acidic	acidic	acidic	acidic	basic	basic
	B	acidic	acidic	acidic	acidic	acidic	basic
Al-III	A	acidic	acidic	acidic	acidic	basic	basic
	B	acidic	acidic	acidic	acidic	acidic	basic
Zn-III	A	acidic	acidic	acidic	basic	basic	basic
	B	acidic	acidic	acidic	acidic	acidic	basic
Mn-III	A	acidic	acidic	acidic	basic	basic	basic
	B	acidic	acidic	acidic	acidic	acidic	basic
K-II	A	acidic	acidic	basic	basic	basic	basic
	B						

the n-butylamine titer required to neutralize the surface acid. It can be seen in this figure that the increasing in the content of aluminum sulfate in the Al catalyst made the catalyst more acidic.

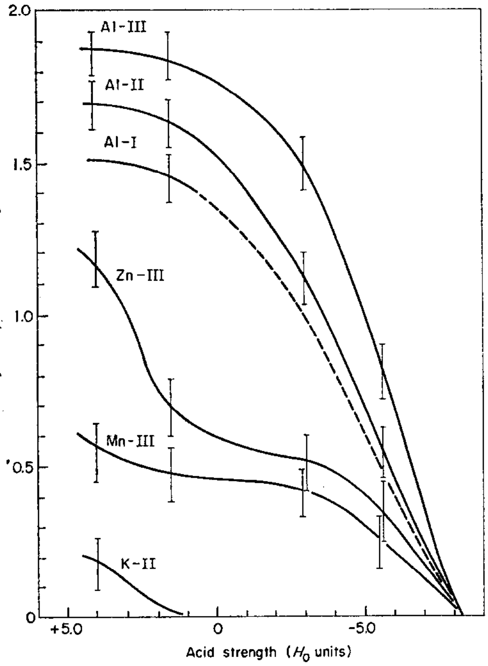

FIG. 6. n-Butylamine titer as a function of the acid strength.

X-Ray diffraction. Results of X-ray diffraction studies are summarized in Fig. 7. As can be seen in this figure, every diffraction pattern of the Al catalysts showed only one broad peak which can be attributed to silica gel, whereas in the diffraction pattern of the mechanical mixture of silica gel and aluminum sulfate octadecahydrate the characteristic peaks of the components appeared.

DISCUSSION

Qualitative Relations between the Catalytic Activity and the Surface Acidity

One of the interesting results obtained in the present research is the regularity in the catalytic activity. According to the experimental results, the catalytic activity decreased in the order of $M^{3+} > M^{2+} > M^{1+}$, where M^{n+} represents an n-valent cation in the catalyst. This dependency of the catalytic activity upon the cation valency in the catalyst resembles the well known fact that, in the hydrolysis of neutral salts, the concentration of hydrogen ion decreases with the decrease in the cation valency in the salts. Further, as pointed out in the previous section, the catalytic activity was found to decrease in the order of Fe > Al > Cr > Cu > Zn > Co > Cd > Ni > Mn >

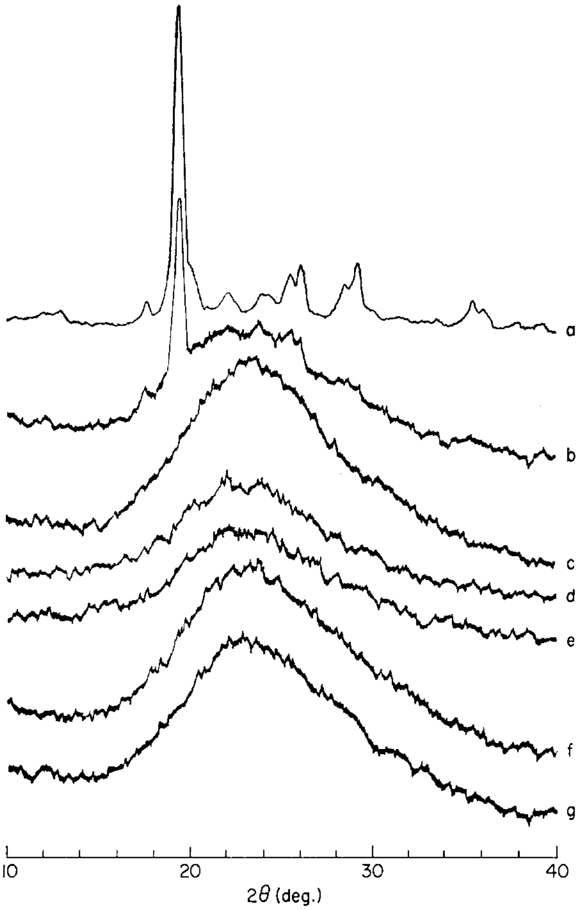

FIG. 7. X-Ray diffraction patterns: a, $Al_2(SO_4)_3 \cdot 18H_2O$; b, mechanical mixture of SiO_2 and $Al_2(SO_4)_3 \cdot 18H_2O$ (7:1 by wt.); c, silica gel; d, Al-II; e, Al-III; f, Al-II; g, Al-I.

Mg > K, Na. This coincides almost completely with the decreasing order of the hydrogen ion concentration in the aqueous solution of the metal salt.

The findings described above permit the supposition that the hydrogen ion on the surface of the catalyst, or the acid site on the catalyst, would play an important role in the catalysis. It is known that the activity of the ion-exchanged zeolite catalyst also decreases in the order of $M^{3+} > M^{2+} > M^{1+}$ (*6–8*). This result is similar to that obtained in the present study. However, it appears that whether the catalytic activity of the zeolite catalyst is due to the surface acidity or to the other factors is not well established. On the contrary, there is much evidence to support an intimate relation between the surface acidity and the activity of the hydration catalyst (*4*). Further, the present supposition is supported by the fact that the catalysts employed in the present study were actually acidic (Table 2).

The surface acidity seems to result from an interaction between silica gel and sulfate. It is known (*9*) that a neutral salt MX, where M is a metal ion and X is a negative ion such as Cl^-, reacts with silica gel in the following manner

$$\mathrm{SiOH} + \mathrm{MX} \rightarrow \mathrm{SiOM} + \mathrm{H}^+ + \mathrm{X}^-$$

A similar reaction between silica gel and a sulfate could be expected to occur at least in the surface region of silica gel. Thus, protonic sites appear on the resultant catalyst. Plank (*8*) considered that the surface acidity of the ion-exchanged zeolite catalyst would result from a reaction

$$M^{n+} + H_2O \rightarrow MOH^{(n-1)+} + H^+$$

This is an interesting consideration. However, according to the present study, the adsorbed water diminished the surface acidity (Table 2). Further, "bound water" in silica gel is considered to take the form of SiOH (*9*). Therefore, the view proposed by Plank seems to be inapplicable to the present case.

If the reaction between silica gel and sulfate results in surface acidity, the magnitude of the acidity should depend on the reactivity of the supported sulfate. In other words, the catalytic activity should depend on the reactivity of the sulfate. According to Iler (*9*), a salt of trivalent metal (Fe or Al) reacts strongly with silica gel. Hence, it can be said that the catalyst composed of silica gel and a sulfate of trivalent metal would be highly acidic and this catalyst would show a high activity. Actually, as pointed out in the previous section, the Fe catalyst, the Al catalyst, and the Cr catalyst showed high catalytic activities, and a high surface acidity of the Al catalyst was also demonstrated. Thus, it may be concluded that the mechanism proposed for the appearance of the surface acidity is plausible.

Quantitative Relations between the Catalytic Activity and the Surface Acidity

Rate Equation

From the point of view of the general importance of a rate equation in comparing the catalytic activity with other quantities such as the surface acidity, efforts were made to derive a suitable rate equation, and after some trials it was concluded that the kinetic data obtained in the present study can be expressed satisfactorily by a rate equation which is derived under the following assumptions: (1) the rate-controlling step is a surface reaction between the adsorbed water molecule and the adsorbed propylene molecule, (2) the surface is energetically homogeneous, (3) the surface is sparsely covered by the adsorbed reactant molecules. These assumptions give

$$r = k_1 p_{H_2O} p_{C_3H_6} - k_2 p_{iso\text{-}C_3H_7OH} \qquad (1)$$

where r (mole/hr ml catalyst) is a reaction rate; p (atm) is a partial pressure of the subscripted vapor; k_1 (mole/hr ml catalyst atm^2) and k_2 (mole/hr ml catalyst atm) are the respective rate constants of the forward reaction and the backward reaction.

On the other hand, the reaction rate in a flow-type reactor is given by

$$r = \frac{P_0}{(T_0 R C_m)(1+z)^2} \frac{dz}{d(1/SV)} \qquad (2)$$

where P_0 is 1 atm pressure; T_0 is 273°K; R (ml atm/mole °K) is the gas constant; C_m is the mean compressibility factor of the feed vapor at the standard state; z (mole fraction) is the concentration of isopropanol in the exit vapor; and SV (hr^{-1}) is a space velocity. Equating (1) with (2)

$$\begin{aligned} r &= \frac{1}{(1+z)^2} \frac{dz}{d(1/SV)} \\ &= 273RC_m(k_1 p_{H_2O} p_{C_3H_6} - k_2 p_{iso\text{-}C_3H_7OH}) \\ &= k_1' p_{H_2O} p_{C_3H_6} - k_2' p_{iso\text{-}C_3H_7OH} \qquad (3) \end{aligned}$$

where $k_1' = 273RC_m k_1$ and $k_2' = 273RC_m k_2$.

At first, the validity of Eq. (3) was tested at $dz/d(1/SV) \rightarrow 0$, where $z \rightarrow 0$. Namely, the initial rate was compared with the experimental data. From Eq. (3), the initial rate is given by

$$\begin{aligned} \{dz/d(1/SV)\}_{1/SV\rightarrow 0} &= k_1' p^\circ_{H_2O} p^\circ_{C_3H_6} \\ &= k_1' m P^2/(1+n+m)^2 \qquad (4) \end{aligned}$$

where p° is a partial pressure of the subscripted species in the feed vapor; P (atm) is the total pressure of the reacting system; n = inert/H_2O (mole ratio); and m = C_3H_6/H_2O (mole ratio). It is possible to show that the value of the term

$$m/(1+n+m)^2$$

in Eq. (4) stays at about 0.23 under the following experimental conditions: $n = 0.0615$ and $m = 0.6712$; $n = 0.0771$ and $m = 0.8401$; $n = 0.089$ and $m = 0.9720$; $n = 0.1093$ and $m = 1.1922$. This result means that at a constant temperature and under a constant total pressure, the initial rate is almost independent of the composition of the feed vapor. As mentioned previously, the experimental initial rate was found to be constant irrespective of the composition of the feed vapor. Thus, the rate equation seems to be satisfactory with respect to the initial rate.

The next problem is to show that Eq. (3) is valid even in cases where $1/SV \neq 0$. For this purpose the integration

$$k'_1 = SV \int_0^z (1+z)^{-2}\left(p_{H_2O}p_{C_3H_6} - \frac{1}{K_{eq}} p_{iso\text{-}C_3H_7OH}\right)^{-1} dz \quad (5)$$

where K_{eq} is the equilibrium constant of the reaction, must be carried out. Considering the fact that $z \ll 1$ under the experimental conditions, $(1+z)^2 = 1$ may be a good approximation. With this approximation, the integration (5) gives

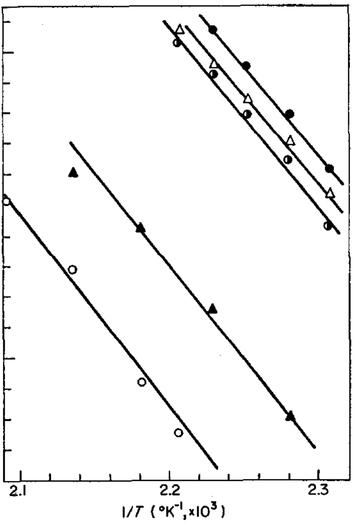

FIG. 8. Arrhenius plots: ●, Al-III; △, Al-II; ◑, Al-I; ▲, Zn-III; ○, Mn-III.

$$z = \left(\frac{1}{2\beta}\right)\left[|\alpha| - (-q)^{1/2} \times \left\{\frac{|\alpha| + (-q)^{1/2}}{|\alpha| - (-q)^{1/2}} \exp\left(\frac{(-q)^{1/2}k}{SV}\right) + 1 \middle/ \frac{|\alpha| + (-q)^{1/2}}{|\alpha| - (-q)^{1/2}} \exp\left(\frac{(-q)^{1/2}k}{SV}\right) - 1\right\}\right] \quad (6)$$

where

$$\alpha = (1 - A) + (m - A)/m - (A^2/PmK_{eq});$$

$$\beta = (1 - A)(m - A)/m;$$

$$q = 4\beta - \alpha^2;$$

$$A = 1 + n + m;$$

and

$$k = k'_1P^2m/(1 + n + m)^2.$$

As mentioned in the previous paragraph, the rate constant k'_1 can be obtained by analyzing the initial rate. Thus, from Eq. (6), it is possible to obtain the value of the concentration of isopropanol in the exit vapor as a function of the reciprocal space velocity. In Fig. 5(b), the calculated results are shown with solid lines, which coincide well with the experimental data.

As an application of the rate equation, the experimental data given in Fig. 4 were analyzed, and Arrhenius plots of the resultant rate constants are shown in Fig. 8. As can be seen in this figure, the respective Arrhenius plots of the Al-I catalyst, the Al-II catalyst, the Al-III catalyst, the Zn-III catalyst, and the Mn-III catalyst have an identical slope, which gives an apparent activation energy of 29.6 kcal/mole. This result indicating a common activation energy for different catalysts is analogous to the fact that different cation molecular sieves have a common activation energy for hexane cracking (*10*). If different catalysts have active sites of the same kind, a common activation energy would result. This deduction is important, and further discussion about it will be given below.

The Catalytic Activity and the Surface Acidity

It seems unlikely that the total acidity, which was defined by the acidity at $H_0 = 4.0$, is directly related to the catalytic activity. As can be seen in Fig. 9, plots of the total acidity vs. k''_1 (the rate constant per unit weight of catalyst) consist of two separate lines. Thus, there is no proportionality between the catalytic activity and the total acidity. According to Hirschler (*11*), the acidity measurements with H_R indicators correlate much better with catalytic behavior than do the results employing Hammett indicators. Therefore, it is suspected that the poor correlation mentioned above is due to the use of Hammett indicators in the present work. However, as can be seen in the following paragraphs, if acidities of a limited strength are compared with the catalytic activity a good correlation between the activity and the acidity as well as a self-consistent interpretation on the experimental results is obtainable. Thus, it appears that the use of Hammett indicators in the present study is not inadequate, though the possibilities that the use of H_R indicators may give some new facts could not be excluded.

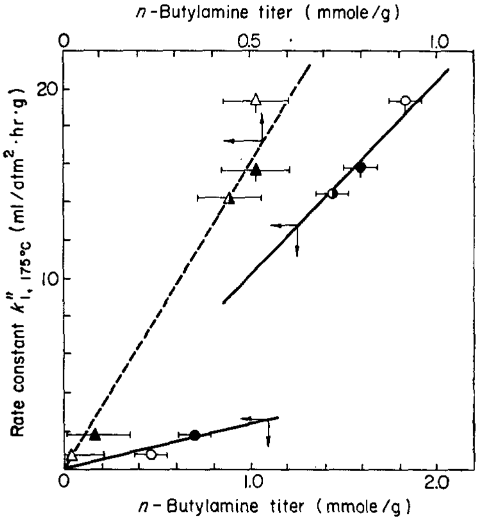

FIG. 9. Relations between the catalytic activity and the surface acidity: ---△--- —○—, Al-III; ---▲--- —●—, Al-II; ---◭--- —◑—, Al-I: ---▲----—●—, Zn-III; ---△--- —○—, Mn-III.

There are some experimental facts which throw some light on the relation between the catalytic activity and the surface acidity. The first fact to be considered is that even the K-II catalyst which was found to be inactive had acidities having H_0 values larger than 1.5. It is apparent from this fact that weak acids of the strength of $H_0 \geq 1.5$ have little contributions against the catalytic activity. The next fact to be considered is that the acidity of acids having H_0 values less than -3.0 disappeared on exposing the sample in a humid atmosphere. This means that the adsorbed water diminishes the surface acidity. Further, the fact enables us to consider that the acids having H_0 values less than -3.0 would not exist on the catalyst under working conditions where water vapor is present as a reactant.

From the discussion above, it is possible to deduce that the acid sites having H_0 values of $1.5 \geq H_0 \geq -3.0$ would be active sites. Generally speaking, the catalytic activity should be proportional to the number of active sites. Therefore, if the deduction is valid a proportionality must be present between the catalytic activity and the surface acidity. Relations between the catalytic activity (k''_1) and the difference between the *n*-butylamine titer at $H_0 = 1.5$ and the titer at $H_0 = -3.0$ are given in Fig. 9 with a dotted line. This figure indicates that k''_1 is proportional to the acidities in the region of $1.5 \geq H_0 \geq -3.0$. Thus, it may be concluded that the acid sites existing in the H_0 region mentioned above are the active sites working for the propylene hydration.

Deductions from this conclusion give results which are consistent with the other results obtained in the present research. For instance, it is unlikely that the energy states of each active site differ widely because only the acid sites having H_0 values in a narrow region act as the active sites. This is consistent with the assumption that the active sites are energetically homogeneous. Further, irrespective of the components and the compositions of the catalysts, a constant activation energy should result from acid sites existing in a given H_0 region. This result agrees with the experimental fact.

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