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## SOLID BASES AND THEIR CATALYTIC ACTIVITY

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### I. Introduction

For the last twenty years, the study on solid acid catalysis has been made extensively and it has made much contribution to the development of both fundamental research and chemical industry, chiefly in the field of petroleum chemistry. Though not much work has been done on solid base catalysis, solid bases are also expected to apply further as useful catalysts for many important reactions. More extensive and quantitative study on basic property of solid materials is now desired to correlate the property with catalytic activity and selectivity and to elucidate the nature of acid-base bifunctional catalysis.

Up to now, as the reactions which are known to be effectively catalyzed by solid bases are the isomerization and polymerization of olefins, the alkylation of aromatics, the stereospecific dehydration of alcohols, aldol type addition

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and condensation *etc.* These reactions are considered to proceed *via* carbanion intermediates and not *via* carbonium ion intermediates as in the case of acid catalyzed reactions. However, the method of measurement of basic property on solid surface is so poor that only several works are reported on the detailed correlation between basic property and catalytic activity of solid.

The present paper reviews the recent works on the surface property, activity and selectivity of solid base catalysts and discusses their characteristics.

## II. Solid Base Catalysts

There are three types of solid bases ; ARRHENIUS, BRÖNSTED, and LEWIS base. Among those are included metal oxides, hydrides, carbonates, hydroxides, amides, alkyl metals, activated carbons, as listed below. Some of them are used as catalysts by supporting with catalyst carriers such as alumina, silica, active carbon, magnesia *etc.*

*Metal*: alkali metal and alkaline earth metal dispersed on silica, alumina, carbon or in oil.

*Hydrides*: hydrides of alkali metal and alkaline earth metal. *e.g.* NaH, CaH<sub>2</sub>.

*Oxides*: oxides of alkali metal and alkaline earth metal and alumina. *e.g.* MgO, CaO, SrO, Al<sub>2</sub>O<sub>3</sub>.

*Hydroxides*: hydroxides of alkali metal and alkaline earth metal.

*Carbonates*: carbonates of alkali metal and alkaline earth metal. *e.g.* MgCO<sub>3</sub>, CaCO<sub>3</sub>.

*Amines, Amides*: LiNH<sub>2</sub>, NaNH<sub>2</sub>, KNH<sub>2</sub>; R<sub>3</sub>N over alumina, H<sub>3</sub>N over alumina.

*Alkyl metals*: alkyl sodium, alkyl lithium (R<sup>-</sup>M<sup>+</sup> type).

*Activated carbons*: carbons activated by heat-treatment or with nitrous oxide, ammonia *etc.*

*Ion exchange resins*: *e.g.* Amberlite IRA-400, OH type, Dowex-3 *etc.*

## III. Basic Property of Catalyst

A complete description of basic property on solid surface requires the determination of basic strength, basicity and nature or structure of basic centers.

### A. Measurement of basic strength

Basic strength of a solid surface is defined as the ability of the surface to convert an adsorbed neutral acid to its conjugate base, *i.e.*, the ability of the surface to donate electron pair to an adsorbed acid. There are two methods

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for measurement of basic strength; indicator method and phenol adsorption method.

i) Indicator method

When an electrically neutral acid indicator is adsorbed on a solid base from nonpolar solutions, the color of the acid indicator is changed to that of its conjugate base, provided that the solid has basic strength enough to give electron pair to the acid. Thus, the basic strength can be measured in general by observing the color change of acid indicators having different pKa values.

For the reaction of an acid indicator AH with an solid base  $\bar{B}$ ,



basic strength  $H'_0$  of  $\bar{B}$  is given as follows according to the equation of HAMMETT and DEYRUP.<sup>1)</sup>

$$H'_0 = pKa + \log(C_A^-/C_{AH}), \quad (2)$$

where  $C_{AH}$  is the concentration of the acidic form of the indicator and  $C_A^-$  the concentration of the basic form.

The color change of an acid indicator begins to be perceptible in the adsorbed indicator layer when about 10% of the basic form is present, *i.e.*, when the ratio  $C_A^-/C_{AH}$  amounts to  $0.1/0.9 \cong 0.1$ . Further increase of the color intensity is imperceptible to the eye; it can only be seen when 90% of the basic form is already present, *i.e.*,  $C_A^-/C_{AH} = 0.9/0.1 \cong 10$ .

Thus, the first color change and the second change of color intensity can be observed when  $H'_0 = pKa - 1$  and  $H'_0 = pKa + 1$ , respectively. If one assumes that the intermediate color appears when 50% of the basic form is formed, *i.e.*  $C_A^-/C_{AH} = 1$ , we have,

$$H'_0 = pKa.$$

According to this assumption, the approximate value of the basic strength on the surface is given by the pKa value of the adsorbed indicator at which the intermediate color appears.<sup>2)</sup> As the indicators which can be used for the above method, we have, at present, bromthymol blue (pKa=7.1, acid form—yellow, basic form—blue) and phenolphthalein (pKa=9.3, acid form—colorless, basic form—red). As the solvents for indicators, nonpolar solvents such as benzene and isooctane are used.

By this method, basic strength of a catalyst (20 mmol Na/100 g silica gel) was found to be  $H'_0 = 4$  when the catalyst was dried at 120°C, but  $H'_0 = 9.3$  when heated at 1000°C. It was also showed that the catalyst of higher sodium content (80 mmol Na/100 g silica gel) changes phenolphthalein to red form even when dried only at 120°C.<sup>2)</sup>

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Other solids on which bromthymol blue is adsorbed and shows blue color are CaO, MgO, Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, KHCO<sub>3</sub>, (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, BaCO<sub>3</sub>, SrCO<sub>3</sub>, 5ZnO·2CO<sub>3</sub>·4H<sub>2</sub>O, KNaCO<sub>3</sub>, Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O and KCN.<sup>3,4)</sup>

MALINOWSKI *et al.*<sup>5)</sup> measured the acid-base strength of magnesium oxide prepared by heating the hydroxide, by using, besides the above acid indicators, bromcresol purple (pKa=6.0), methyl red (5.2) and bromphenol blue (3.8). The results are shown in Fig. 1, where the basic strength decreases and acid strength increases as the temperature of heat-treatment is raised.

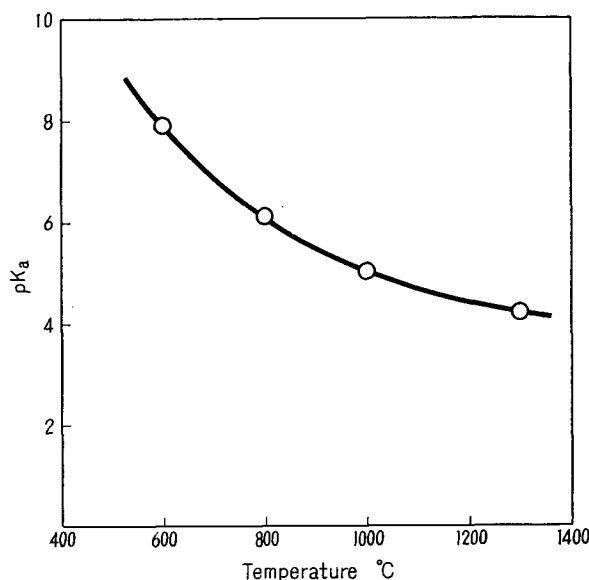


Fig. 1. pKa of MgO surface *vs.* ignition temperature.

There are, besides, a series of spectroscopic studies in UV region on 1,3,5-trinitrobenzene adsorbed on magnesium oxide,<sup>6)</sup> *o*-nitrophenol adsorbed on alkaline earth metal oxides,<sup>7,8)</sup> and three mono-nitrophenols adsorbed on alkali metal carbonates.<sup>9)</sup> In these studies, absorption maxima of the reflectance spectra may also be correlated with basic (in wide sense) strength of a solid material (*cf.* III, C, ii).

ii) Phenol vapor adsorption method

Phenol, a weak acid, which is stable at relatively high temperature is used as an adsorbate. The phenol vapor is adsorbed at saturation on a solid at a definite vapor pressure at a constant temperature and then the system is evacuated at elevated temperatures (100, 200, 300, 380°C). At each temperature, the amount of adsorbates remained on the solid surface is measured.

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A solid on which adsorbed phenol is difficult to desorb at higher temperature can be said to have high basic strength. Some metal oxides are classified as follows by their basic strength thus obtained: a) strong: CaO, b) moderate: BeO, MgO, ZnO, c) weak: silica gel, aluminosilicate.<sup>10)</sup>

### B. Measurement of basicity

Let us define basicity as the number of basic sites per unit weight or unit surface area of a solid. There are four kinds of the methods for basicity measurement.

i) Titration method

Similarly as the acidity of a solid is determined by the *n*-butylamine titration,<sup>11)</sup> the basicity of a solid can be measured by titrating the solid suspended in benzene, on which an acid indicator was adsorbed in the form of its conjugate base, with benzoic acid dissolved in benzene.<sup>12)</sup> Benzoic acid titers are a measure of the amount of basic sites (in mmol/g or mmol/m<sup>2</sup>) having the basic strength of the pK<sub>a</sub> value of the indicator used.

The basicity of some metal oxides measured by this method, using bromthymol blue (pK<sub>a</sub>=7.1) as an indicator is shown in Table 1.<sup>12)</sup> The basicity of alkaline earth metal is changed by heat-treatment. Recently, SAITO *et al.*<sup>13)</sup> found that the basicity of Ca(OH)<sub>2</sub> decreases with increasing temperature of heat-treatment in the range of room temperature ~350°C, but increases at higher temperature and attains maximum value at 550°C and then begins to decrease again.

By the same method, NIWA *et al.*<sup>14)</sup> measured the basicity of slugs such

TABLE 1 Basicity of metal oxides

Oxides	Temperature of heat-treatment (°C)	Time of heat-treatment (hr)	Basicity (mmol/g)
MgO	untreated	—	0.033
	300	3	0.036
	500	3	0.069
	700	3	0.051
CaO	untreated	—	0.007
	650	3	0.073
ZnO	untreated	—	0
	300	3	0
	400, in vacuum	3	0

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TABLE 2 Basicity of SiO<sub>2</sub>-CaO-MgO

No.	Composition of slag (mol %)			Basicity (mmol/g × 10 <sup>3</sup> )	BL*
	SiO	CaO	MgO		
1	44.2	55.7	0	1.37	5.581
2	44.8	32.3	22.9	1.38	0.043
3	45.2	27.1	27.7	1.14	-0.105
4	46.0	39.3	14.7	1.27	0.063
5	46.8	33.7	19.5	1.22	-0.134
6	46.5	34.1	19.4	1.25	-0.095
7	51.3	36.3	12.4	0.44	-0.555
8	51.0	15.0	33.9	-6.2	-0.855
9	52.7	32.4	14.9	-5.7	-0.782

\* BL (basicity) =  $\sum a_i N_i$ , where  $N_i$  is the mole fraction of each component and  $a_i$  the constant proper to each component (ref. 15).

as SiO<sub>2</sub>-CaO-MgO, SiO<sub>2</sub>-CaO-TiO<sub>2</sub>, and CaO-Al<sub>2</sub>O<sub>3</sub>-MgO, an example of the results being given in Table 2. As shown in the Table, the basicity decreases in the order of No. 1, 2, 4, 6, 5, 3, 7, 9, 8, while the values calculated by MORI's expression<sup>15)</sup> for slug basicity given in the last column are in the order of No. 1, 4, 2, 6, 3, 5, 7, 9, 8. The order of both experimental and calculated basicity values is almost the same except No. 2 and 4, and 3 and 5.

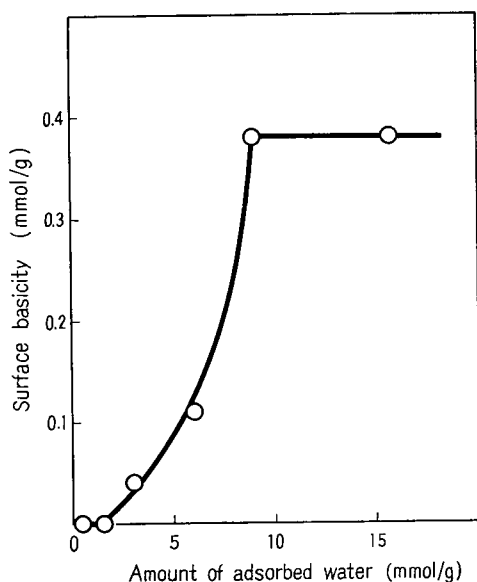


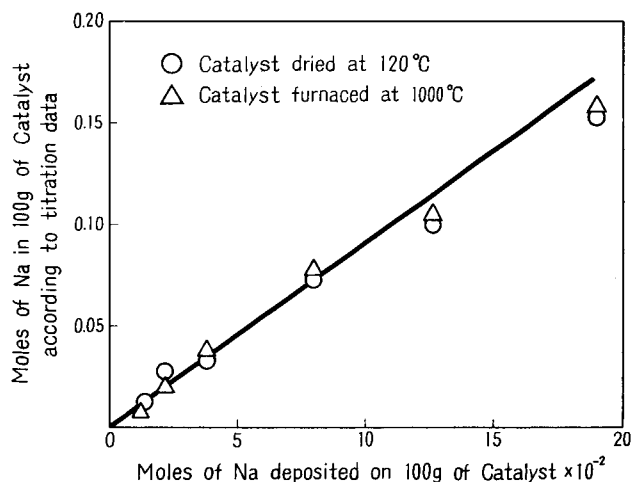
Fig. 2. Surface basicity vs. amount of water adsorbed on Al<sub>2</sub>O<sub>3</sub> at room temperature.

An interesting correlation between the amount of water adsorbed on alumina and the basicity of the surface was observed also by the benzoic acid titration method, using bromthymol blue as an indicator. As shown in Fig. 2,<sup>16)</sup> the basicity increases sharply with increase of the amount of adsorbed water in the range of 3 to 8 mmol/g and then attains a constant value. The basic sites begin to appear by water adsorption of the amount enough to

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poison all acid sites of the alumina. Such an appearance of basicity due to water adsorption was never observed for silica gel or silica-alumina.

MALINOWSKI and SZCZEPANSKA<sup>2)</sup> proposed several titration methods which can be carried out in aqueous solution. One is the titration of the catalyst suspension in water with sulfuric acid solution and another the potentiometric titration in anhydrous acetic acid with perchloric acid solution in anhydrous acetic acid. The basicity of silica containing various amounts of sodium, determined by the former method, is plotted against the amount of sodium impregnated on silica in Fig. 3.<sup>2)</sup> This gives *ARRHENIUS* basicity which is



**Fig. 3.** Quantity of Na found by titration in water vs. quantity of Na impregnated on silica.

**TABLE 3** Basicity, surface area and catalytic activity of nitrous oxide-activated charcoal.

Temperature of heat-treatment (°C)	Surface area (m <sup>2</sup> /g)	Basicity (pH)	Rate of decomposition of hydrogen peroxide (ml/day)
untreated	264	7.1	2
300	164	7.1	75
400	187	7.2	33
500	210	7.9	53
600	219	9.0	93
700	453	9.8	372
800	636	9.9	721
900	860	8.8	713

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due to the presence of  $\text{OH}^-$  ions formed in the solution owing to hydrolysis of the  $\text{Si-ONa}$  compound (salt of weak acid and strong base) to  $\text{Si-OH}$  and  $\text{NaOH}$ .

These methods in aqueous solution, however, have to await a further investigation, because any interaction of polar solvent with basic site may occur, depending on the kinds of solid used.

ii) Exchange method

Similarly as the surface acidity is determined by measuring the amount

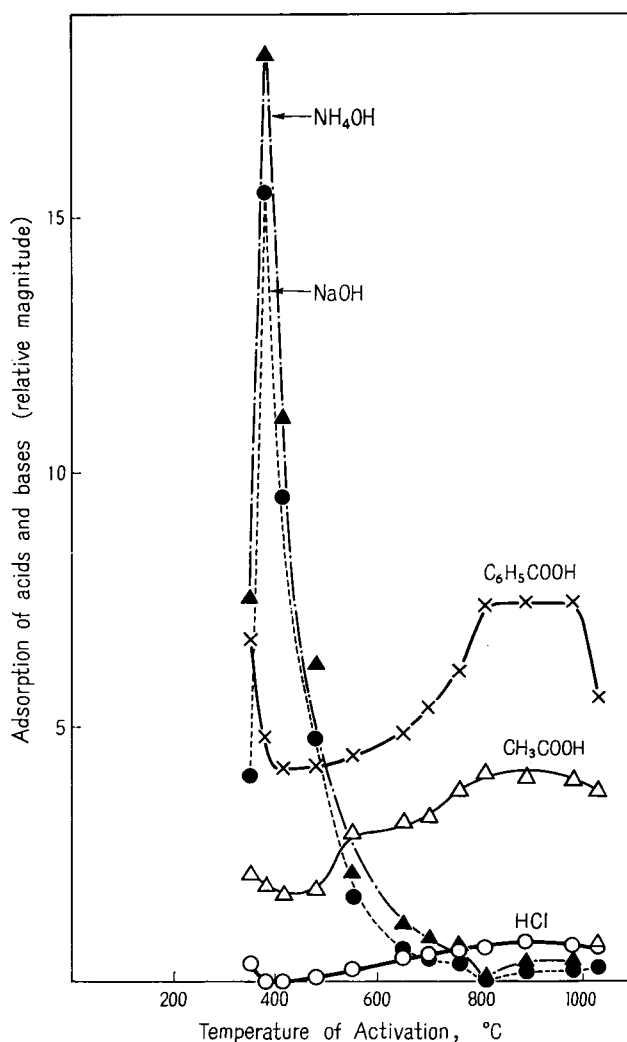


Fig. 4. Adsorption of acids and bases on pure charcoal

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of proton released in solution by the exchange of proton of the surface with cations such as  $K^+$ ,  $NH_4^+$  etc.,<sup>17)</sup> the basicity of some solids can be measured by the exchange of hydroxide ion of the surface with anions. NARUKO measured the basicity of carbon activated with nitrous oxide<sup>18)</sup> or ammonia<sup>19)</sup> by putting 0.1 g of active carbon into 100 ml of 0.1 N KCl aqueous solution (pH=7) and by observing pH variation of the solution after 24 hours shaking by means of pH meter.

The basicity of charcoal activated with nitrous oxide is shown in Table 3. The basicity increases with increasing temperature of heat-treatment, attains a maximum value at 800°C and then decreases at higher temperature.

iii) Acid adsorption method

The basicity of pure sugar charcoal was obtained by measuring the adsorbed amount of acids such as benzoic acid, acetic acid and hydrochloric acid in water.<sup>20)</sup> As shown in Fig. 4, the basicity attains maximum value when the charcoal was heat-treated at about 900°C, while the acidity maximum appears at 400°C.

Recently SCHWAB<sup>21)</sup> found that boron trifluoride (LEWIS acid) covers 60~80% of BET surface area of alumina in 30 mmHg at 400°C. Since ammonia covers only 5~8% for the same alumina, the basicity of the alumina is larger than the acidity.

The number of carbon dioxide molecules adsorbed per unit surface area may be also considered a measure of the basicity at the surface.<sup>22)</sup>

iv) Calorimetric titration

The calorimetric determination of surface acidity was reported by TRAMBOUZE *et al.*<sup>23)</sup> and TOPCHIEVA *et al.*<sup>24)</sup> Similarly, the basicity can be determined by observing the temperature increase due to heat of the reaction of solid bases with acid in benzene. A titration curve for the basicity measurement of silica-alumina is given in Fig. 5.<sup>25)</sup> Taking 3 ml as the amount of trichloroacetic acid required

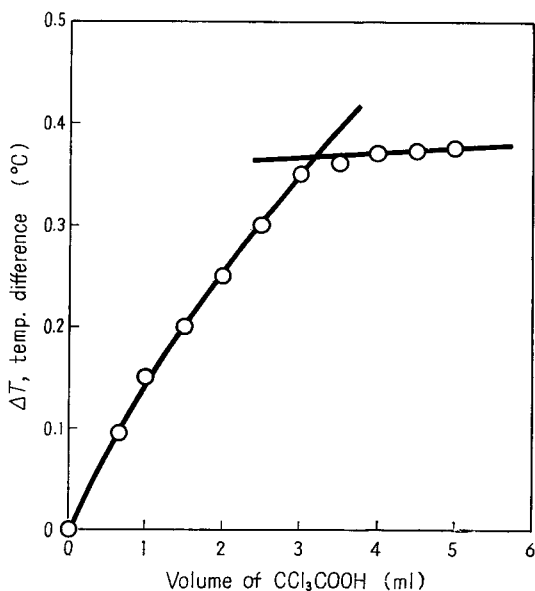


Fig. 5. Temperature increase due to heat of reaction of  $SiO_2 \cdot Al_2O_3$  (4.15 g) with trichloroacetic acid in benzene

for neutralizing basic sites of the catalyst, the basicity is estimated to be about 0.6 mmol/g.\*)

### C. Nature of basic centers

The nature or structure of basic centers on solid surfaces is not fully studied and the solid bases subjected to the study are limited to alumina, magnesia and activated carbon.

#### i) Alumina

The basic site as well as the acid site on the dehydrated surface of alumina could be pictured by a model<sup>26)</sup> shown in Fig. 6. The LEWIS acid site is explained as not fully coordinated aluminum atom formed by dehydration and the BRÖNSTED acid site as the LEWIS acid site which adsorbed moisture, while the basic site is considered to be negatively charged oxygen atom.

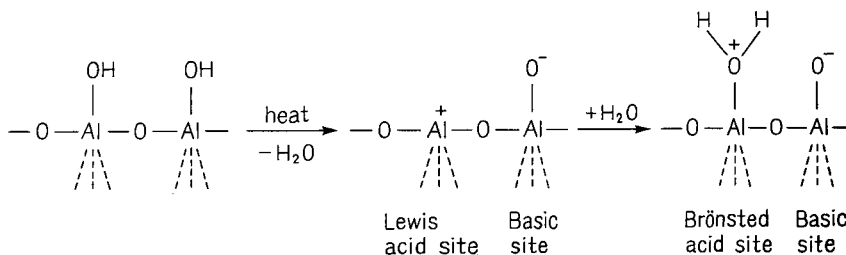


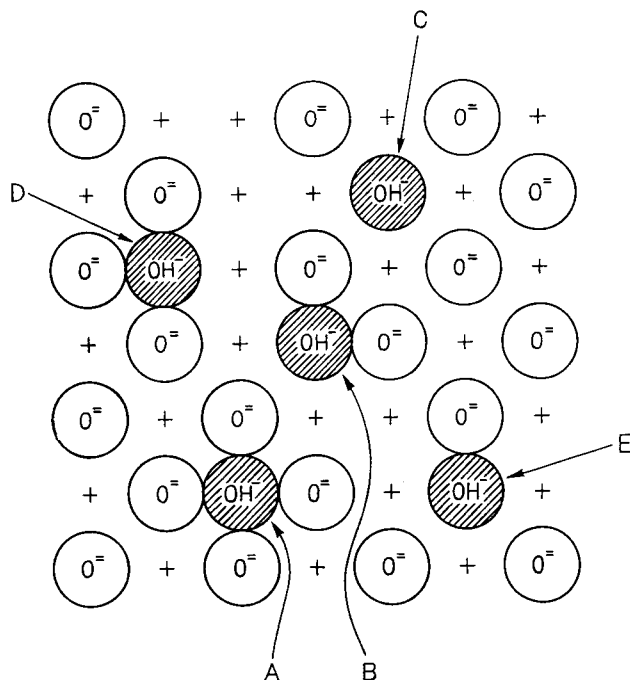
Fig. 6. Acidic and basic site of  $\text{Al}_2\text{O}_3$ .

Recently PERI proposed a detailed model<sup>27)</sup> for the surface of  $\gamma$ -alumina<sup>28)</sup> prepared by heating aluminum hydroxide. The model for the alumina heat-treated at 800°C is shown in Fig. 7, where five types of isolated hydroxyl groups A, B, C, D and E are seen, which are differing in the nearest neighbor configuration and covering 10% of surface. The observed five absorption maxima (3800, 3780, 3744, 3733 and 3700  $\text{cm}^{-1}$ ) in infrared spectra could be assigned respectively to the sites of A, D, B, E and C. Their sites differ in local charge density; type A with 4  $\text{O}^{-2}$  ions as neighbors is most negative (basic site) and type C without neighbors is most positive (acidic site).<sup>28)</sup> PERI<sup>29)</sup> also assumes the existence of "acid-base" sites or ion-pair sites on dry  $\gamma$ -alumina from infrared study on the adsorption of ammonia.

YAMADAYA *et al.*<sup>16)</sup> attributed their observed basic property of alumina to weakly adsorbed free OH groups, and not to the remaining OH groups on the surface after dehydration, on the basis of the observation that the basic

\*) An attempt to measure basicity by titrating with benzoic acid using bromthymol blue as an indicator failed in the case of  $\text{SiO}_2\text{-Al}_2\text{O}_3$ , since the adsorbed indicator did not give its basic color (see ref. 12).

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**Fig. 7.** Types of isolated hydroxyl ions  
(+ denotes  $Al^{+3}$  in lower layer)

property begins to appear when water molecule corresponding to mono-molecular layer adsorption was adsorbed and becomes constant with the adsorption of water corresponding to termolecular layer (see Fig. 2).

ii) MgO

The presence of several types of basic centers at the surface of partially dehydrated magnesium hydroxide are discussed by KRYLOV *et al.*<sup>30)</sup> on the basis of the study on adsorption and isotope exchange of carbon dioxide at the magnesium oxide and at the partially dehydrated magnesium hydroxide surfaces. These are (a) strongly basic  $O^{2-}$  centers which during adsorption are transformed to  $CO_3^{2-}$  ions in agreement with the mechanism postulated by Garner ; (b) strongly basic centers derived from the  $O^{2-}$  ions adjacent to the surface OH groups ; and (c) surface OH groups constituting weakly basic centers. According to a recent work made by MALINOWSKI *et al.*,<sup>22)</sup> the type (c) centers are ruled out as a possibility, at least for the specimens ignited at temperatures higher than  $600^\circ C$  in which no free hydroxyl groups were detected. Recently, the transfer of an electron from the surface of magnesium oxide to the adsorbed electron acceptor molecule, forming ions and ion radicals,

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which are stabilized by the surface of the adsorbent under vacuum conditions, was detected according to the absorption spectra and ESR signals.<sup>31-33</sup> This also indicates the existence of basic (in wide sense) sites on magnesium oxide.

KORTÜM<sup>6</sup>) found that 1,3,5-trinitrobenzene (I) which is colorless on silica gel becomes red ( $\nu_{\max} = 21500 \text{ cm}^{-1}$ ) on magnesium oxide and the red becomes colorless when dissolved out with methanol. This absorption maximum is the same as that in alkaline ethanol solution. Thus, the action of magnesium oxide is considered to be analogous to that of hydroxide ion as shown in Fig. 8.

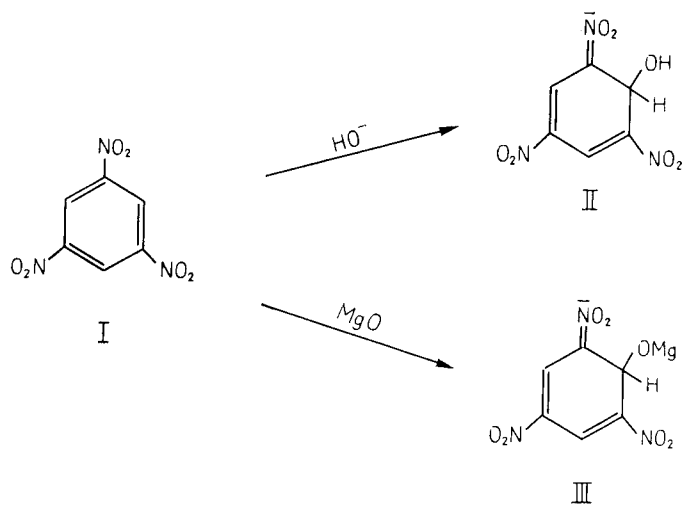
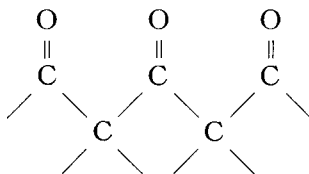


Fig. 8. Adsorption of 1,3,5-trinitrobenzene on MgO.

### iii) Carbon

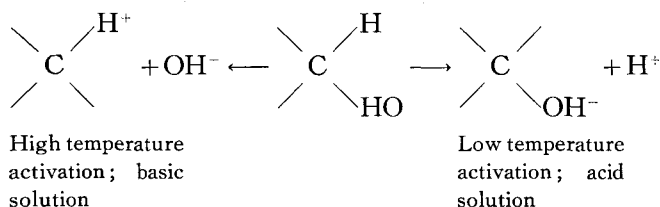
As shown in Fig. 3, activated carbon has not only base-adsorption capacity, but also acid-adsorption capacity. These properties are considered due to the presence of chemisorbed oxygen on charcoal or oxygen complex.<sup>34-38</sup> SHILOV<sup>39</sup>) says that the basic property is due to the formation of the oxygen complex as shown below.



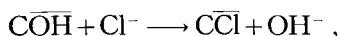
FRUMKIN<sup>40</sup>) assumes that charcoal would be regarded as functioning as a reversible electrode, either hydrogen or hydroxyl according to the temperature

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of activation. This may be expressed as follows.



The appearance of the basic property of nitrous oxide-activated charcoal shown in Table 3 is considered due to the following three reasons. a) The solution becomes alkaline due to  $\text{OH}^-$  released in the solution by anion exchange as below.



where  $\overline{\text{OH}}$  and  $\overline{\text{Cl}}$  denote respectively the hydroxide and chlorine on the surface of the carbon. b) Due to the decrease of proton concentration in solution by the selective adsorption of proton to  $\pi$ -electron of carbon. c) Due to the decrease of proton concentration in solution by proton attraction of anion adsorbed on carbon.<sup>41)</sup>

The fact that the basicity changes, as shown in Table 4,<sup>18)</sup> depending on the kinds of anion used excludes the reason of b). Thus, the basicity is considered due to anion exchange or anion adsorption.

TABLE 4 Basicity of activated carbon

Temperature of heat-treatment (°C)	Basicity (pH)		
	KCl	KBr	KI
untreated	7.1	7.3	7.9
800	9.9	10.1	10.9

#### IV. Correlation between Basic Property and Catalytic Activity

A parallel relation was found between the basic strength of various solids measured by phenol vapor adsorption method and their catalytic activity for the dehydrogenation of isopropyl alcohol.<sup>10)</sup>

MALINOWSKI *et al.* investigated the reactions of formaldehyde with nitromethane,<sup>42)</sup> acetaldehyde,<sup>43)</sup> acetone<sup>44)</sup> or acetonitrile,<sup>45)</sup> over the silica gel catalysts containing various amounts of sodium at 275°C and found the linear relation between the apparent reaction rate constants and the amounts of sodium im-

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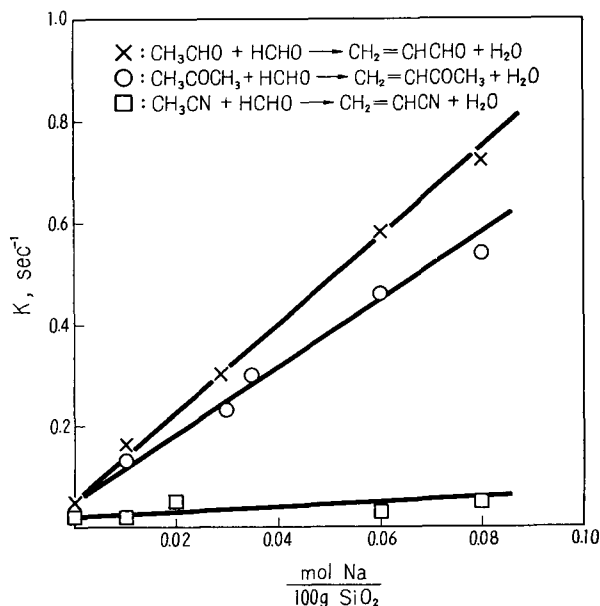
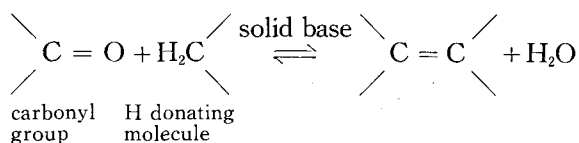


Fig. 9. Correlation between reaction rate constant and sodium concentration in silica catalyst.

pregnated in silica gel, as shown in Fig. 9.<sup>46)</sup> Since linear relations exist between the sodium concentration in silica catalyst and the basicity or basic strength of the catalyst as discussed in the foregoing section, the reaction rates is directly influenced by basic property of catalysts. On the other hand, a linear relation was also found between the rate constants and pK<sub>A</sub> value of hydrogen donating molecules such as CH<sub>3</sub>CHO, CH<sub>3</sub>COCH<sub>3</sub>, CH<sub>3</sub>CN.<sup>46)</sup> Consequently, the reaction rate V is governed not only by basic property of the catalyst X<sub>B</sub>, but also by the acid strength of hydrogen donating molecule K<sub>A</sub>.



$$V \propto K_A X_B$$

More detailed relationship between V and X<sub>B</sub> was examined for the reaction of formaldehyde with acetaldehyde, by keeping K<sub>A</sub> constant. As shown in Fig. 10,<sup>47)</sup> the rate constant increases linearly with increasing sodium content of catalyst in the range of the content below 0.81 mmol/g. Since the reaction occurs even with a catalyst containing no sodium, two types of active centers

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for this reaction are considered to exist. One is "sodium active site (-Si-O-Na)" formed on the catalyst containing sodium and the other is active sites containing no sodium. This is supported by the fact that the observed activation energy (10~12 kcal/mol) with the catalyst containing Na (0.187~1.875 mmol/g) differs from the value (3 kcal/mol) with pure silica gel (Na, K content 0.003 mmol/g). The constancy of activation energy in the range of Na content (0.187~1.875 mmol/g) indicates that reaction rate is proportional to the amounts of the active center containing sodium. In Fig. 10, the rate constant decreases with increasing sodium content in the range of 1.25~1.875 mmol/g. This is considered due to the decrease of the sodium active centers by partial disruption of silica gel structure with treatment of high concentration of sodium hydroxide.

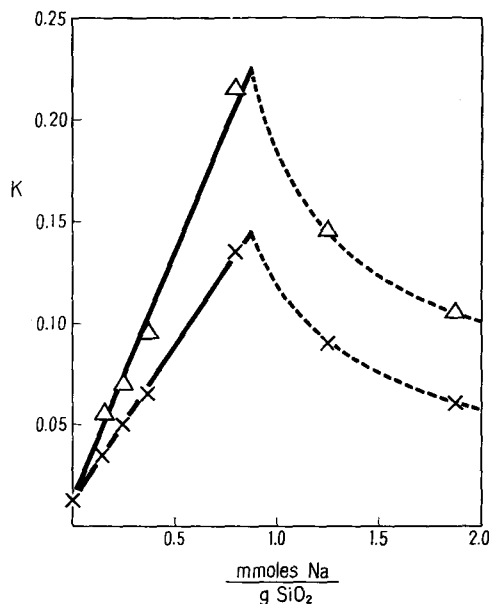


Fig. 10. Correlation between reaction rate constant and sodium concentration in silica catalyst.

NARUKO<sup>18)</sup> observed a parallel relation between the basicity and the catalytic

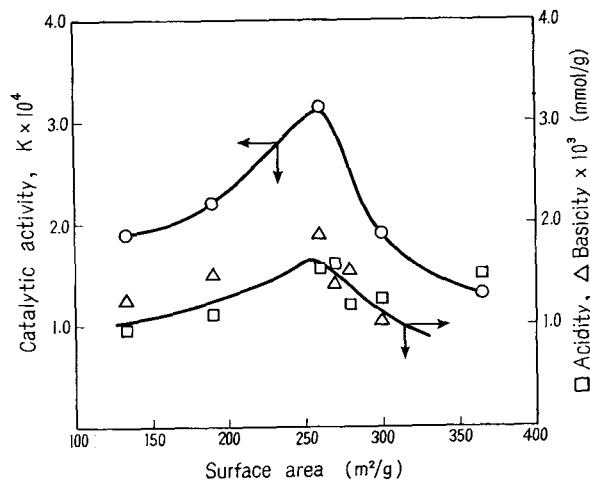


Fig. 11. Catalytic activity, acidity and basicity of various Al<sub>2</sub>O<sub>3</sub>.

activity of nitrous oxide-activated charcoal for the decomposition of hydrogen peroxide (see Table 3).

YAMADAYA *et al.*<sup>16)</sup> measured specific surface area (BET), basicity (by titration method using bromthymol blue) and the catalytic activity for the dehydration of alcohol of alumina prepared under various conditions. As the result is shown in Fig. 11, the basicity increases with increasing surface area in the range of 150~250 m<sup>2</sup>/g and then decreases. The change is approximately parallel with that of the catalytic activity.

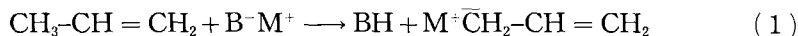
## V. Reactions Catalyzed by Solid Bases

In this section, it will be briefly described that what kinds of solid base catalysts have been used for what kinds of reactions. In some cases, the catalysts are compared with solid acid catalysts or homogeneous base catalysts to characterize the catalytic action of solid bases. Acid-base bifunctional catalysis and some reaction mechanism involving carbanion intermediates are also discussed.

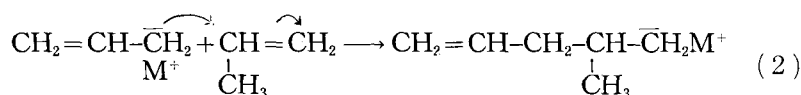
### i) Polymerization, isomerization and alkylation

The oxides, carbonates and hydroxides of alkali and alkaline earth metal (MgO, CaO, SrO, Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, CaCO<sub>3</sub>, SrCO<sub>3</sub>, NaOH, Ca(OH)<sub>2</sub>, *etc.*) were found to polymerize formaldehyde,<sup>48)</sup> ethylene oxide,<sup>49)</sup> propylene oxide,<sup>50,51)</sup> lactam<sup>52)</sup> and  $\beta$ -propiolactone<sup>53)</sup> to form their high polymers. It is interesting to note that the catalytic activity of Ca(OH)<sub>2</sub> is less than that of CaO for  $\beta$ -propiolactone under the same reaction condition.<sup>53)</sup> The polymerization of lactam is considered to be catalyzed by the complex formed from the monomer and solid base<sup>54)</sup> and in fact, the bond formation of the alkali metal with the nitrogen atom of the monomer is revealed by the IR investigation.<sup>55)</sup>

Dimerization of olefins, in particular, the synthesis of hexane from propylene was studied by using solid bases such as Na/K<sub>2</sub>CO<sub>3</sub> (reaction temp. 100°C),<sup>56)</sup> KH dispersed in mineral oil (98~100°C)<sup>57)</sup> and KNH<sub>2</sub> on alumina (200~206°C).<sup>58)</sup> The reaction is considered to proceed *via* carbanion intermediates as illustrated below.

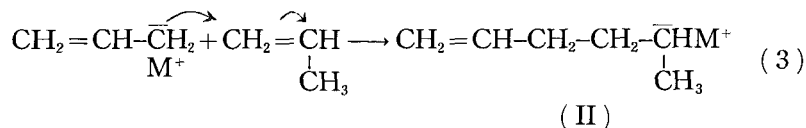


(B = H, NH<sub>2</sub>, alkyl, allyl, alkenyl *etc.*, M = alkali metals)

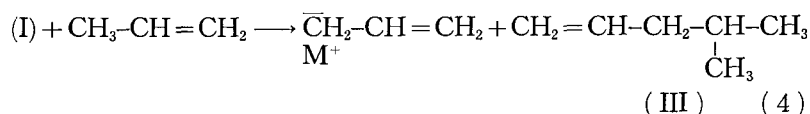


(I)

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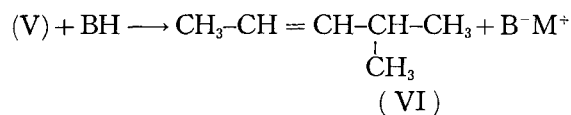
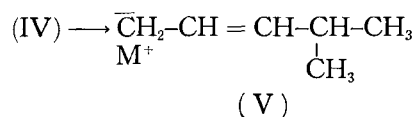
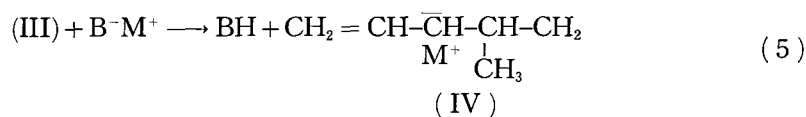


Chiefly,



The allyl anion formed by Eq. (1) reacts with propylene by Eq. (2) or (3), but gives (III) as a chief product because of the stability of primary carbanion (I).\*

Allyl anion produced by Eq. (4) reacts also with propylene to give dimer. Further reaction like Eq. (5) takes place to give 4-methyl-2-pentenes (VI).



Namely, the isomerization of olefin with base catalyst takes place and the product distribution of olefin shows that at thermodynamical equilibrium after a long contact time.

A solid base like Na/Al<sub>2</sub>O<sub>3</sub> which has large surface area is very active for the isomerization of olefins. For example, the isomerization of 1-pentene attains its equilibrium in 60 min even at 30°C, and that of 1-butene in only 0.6 min at 25°C.<sup>59,60)</sup>

The isomerization of *trans*-crotonitrile to *cis*-isomer was recently investigated by using solid base catalysts such as Al<sub>2</sub>O<sub>3</sub>, MgO, CaO, Na<sub>2</sub>CO<sub>3</sub> and NaOH supported on silica gel and solid organic compounds.<sup>61)</sup> The observed facts that inorganic or organic compounds such as Al<sub>2</sub>O<sub>3</sub>, potassium 2-naphthol-3-carboxylates, sodium salicylates *etc.* which have both acidic and basic groups

\* ) The order of the stability of carbanions is primary > secondary > tertiary, in contradiction to that of carbonium ions.

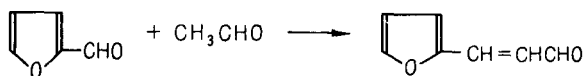
are catalytically active, but NaOH or Na<sub>2</sub>CO<sub>3</sub> without carrier, silica alone and potassium biphthalate which have either only basic or only acidic property are inactive indicate that this isomerization undergoes an acid-base bifunctional catalysis.

Alkylation of aromatics with olefins was also catalyzed by solid bases such as Na/Al<sub>2</sub>O<sub>3</sub>, NaH, K/graphite *etc.* It is of interest to note that  $\alpha$ -carbon of side chain of aromatics having benzylic hydrogen is alkylated over the base catalysts, while aromatic ring is alkylated over acid catalysts. The side chain alkylation catalyzed by solid bases is also considered to proceed *via* carbanion intermediates.<sup>59)</sup>

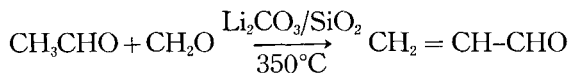
ii) Condensation, addition and dehydrohalogenation

As stated in foregoing section, a detailed kinetic work on aldol type condensation over NaOH/SiO<sub>2</sub> catalyst has been made by MALINOWSKI and BASINSKI.<sup>47)</sup> The condensation of propionaldehyde is catalyzed by basic lithium phosphate, Ca(OH)<sub>2</sub> *etc.*<sup>62)</sup> Although CANNIZZARO reaction as a side reaction is accompanied in the case of Ca(OH)<sub>2</sub>, basic lithium phosphate shows high selectivity. The formations of aldol from acetaldehyde and of diacetone alcohol from acetone are catalyzed also by anion exchange resin (Amberlite IRA-400, OH type).

MgO, CaO and K<sub>2</sub>CO<sub>3</sub> was used as catalysts for the formation of 2-furylacrolein from furfural and acetaldehyde in gaseous phase<sup>63)</sup> and Li<sub>2</sub>CO<sub>3</sub>/SiO<sub>2</sub> for the synthesis of acrolein.<sup>64)</sup> KNOEVENAGEL reaction<sup>65)</sup> and MICHAEL condensation<sup>66)</sup>



(yield: MgO, 70.0%; CaO, 36.0%; K<sub>2</sub>CO<sub>3</sub>, 25.6%)



(yield: 55~53%)

takes place easily in the presence of weakly basic Amberlite IR-4B, Dowex-3, polyvinylpyridine.

Addition reaction of alcohol to acrylonitrile,<sup>67)</sup> hydrogen cyanide to ketone,<sup>68)</sup> nitromethane to aldehyde<sup>69)</sup> and of epoxide to phenol<sup>70)</sup> are catalyzed by anion exchange resins.

The dehydrochlorination of 1,1,2-trichloroethane is catalyzed by alkaline earth metal oxides. The ratios of 1,1-dichloroethylene to 1,2-dichloroethylene formed and of *trans*- to *cis*-1,2-dichloroethylene were found to increase in the

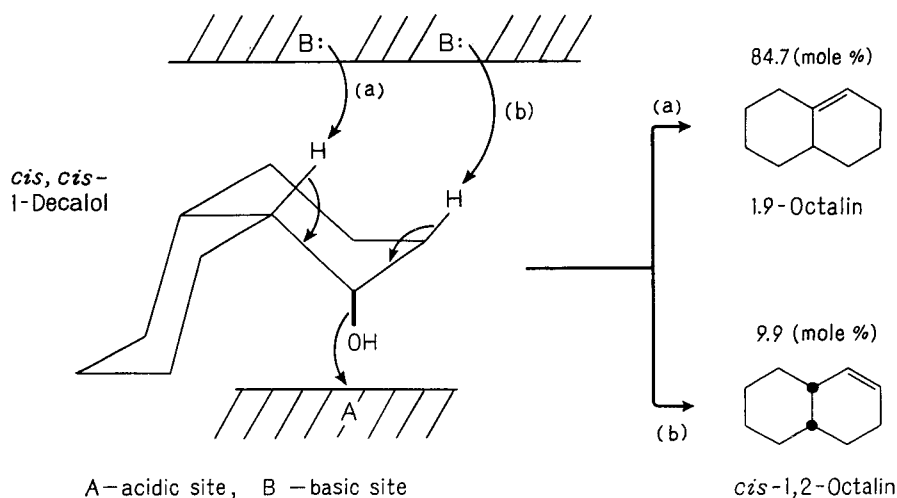
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order of MgO, CaO and SrO.<sup>71)</sup> The eliminations of HCl from 1, 2-dichloro-2, 2-diphenylethane<sup>72)</sup> and 2, 3-dichlorobutane<sup>73)</sup> were also studied with basic oxide catalysts (CaO, Al<sub>2</sub>O<sub>3</sub>).

iii) Dehydration of alcohol

The dehydration of various types of alcohols with alumina catalysts has been extensively studied and the reaction mechanism and the nature of alumina were discussed recently by PINES and MANASSEN.<sup>74)</sup> They summarize that the dehydration of most alcohols (menthols, alkylcyclohexanols, decalols, bornanols, 2-phenyl-1-propanol *etc.*) undergoes *trans*-elimination and requires the participation of both the acidic and basic sites of the alumina and that for this reason alumina may act as a "solvating" agent as it must surround the alcohol molecule, whereby the acid sites of the alumina would act as a proton donor or electron acceptor and the basic sites as the proton acceptor or electron donor.

As a typical example, the elimination scheme of *cis, cis*-1-decalol is shown in Fig. 12. The formation of 1, 9- and *cis*-1, 2-octalins clearly indicates that the dehydration undergoes a *trans*-elimination over alumina acting as a solvating agent and an acid-base bifunctional catalyst.

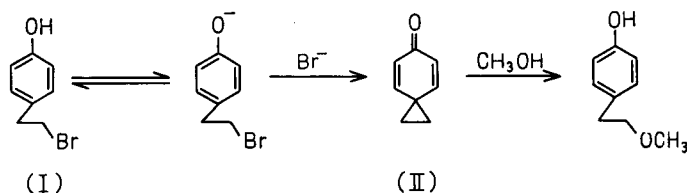


**Fig. 12.** Dehydration of *cis, cis*-1-decalol over Al<sub>2</sub>O<sub>3</sub> catalyst.

iv) Synthesis of unstable intermediates

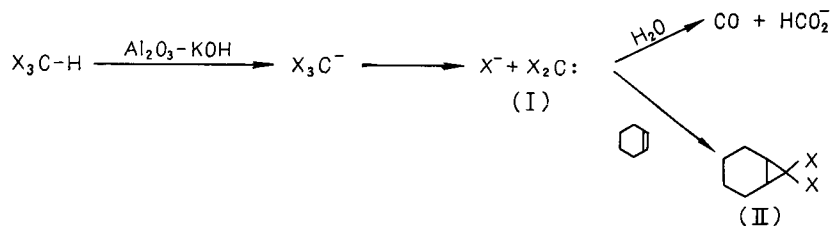
Spiro [2, 5] octa-1, 4-dien-3-one intermediate (II) which is easily solvated can not be obtained in the presence of homogeneous bases such as *t*-BuOK in *t*-BuOH, NaH in ether and NaOH in aqueous solution, but is obtained by passing ether solution of (I) through a column packed with KOH/Al<sub>2</sub>O<sub>3</sub>.<sup>75)</sup>

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Other acetylenic compounds having a group sensitive to alkali<sup>76)</sup> or perchloro compound<sup>77)</sup> can be also obtained by using basic alumina catalysts. For the hydrolysis of cholestan-3 $\beta$ -yl 3:5-dinitrobenzoate,  $\text{KOH}/\text{Al}_2\text{O}_3$  is more catalytically active than homogeneous base<sup>78)</sup> and for the hydrolysis of toluene-sulfonate the selectivity of solid base catalyst ( $\text{KOH}/\text{Al}_2\text{O}_3$ ) differs from that of homogeneous base ( $\text{AcOK}-\text{AcOH}$ ).<sup>79)</sup>

The yield of 7,7-dihalobicyclo [4.1.0] heptane (II, X=Cl or Br) from haloform and cyclohexene was found to be 12~15% in the case of  $\text{KOH}/\text{Al}_2\text{O}_3$ ,<sup>77)</sup> but less than 1% with  $\text{KOH}$  in aqueous solution.<sup>80)</sup>



The difference in yield is explained by taking into account that water molecule remained in  $\text{Al}_2\text{O}_3-\text{KOH}$  prepared by calcination is hard to react with carbenes (I), since the water molecule is tightly bound to the catalyst, but in aqueous solution free water molecule is easy to react with carbenes.

## VI. Summary

The characteristics and advantages of solid base catalysts have been demonstrated in comparison with solid acid and homogeneous base catalysts. The reactions with solid base catalysts proceed, in general, *via* carbanion intermediates in contrast with carbonium ion intermediates in the case of solid acid catalyzed reactions. The distinct difference in catalytic action between solid acid and base catalyst was seen in isomerization and alkylation reactions. Compared with homogeneous bases, solid bases as catalysts have the advantages that their separation from reaction mixture is easy and their property can be changed by heat-treatment or poisoning so as to get a good catalyst for a certain reaction. In some reactions, it was pointed out that the catalytic

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activity and selectivity of solid bases is higher than those of usual bases of liquid form.

It is again emphasized that more extensive and quantitative study on the measurement of basicity and basic strength and on the nature of basic centers is required not only to find optimum base catalysts or acid-base bifunctional catalysts, but also to elucidate the reaction mechanisms.

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