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Properties of Magnesium Oxides Prepared from Various Salts and Their Catalytic Activity in 1-Butene Isomerization

Tsuneo Matsuda,* Jun Tanabe, Nobuatsu Hayashi, Yoh Sasaki,
Hiroshi Miura, and Kazuo Sugiyama
Department of Applied Chemistry, Faculty of Engineering, Saitama University, Saitama 338

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The basicity, one-electron donor property, and surface area were examined on the magnesium oxide catalysts prepared from six different kinds of magnesium salts. Magnesium oxide prepared from magnesium nitrate, oxalate, and acetate exhibited strong basicity and relatively large surface area and, on the other hand, MgO prepared from magnesium chloride, carbonate and sulfate had relatively weak basicity and small surface area. Number of one-electron donor centers hardly changed in the variety of magnesium oxides, except the one prepared from magnesium chloride. Magnesium oxide prepared from chloride showed both the lowest basicity with less strength than $H_-=15.0$ and surface area in the six kinds of catalysts. In order to examine the influence of remaining anions in MgO a variety of catalysts were prepared by the addition of ammonium chloride, sulfate, and carbonate, respectively in MgO prepared from the nitrate. Ammonium chloride brought the greatest influence on the basicity, one-electron donor property, and surface area. Thus the remaining chloride ion greatly affected such properties as cited above. Sodium nitrite which decomposes at higher temperature than 320 °C was added to the magnesium oxides for the examination of the effect of the sodium cation. The amount of the basicity with a moderate strength ($H_-=15.0$—22.3) increased by the addition of $NaNO_2$. This was ascribed to the formation of the moderate strength of basicity by the interaction of Na_2O, one of the decomposed products of $NaNO_2$ and MgO. Isomerization of 1-butene was carried out on the six kinds of catalysts at 30 °C. The magnesium oxides prepared from nitrate, oxalate, and acetate salts (group A) exhibited isomerization activity and the ones from chloride, sulfate, and carbonate (group B) did not entirely. The isomerization activity could be correlated with the stronger basicity than $H_-=22.3$. Temperature pregrammed desorption curves of acetic acid adsorbed on the catalysts indicated two peaks at around 350 and 420 °C in group A catalysts and only one at 350 °C in group B. The desorbed peak at around 420 °C was assigned to the adsorbed acetic acid on the stronger basic sites than $H_-=22.3$.

It is well known that magnesium oxide is characterized by extremely strong basicity[1-3] and one-electron donor property.[4] Kijenski and Malinowski[5,6] reported that magnesium oxide prepared from magnesium nitrate exhibited such strong basicity as $H_-=33.0$ and that magnesium oxide doped with sodium vapor had further stronger basicity than $H_-=35.0$. Accordingly we examined at first the basicity of magnesium oxide prepared from basic magnesium carbonate, on which sodium vapor was doped as a trace experiment of Kijenski and Malinowski. The results, however, did not entirely show stronger basicity than $H_-=35.0$. Kijenski[7] suggested to us that a trace of remaining carbonate ion in MgO, when it was prepared by from basic magnesium carbonate, would hinder the formation of the stronger basic sites. Consequently, it was considered that the remaining anions, when MgO was prepared from the different magnesium salts, would greatly affect the strength of basicity. On the basis of the consideration basicity, one-electron donor property and surface area of magnesium salts were undertaken to examine in this study. On the six kinds of MgO catalysts isomerization of 1-butene was carried out and their activity was connected with such physicochemical properties of the catalysts as basicity, one-electron dnor and safaoe area. Temperature progammed desorption (TPD) method of acetic acid adsorbed on the catalysts was also undertaken forthe examination of basicity distribution, as anothermethod from a titration method.

Experimental

Materials. Magnesium oxides were prepared from six different magnesium salts as shown in Table 1. In each of the saturated aqueous solutions of magnesium nitrate, chloride, and sulfate, two times as dilute aqueous ammonia as the concentrated one was gradually added to precipitate magnesium hydroxide. The precipitates were washed well with distilled water; 5 times in the case of nitrate, 11 times in chloride, and 8 times in sulfate, respectively. Thus even by

Table 1. Basicity, number of one-electron donor centers, and specific surface area of MgO prepared from six different magnesium salts

Magnesium salts	Basicity H_-/mmol g^{-1}						Number of one-electron donor centers spins g^{-1} × 10^{18}	Surface area m^2 g^{-1}
	9.3—15.0	15.0—17.2	17.2—22.3	22.3—27.0	27.0—33.0	Total		
$Mg(NO_3)_2$	0.08	0.01	0.04	0.05	0.03	0.21	1.8	85.7
$MgSO_4$	0.18	0.01	0.01	—	—	0.20	2.1	86.3
$MgCl_2$	0.04	trace	—	—	—	0.04	0.047	19.0
$MgCO_3$-$Mg(OH)_2$	0.02	0.11	—	—	—	0.13	1.8	59.4
MgC_2O_4	0.03	0.12	0.03	0.04	0.03	0.25	1.2	140
$Mg(CH_3COO)_2$	0.04	0.03	0.03	0.03	0.02	0.15	2.1	117

washing with water so well every trace of anion could not be eliminated in every case. Magnesium acetate was dissolved in 6 mol dm^{-3} acetic acid solution, in which the aqueous ammonia of the same concentration as that indicated above was added to precipitate magnesium hydroxide. The precipitate was also washed 5 times with the distilled water All precipitates described above were dried at 120 °C for 12 h and then calcined at 550 °C for 20 h in air. Both magnesium oxalate and basic magnesium carbonate were decomposed to MgO at 550 °C for 20 h in air. Thus prepared samples were analyzed by X-ray diffraction (Rigaku Denki DS type, target Cu $K\alpha$) and could be confirmed to be MgO, and designated as MgO–N (MgO prepared from magnesium nitrate), MgO–Cl (from chloride), MgO–S (from sulfate), MgO–C (from basic carbonate), MgO–O (from oxalate), and MgO–A (from acetate), respectively. Additional compounds of anions and $NaNO_2$ in MgO were prepared as folows; $Mg(OH)_2$ prepared from magnesium nitrate according to the method described above was impregnated in the solutions of ammonium chloride, sulfate, and carbonate, respectively and then evaporated to dryness on the water bath. Thus prepared $Mg(OH)_2$ containing anions was also decomposed at 550 °C for 20 h in air. Sodium nitrite was mixed with MgO and then their mixture was calcined at 400 °C for 2 h under evacuation.

Measurement of Basicity and One-electron Donor Centers. Before the measurements, MgO catalysts were treated at 400 °C for 2 h in a vacuum. The basicity of the catalysts was determined by the titration method with the solution of benzoic acid in benzene (0.05 mol dm^{-3}) in the presence of appropriate Hammett indicatores. The following was applied as basicity indicators;[3,4] phenolphalein ($H_-=9.3$), 2,4-dinitroaniline ($H_-=15.0$), 4-chloro-2-nitroaniline ($H_-=17.2$), aniline ($H_-=27.0$), and triphenylmethane ($H_-=33.0$). By the way the basicity of MgO treated at 500 °C for 2 h in a vacuum showed nearly the same values as the one treated at 400 °C. This agreed with the results of the report of Kijenski that the basicity hardly changed by heat-treatment at the temperature of less than 500 °C.[7] The number of one-electron donor centers was determined by the mesurement of concentration of the anion radical formed by tetracyanoethylene adsorption (in benzene solution) on MgO surface. ESR spectrometer in X-band (Varian E-Line Modulation 100 KHz) was used to record the signal of the resulting radical at room temperature. Spin concentrations were determined by comparison of the area obtained by double integration of the first derivative curves for the sample and for a standard of 2,2-diphenyl-1-picrylhydrazyl benzene solution.

All the reagents used in this study were special grade from Wako Junyaku Co. and used without further purification except benzene and benzoic acid. Benzene and benzoic acid were purified by rectification after reflux in the presence of molecular sieve and recrystallization from water, respectively.

1-Butene Isomerization. 1-Butene isomerization was carried out at 30 °C in a closed system with a volume of 181 cm^3 which was directly connected to a gas chromatograph. The catalysts were evacuated at 500 °C for 2 h before the reaction. Reaction products were analyzed by gas chromatograph equipped with a thermal conductivity detector at 0 °C. The column consisted of 4 m long stainless steel tube (2 mm i.d.) packed with VZ-7. The reaction products released from the system were detected time dependently. The amount of 1-butene fed in the reactor was usually 2.97 mmol and catalysts used was 0.1 g.

TPD of Adsorbed Acetic Acid. TPD of adsorbed acetic acid on MgO consisted of a step-wise heating procedure (5 °C min^{-1}) under flowing N_2 (30 cm^3 min^{-1}). The catalyst (0.2 g) was heated at 550 °C for 2 h under vacuum before adsorption of acetic acid at 35 °C for 30 min. Desorbed compounds were detected by gas chromatograph equipped with the column packed with SiO_2 sand.

Results

Basicity and One-electron Donor Centers of Six Kinds of MgO. The basicity, number of one-electron donor centers and specific surface area of magnesium oxides were summarized in Table 1. The MgO–N, MgO–O, and MgO–A (group A) showed stronger basicity than $H_-=22.3$, but MgO–Cl, MgO–S, and MgO–C (group B) showed a weaker one than that value. However, one could not find stronger basicity than $H_-=35$ in the former catalysts. The MgO–O exhibited both the highest basicity and surface area, and in group B, basicity and surface area of MgO–Cl were the lowest. In the catalysts of group B a trace of anion can be considered to be left. Thus a trace of remaining anions, especially chloride ion, greatly affects basicity and surface area towards the decrease of their values. Number of one-electron donor centers was not almost concerned with the remaining ions except chlorine and was nearly constant.

Additional Effects of Anions and $NaNO_2$. The influences of anions were further examined by the addition of ammonium chloride, sulfate, and carbonate in MgO–N as a standard, since this had a broad distribution of basicity. As shown in Table 2 a large influence

TABLE 2. BASICITY, NUMBER OF ONE-ELECTRON DONOR CENTERS, AND SPECIFIC SURFACE AREA OF MgO ADDED WITH ANIONS

Amount of anion added to 1 g MgO / mmol		Basicity H_-/mmol g^{-1}						Number of one-electron donor centers / spins g^{-1} × 10^{18}	Surface area / m^2 g^{-1}
		9.3—15.0	15.0—17.2	17.2—22.3	22.3—27.0	27.0—33.0	Total		
Cl^-	0.12	0.05	0.01	trace	trace	—	0.06	0.6	34.1
	0.28	0.05	trace	—	—	—	0.05	0.6	24.2
	0.58	0.06	trace	—	—	—	0.06	0.3	21.9
SO_2^{4-}	0.11	0.16	0.04	0.14	0.01	0.02	0.37	2.9	107
	0.30	0.18	0.07	0.13	trace	trace	0.38	1.4	110
	0.58	0.20	0.10	0.06	trace	—	0.36	1.7	114
CO_2^{3-}	0.08	0.02	0.07	0.10	0.02	0.01	0.22	1.9	85.9
	0.29	0.10	0.09	0.11	0.01	0.02	0.33	2.1	85.9
	0.58	0.18	0.07	0.09	0.04	trace	0.38	1.9	82.5

TABLE 3. BASICITY OF MgO ADDED WITH $NaNO_2$

Amount of $NaNO_2$ added to 1 g MgO[a)] mmol	Basicity H_-/mmol g^{-1}					
	9.3—15.0	15.0—17.2	17.2—22.3	22.3—27.0	27.0—33.0	Total
0	0.08	0.01	0.04	0.05	0.03	0.21
0.3	0.08	0.02	0.07	0.03	0.01	0.21
0.9	0.08	0.14	0.06	0.03	0.01	0.32
1.8	0.01	0.17	0.06	trace	trace	0.24

a) MgO was prepared frommagnesium nitrate.

TABLE 4. BASICITY OF MgO–N, MgO–Cl, MgO–S, AND MgO–C ADDED WITH $NaNO_2$[a)]

Catalysts	Basicity H_-/mmol g^{-1}					
	9.3—15.0	15.0—17.2	17.2—22.3	22.3—27.0	27.0—33.0	Total
MgO–N	0.08	0.14	0.06	0.03	0.01	0.32
MgO–Cl	0.01	0.03	0.01	trace	—	0.05
MgO–S	0.07	0.11	0.02	trace	—	0.20
MgO–C	0.01	0.12	0.02	trace	—	0.15

a) Added amount of $NaNO_2$ is 0.9 mmol/g-MgO.

of chloride ion could also be detected in this case. By addition of only 0.12 mmol as chloride ion per gram of MgO the stronger basic sites than $H_-=17.2$ rapidly diminished. The influences of other ions as sulfate and carbonate were not so remarkable as those of the chloride ion, but stronger basic sites decreased to a large extent in all ions. On the contrary total basicity increased by addition of ammonium salts. Surface area increased by addition of $(NH_4)_2SO_4$ and decreased by NH_4Cl and hardly changed by $(NH_4)_2CO_3$. The extent of the influence of anions on the surface area was in the order; $Cl^- > SO_4^{2-} > CO_3^{2-}$. It could be also confirmed that the number of one-electron donor centers was hardly changed by the addition of anions.

Instead of anions, cation was added to magnesium oxides to examine its influence on physicochemical properties. The results were summarized in Tables 3 and 4. With increase of the added amount of $NaNO_2$ basicity with a moderate strength ($H_-=15.0$—17.2) increased and total basicity attained a maximum of 0.9 mmol/g MgO of $NaNO_2$ (see Table 3). By addition of $NaNO_2$ into the group B catalysts, strong basic sites which did not exist before addition appeared. Total basicity hardly changed except MgO–N. It was confirmed by titration method that $NaNO_2$ did not exhibit any basicity. When $NaNO_2$ was decomposed in air or under vacuum, a fused solid was obtained. The solid was very hard and deliquesced during grinding in air. Therefore, measurement of the basicity of the decomposed solid did not suceed.

1-Butene Isomerization. Isomerization of 1-butene was carried out on the six kinds of MgO catalysts at 30 °C. The group A catalysts alone exhibited isomerization activity and group B did not entirely. Time dependency of 1-butene conversion was shown in Fig. 1. The slope between 2 and 7 or 8 min in a plot of conversion *vs.* reaction time was taken as an initial rate. The good correlation between the rate and the basicity

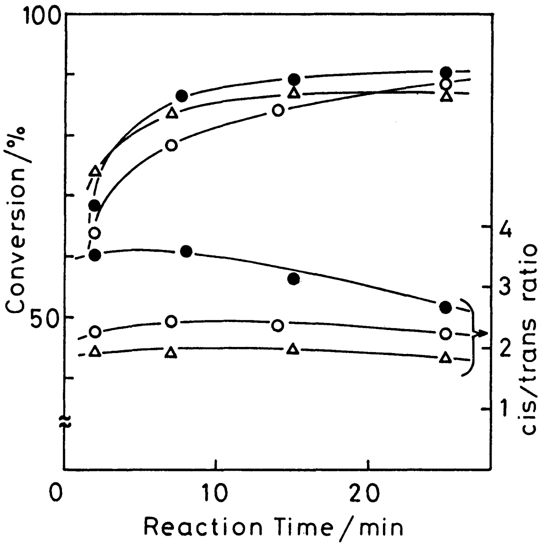

Fig. 1. Conversion-time and *cis*/*trans* ratio plots of 1-butene isomerization.
○: Reaction over MgO prepared from magnesium nitrate, ●: magnesium oxalate, △: magnesium acetate.

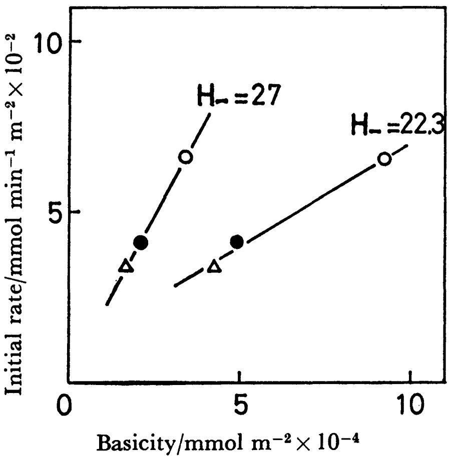

Fig. 2. Relationship between initial rate and basicity with the strength$\geq H_-=22.3$ or 27.
Symbols are the same as those in Fig. 1.

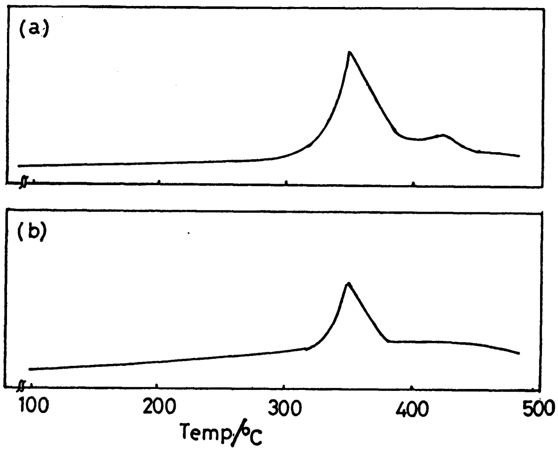

Fig. 3. Typical TPD curves.
(a): MgO–N, (b): MgO–Cl.

stronger than $H_-=22.3$ or 27 per each unit surface area was obtained as shown in Fig. 2.

TPD Measurement. With the aim of examining the basicity distribution by another method except the titration method, and of comparing the results of both methods TPD was carried out. The typical results are shown in Figs. 3(a) and (b). Group A catalysts exhibited two desorbed peaks at near 350 and 420 °C, repectively (Fig. 3(a)). Group B which was inactive for the isomerization exhibited only a peak at 350 °C (Fig. 3(b)). The TPD curve of the catalyst prepared by addition of NH_4Cl in MgO–N was entirely similar to that of Fig. 3(b). It could be demonstrated that the desorbed peak at higher temperature was diminished by the chloride ion left in MgO. By the TPD method a detailed basicity distribution could not be obtained, but a broad one.

Discussion

Basicity nad One-electron Donor Centers of Six Kinds of MgO, Additional Effects of Anions and $NaNO_2$. It is obvious from the results in Tables 1 and 2 that the remaining anions during the preparation of MgO remarkably affect the basicity, one-electron donor centers (only in the case of Cl^-) and surface area. The added ammonium salts decompose evolving gases[8] by heating at 550 °C. In the decomposition of ammonium chloride both NH_3 and HCl are evolved. The strong acid, HCl will interact with MgO to shrink MgO, reducing its basicity and surface area. Chloride ion in HCl probably sinters MgO particles to reduce surface area, as it is known that Cl^- sinters UO_2 particle.[9] The effect of NH_3 would be much smaller than Cl^- in this case. Ammonium sulfate and carbonate decompose as follows:[8]

$$(NH_4)_2CO_3 \longrightarrow 2NH_3 + CO_2 + H_2O,$$
$$(NH_4)_2SO_4 \longrightarrow NH_3 + (NH_4)HSO_4.$$

As the effect of NH_3 seems to be stronger than that of CO_2 or $(NH_4)HSO_4$, more basic sites are produced than acidic sites. The increase of surface area by addition of ammonium sulfate is not due to NH_3, but to sulfate ion, because it was not found in the case of ammonium carbonate.

The basic center is considered mainly to consist of surface O^{2-}.[10,11] Chloride ion added will reduce the electron density of surface O^{2-} by its large electron negativity, leading to the decrease in basicity of MgO. One-electron donor centers consist of anion vacancies in MgO, in which free electron enters.[11,14] Cordischi *et al.*,[15] however, proposed a model of the electron donor surface site consisting of dual site (O^{2-}_{cus}, OH^-), where O^{2-}_{cus}, indicates O^{2-}_{cus} ions in a coordinatively unsaturated site. Thus the accurate structure of one-electron donor centers is still obscure. In either case chloride ions existing in MgO will also attract electron by strong electron affinity, reducing the number of one-electron donor centers. The effect of both sulfate and carbonate ions with weak electron affinity hardly affect the electron donor property. This also agrees with the results in the literature.[15] Both sulfate and carbonate ions do not affect one-electron donor property, as already described, but certainly do the strong basicity, (see Tables 1 and 2) *i.e.*, both affect only the strong basic site to reduce the strength. The strong basic sites ($>H_-=17.2$ or 22.3) will be high in charge density, onto which electrons will easily transfer. Therefore the sites might be affected even by weaker ions such sulfate and carbonate, or one could consider that both ions occlude the strong basic sites. That MgO–S, MgO–C, and MgO added with $(NH_4)_2SO_4$ or $(NH_4)_2CO_3$ had larger surface area than MgO–Cl might be associated with less sintering effect of both ions than Cl^-. Rather larger surface areas of MgO–O and MgO–A might be due to the evolving gases in the decomposition of organic radicals in magnesium salts. Thus, this study provides usuful indications of suitable methods for preparing magnesium oxide having the most favorable catalytic and surface properties.

Sodium nitride decomposes according to the following reaction at more than 320 °C.[16]

$$2NaNO_2 \longrightarrow Na_2O + N_2O_3(=NO+NO_2)$$

and a mechanical mixture or interacted products between them will be formed. By addition of $NaNO_2$ the concentration of the moderate basicity increased, but further addition caused a decrease of the strong basicity, as shown in Table 3. These indicate that Na_2O interacts with the strong basic sites in MgO to reduce the basicity, resulting in the increase of the moderate strength by the increment of Na_2O. Additional details of the interaction of $NaNO_2$ cannot be provided at present, but will be further studied in the future.

1-Butene Isomerization and TPD. As shown in Fig. 2 a good correlation of the initial rate with the stronger basicity than $H_-=22.3$ or 27 indicates that 1-butene isomerization proceeds on such strong basic sites. Therefore the isomerization is inactive on the group B catalysts existing only on weak basic sites. This fact agrees with the results of isomerization of 1-pentene on MgO doped with metalic sodium,[6] requiring stronger basic sites than $H_-=35$. By the reactivity of 1-butene and pentene the isomerization of the former would occur on the weaker basic sites than those in the case of the latter. The reaction mechanism of 1-butene isomerization will be started with proton abstration from the alkene molecule by the stronger basic site than $H_- = 22.3$. Therefore a mechanism similar to that proposed by Pines and Schaap[17] can also hold in this case. As a result an allyl-type carbanion as an intermediate would be formed:

$$CH_2{=}CH{-}CH_2{-}CH_3 + O^{2-} \longrightarrow \underset{\ominus}{\underline{CH_2{-}CH{-}CH{-}CH_3}} + OH^-,$$

where O^{2-} indicates the basic site. With back donation of one proton from OH^- the intermediate would transform into 2-butene.

$$\underset{\ominus}{\underline{CH_2{-}CH{-}CH{-}CH_3}} + OH^- \longrightarrow CH_2{-}CH{=}CH{-}CH_3 + O^{2-},$$

It was concluded by Kijenski and Malinowski that the one-electron donor center was independent from the basic site.[6] Cordischi and Indovina reported that there existed a parallelism between basic and one-electron donor properties.[18] In either case the catalytic activity of alkene isomerization and cumene dehydrogenation was unambiguously associated with the one-electron donor center.[6] The center will similarly attract a proton from 1-butene to proceed the reaction, probably in the same way as indicated by Kijenski and Malinowski.[6] As suggested by this study, however, isomerization mainly proceeds on the strong basic sites already described.

The ratio of *cis* to *trans* isomers was rather low in comparison with such a value of 18, as indicated by Tanabe *et al.*[2] This difference might be either due to the concecutive reaction from *cis* to *trans*, as the conversion of 1-butene was so high, or to the thermodynamical stability of *trans* isomer.

TPD curve of the group A catalysts is characterized by two desorption peaks of 350 and 420 °C as shown in Fig. 3(a). The desorption peak at high temperature corresponds to the stronger basicity than $H_- = 22.3$ or 27 in comparison with the results of 1-butene isomerization. It should be noted that TPD of adsorbed acetic acid can provide a suitable method to detect the existence of the basicity stronger than $H_- = 22.3$. By the way the TPD of adsorbed CO_2 and gaseous HCl did not succeed, because no desorption peak appeared upto 550 °C, but that of magnesium acetate exhibited similar behavior as in Fig. 3(b). Consequently magnesium acetate by adsorption of acetic acid was not formed, which was also confirmed by X-ray analysis. Detailed basicity distribution may be obtained by the TPD method of other acidic compounds adsorbed.

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