

Participation of Surface Radical Species with Base Catalytic Activity of Na Metal Doped MgO

Hiromi Matsuhashi* and Kazushi Arata

Department of Science, Hokkaido University of Education, 1-2 Hachiman-cho, Hakodate 040, Japan

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Participation of F^+ centers with the formation of superbases was studied. Two kinds of ESR signals were observed with Na metal doped MgO, which was thermally activated at 773, 873, and 973 K. A relationship was found between double bond migration activity of 3-methyl-1-butene and ESR signal intensity which was observed at low magnetic field. This radical species was assigned to an F^+ center formed on an unstable MgO surface. The maximum activity was obtained when two electrons were trapped in an anion vacancy. It was concluded that the F^+ and F centers played the most important role for the formation of superbases sites.

Introduction

Materials that possess base sites stronger than $H_- = 26$ are called superbases. The highest basicity of MgO, which was thermally activated in a vacuum, was almost equal to $H_- = 26$.¹ The basicity of MgO was enhanced by alkali metal doping, and superbase sites were formed. Kijenski *et al.* measured the basicity of Na, K, and Cs metal doped MgO in H_- scale and confirmed that those materials have superbase sites stronger than $H_- = 35$.² An existence of superbase sites on Na metal doped MgO was also ascertained by measuring the catalytic activity for methyl formate decomposition to CO and methanol.³

On the other hand, paramagnetic centers in MgO induced by electrons, which were released from alkali metal doped on the surface, have been studied by the ESR technique. The same kinds of paramagnetic centers as above were also generated by γ -rays or neutron irradiation.⁴ Giamello *et al.* reported that paramagnetic Fs^+ center, consisting of one electron trapped in a surface anion vacancy, was formed by doping with Li and Mg metals.⁵

Fs^+ centers have strong one-electron donor properties. The one-electron donor properties of Na metal doped MgO was studied using the method of adsorption of organic electron acceptors (tetracyanoethylene and nitrobenzene); the catalytic activities for dehydrogenation of isopropylbenzene and hydrogenation of alkenes were most probably connected with the presence of very strong one-electron donor centers.² As is described above, there seems to be a relation between the formation of Fs^+ centers on the surface and the generation of superbasicity. From the point of view, it is important to clarify the role of surface radicals for understanding the surface properties of MgO.

In this study, the catalytic activity of Na metal doped MgO was examined in the double bond migration of 3-methyl-1-butene, and the participation of Fs^+ centers for catalytic activity is discussed on the basis of ESR measurement of surface radicals induced by the doping of Na metal together with X-ray irradiation.

Experimental Section

The magnesium oxide used in this study was prepared as follows. Pure MgO (10 g, Merck, analytical grade) was placed in a beaker and boiled for 1 h with 100 mL of distilled water

to obtain $Mg(OH)_2$, followed by drying at 373 K, and powdered to 32-60 mesh. Then 0.1 g of $Mg(OH)_2$ was placed in a preparation apparatus made of glass with a piece of quartz wool. Thermal decomposition of hydroxide and activation were carried out in a vacuum to obtain a oxide of high surface area. Three temperatures were chosen for the activation: 773, 873, and 973 K. Heat treatment was conducted for 3 h. The surface area of MgO samples was *ca.* 140 m^2/g for all activation temperatures.⁶

After the activation, Na metal doping was performed as follows. Magnesium oxide was cooled to room temperature and mixed with NaN_3 powder kept in another part of the preparation apparatus. The mixed powder was heated again at 673 K in vacuum until NaN_3 decomposition was completed. The color of the sample turned from white to light blue-violet when a large amount of NaN_3 was used. Then the sample was transferred to a U-tube with two breakable seals attached near the top of each side for measuring of catalytic activity or to a glass tube for ESR measurement. The sample was sealed and kept under high vacuum. The amount of Na doped on the MgO surface was determined by a Hitachi 207 atomic absorption spectrometer. The sample was weighed and dissolved in dilute HCl solution for atomic adsorption analysis. Hereafter, Na metal doped MgO will be indicated by the label Na/MgO.

X-ray irradiation to MgO that was not treated with Na metal was carried out as follows. After activation with a similar method to that described above, the sample was transferred to a glass tube connected to the ESR tube. The sample was exposed to $Cu K\alpha$ X-ray through the thin glass wall at room temperature. All ESR data were obtained on a JEOL JES-FE1XG ESR spectrometer with 1 mW microwave power.

An all-glass recirculation system was employed for carrying out the double bond migration of 1-butene and 3-methyl-1-butene. Both reagents were purified by passing through 3A molecular sieves. The reaction temperature was 273 K, and the starting pressure of the reagent was 100 Torr. Products were analyzed periodically by GLC: a 3 m column packed with VZ-7 was operated at room temperature. The catalytic activity was estimated by the reactant conversion at 5 min after the reaction started.

Results

Time dependence of the composition in double bond migration of 1-butene over Na/MgO is shown in Figure 1a. Rapid increase of *cis*-2-butene concentration was observed at the initial

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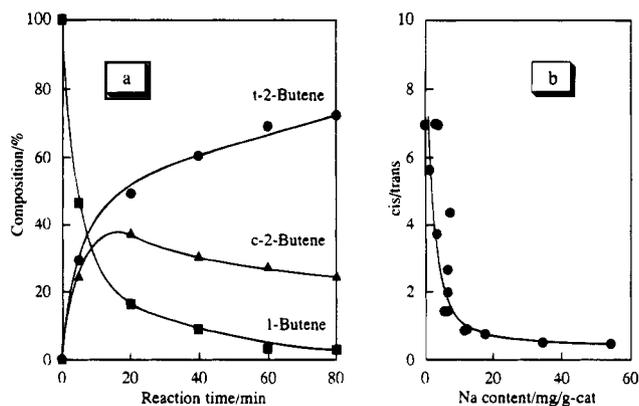


Figure 1. (a) Catalytic activity and selectivity of Na/MgO for double bond migration of 1-butene at 273 K. (b) The same after 5 min reaction.

stage of the reaction. After that, *cis*-2-butene was converted into *trans*-2-butene soon. This means that 1-butene converted to *trans*-2-butene through *cis*-2-butene. This feature of time dependence has been commonly observed with solid base catalysts.⁷

The reaction selectivity of Na/MgO is shown in Figure 1b. The formation of *trans*-2-butene increased with the increase of Na content. The ratio of *cis* and *trans* isomers (*cis/trans*) was very large in low Na content as is generally observed with base catalysts.⁷ The *cis/trans* ratio decreased with increase of the amount of Na. On Na/MgO containing more than 12 mg/g-cat of Na, the *cis/trans* ratio was smaller than 1. According to Walling *et al.*, the *cis* isomer is the most favored product in radical reaction mechanisms.⁸ In contrast to this, a large amount of *trans* isomer was formed in our study. The time dependence of product composition shown in Figure 1a indicates that the relative reaction rate of *cis*-2-butene to *trans*-2-butene is very high. The double bond migration of *cis*-2-butene to *trans*-2-butene was catalyzed by very strong base sites.⁹ Therefore, it appears that Na/MgO acts as a base catalyst for the double bond migration, basicity of the active site being very high.

The reaction rate of 1-butene on Na/MgO was too high to compare the activities of catalysts. Instead of this reaction, double bond migration of 3-methyl-1-butene was selected as a test reaction, because the reaction rate of 3-methyl-1-butene was expected to be much lower than that of 1-butene. In the case of base catalyst, the first step of double bond migration is proton abstraction to form allyl anion. The reaction rate is determined by electron density of site for hydrogen abstracted as proton. On 3-methyl-1-butene, the electron density of hydrogen at γ -position is high due to the inductive effect of methyl group. Therefore, the proton abstraction on 3-methyl-1-butene takes place with difficulty in contrast with that on 1-butene as is shown in Figure 2.

Variation of the conversion in 5 min for the double bond migration of 3-methyl-1-butene on Na/MgO as a function of the amount of Na is shown in Figure 3. The maximum activity was obtained when 27.0, 7.2, and 6.9 mg/g-cat of Na were doped on magnesium oxides activated at 773, 873, and 973 K, respectively. The absolute maximum activities of the samples activated at 873 and 973 K were almost same. On the catalyst activated at 773 K, the absolute activity was low as compared with those of others.

The catalytic activity decreased as the amount of Na doped on MgO increased in all samples. As a reason for the decrease of catalytic activity, deposition of Na metal particles on an active site could be assumed; Na particles are known to be formed on the MgO surface as amount of Na increases.¹⁰ However, the detailed reason is not clear in this study.

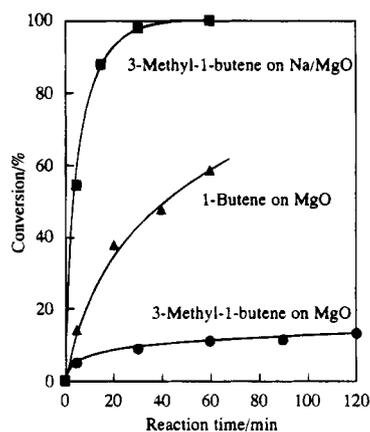


Figure 2. Double bond migration of 1-butene and 3-methyl-1-butene over MgO and Na/MgO activated at 773 K.

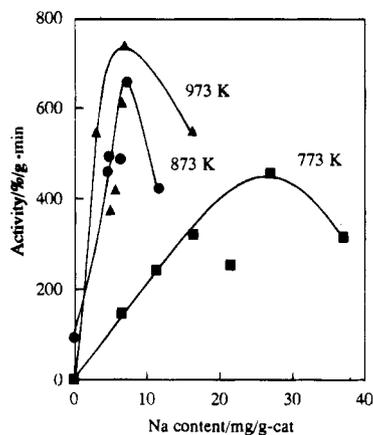


Figure 3. Variation of the activity of Na/MgO for double bond migration of 3-methyl-1-butene as a function of Na content.

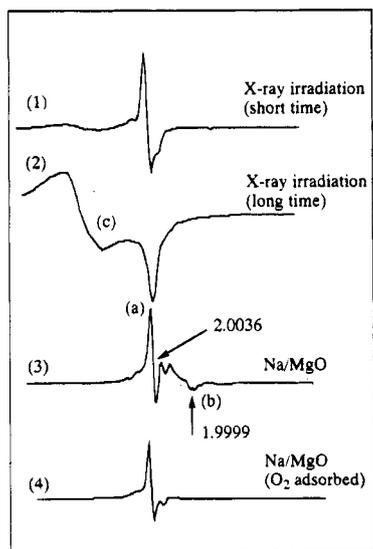


Figure 4. ESR spectra of X-ray irradiated MgO and of Na/MgO.

Figure 4 shows the ESR spectra of paramagnetic centers produced by Na metal doping or by X-ray irradiation. Three different paramagnetic centers termed a, b, and c were observed. By the short-time irradiation of X-ray (40 kV, 100 mA, for 30 min) to MgO activated at 773 K, only the (a) center was formed. The *g* value of this center, where the first derivative curve crosses the base line, was 2.0036. The (a) center was observed on the MgO surface that was activated at low temperature around 673 K.⁴ At the activation temperature used in this study, the formation of MgO lattice should be incomplete. Thus, the

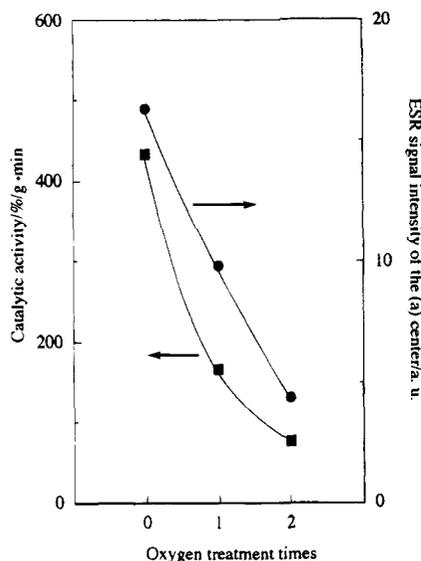


Figure 5. Effect of O₂ adsorption on catalytic activity for the double bond migration of 3-methyl-1-butene and signal (a) intensity.

(a) center is coincident with an F^{s+} center formed with a trapped electron in oxygen vacancy constructed on the unstable surface.⁴

By Na metal doping, both the (a) and the (b) centers were formed. From the shape of the spectrum, it is concluded that the (b) center holds an unpaired electron in uniaxial symmetry. The perpendicular composition of the *g* value was 1.9999, but the parallel composition was not clear. On the basis of the similarity of the shape of the spectrum, the (b) center can be assigned to a single electron trapped in a kind of anion vacancy on the surface of MgO which was activated at the high temperature of 1073 K, it being usually called an F^{s+} center.⁵ The (b) center was rapidly and irreversibly destroyed by small amounts of oxygen, while this treatment was less effective for the signal intensity of the (a) center (Figure 4 (4)). The (c) center was observed when MgO was exposed to X-rays for a long time (80 kV, 120 mA, for 3 h). This center was not formed by Na metal doping. From the characteristics of the (c) center, the spectrum was assigned to an F^{s+} center constructed by a trapped electron in an oxygen vacancy on the MgO surface, whose activation temperature was 873 K or higher and gave the face-centered cubic structure.⁴

The oxygen treatment showed a similar aspect on the change of catalytic activity and ESR signal intensity of the (a) center. As is shown in Figure 5, the reaction activity for double bond migration of 3-methyl-1-butene was depressed by the treatment with 2 Torr of oxygen, but the deactivation degree was not large. From this result, participation of the (a) center for the construction of superbase site is deduced.

A relation between the ESR signal intensity of the (a) center and content of Na on MgO is shown in Figure 6. The maximum intensity was obtained when 3.1, 3.2, and 12.0 mg/g-cat of Na content for the activation temperature of 973, 873, and 773 K, respectively. In all activation temperatures, the amount of Na to show the maximum activity for the isomerization of 3-methyl-1-butene (Figure 3) was almost twice as much as the quantity that gave the maximum signal intensity. It means that the maximum activity is obtained when two electrons are trapped in one anion vacancy.

Discussion

In our study, three kinds of paramagnetic centers, termed (a), (b), and (c) were observed on MgO. The (a) and the (b) centers were formed with an electron that were released from Na metal

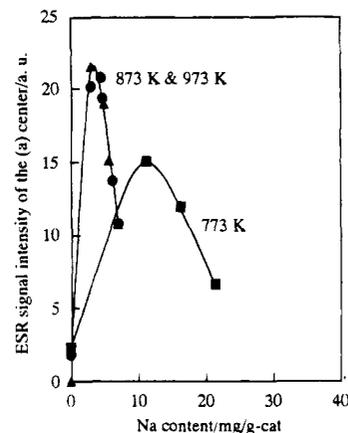
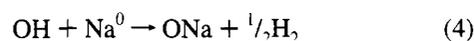
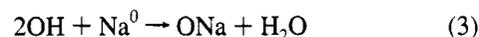
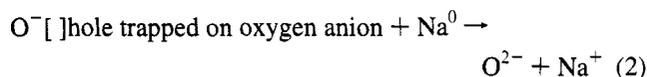
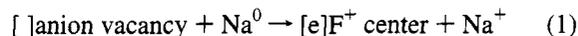


Figure 6. Variation of ESR signal intensity of the (a) center on Na/MgO as a function of Na content.

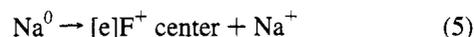
and were trapped in different kinds of oxygen vacancies. As was reported, the oxygen vacancy for the (a) center was formed on an unstable surface, it being probably not well dehydrated,⁴ while that for the (b) center was formed on the well-dehydrated and stable surface. Since the (b) center was not observed on X-ray irradiated MgO, the vacancy was probably generated during the adsorption process of Na ion, as proposed by Giamello *et al.*⁵

In contrast to the above, the formation of the (c) center was certainly not connected with the construction of superbase sites.

Kijenski *et al.* proposed the generation mechanism of superbase sites on MgO as follows.²



Here, another reaction must be considered.⁵



Equation 1 describes the formation of the F⁺ center with the electron released from Na and the oxygen vacancy. Equation 2 is the reaction of surface O⁻ ion and Na metal. Reaction 3 shows that a Na metal is adsorbed on the remained oxygen after the dehydration of two hydroxyl groups on the surface; no ESR signal of F⁺ center is observed with the species. Equation 4 is the replacement reaction of Na⁺ and H⁺ of the surface hydroxyl group. Equation 5 shows the formation mechanism of F⁺ center which is newly generated by the adsorption of Na.

The (a) center is supposed to be formed by reaction 1 because the same paramagnetic center was generated by X-ray irradiation. Due to the absence of the paramagnetic center of O⁻ in all samples before the Na doping, reaction 2 is excluded.

As is shown in Figure 6, the ESR signal intensity of the (a) center observed on Na/MgO activated at 773 K was close to that of the samples activated at 873 and 973 K. This behavior shows that the number of oxygen vacancies is closely coincident. However, a large amount of Na was needed to obtain the maximum intensity for the sample activated at 773 K. It seems that the decomposition of surface OH group on that sample was not enough because of the relatively low activation temperature; replacement of proton with Na⁺ (eq 4) should proceed mainly

when a small amount of Na was doped. On these samples, the effect of doped Na on the catalytic activity was small. Therefore, ONa formed by reaction 4 does not act as a superbase site.

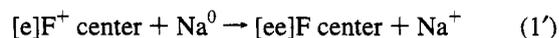
The Na metal adsorbed on the remained oxygen formed by reaction 3 does not give any F^+ center. A relationship was found between the catalytic activity and signal intensity of the (a) center. Therefore, this species does not give the superbase site even if it was formed.

The (b) center was newly generated owing to the doping of Na and not observed when MgO was irradiated with X-rays. The result of the O_2 adsorption experiment shows that the (b) center is not related with the superbase sites formation, and therefore reaction 5 is also excluded. From these considerations, it can be concluded that the superbase sites are produced by reaction 1.

The ionic character of Mg^{2+} in MgO decreases with decreasing the coordination number.¹¹ The active sites of MgO are constituted with the coordinative unsaturated surface ions of Mg^{2+} and O^{2-} . The ionic character of the surface ions is low compared to those in the bulk. Particularly, the absolute positive charge of Mg^{2+} that is located around the anion vacancy is much lower. An electron which is trapped in the anion vacancy would show analogous aspect to O^{2-} for the electron density of Mg^{2+} . When an anion is put in the anion vacancy, the coordination number of Mg^{2+} is increased. Similarly, the trapping of electron in the anion vacancy provides an increase of an apparent coordination number of Mg^{2+} . As a result of this effect, the absolute positive charge of Mg^{2+} is increased. Further, the absolute negative charge of O^{2-} that is located at the next position of the Mg^{2+} is also increased by this effect, resulting in O^{2-} showing superbasicity.

In our experiment, the second electron released from an excess Na should be trapped in the F^+ center, and the F^+ center

is converted into diamagnetic F center, which is inactive for the ESR measurement. As a result of the F center formation, a decrease of the signal intensity of the F^+ center is observed with high content of Na.



The electrical induction effect increases when the two electrons are trapped. This proposition can be supported by the results shown in Figures 3 and 6. The amount of Na that gave the maximum activity was almost double of that which gave the maximum intensity of the (a) center signal. In conclusion, reactions 1 and 1' play the most important role for the formation of superbase sites; the superbasic sites are O^{2-} adjacent to $Mg^{2+}-[e]$ or to $Mg^{2+}-[ee]$.

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