The Effect of Potassium on the Surface

Properties of MgO

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(Received, April 12, 1990)

Abstract

The effect of potassium on the adsorption properties of CO_2 and H_2O on MgO has been studied by TPD (Temperature Programmed Desorption) and IR (Infrared) Spectroscopies. It is demonstrated that a dose of potassium with MgO causes (1) appearence of a new site for CO_2 species, (2) inhibition of adsorption of water and (3) that potassium exists as potassium oxide (K_2O) after treating with air at 600°C.

1. Introduction

The study of the surface properties of MgO, which is a typical basic metal-oxide and a ceramic material, is one of intriguing themes from the point of view of the characterization of functional solid surfaces. A large number of reports on this issue have been presented so far. We have also investigated the adsorption properties of CO and CO_2 and kinetics of CO–N_2O reaction on MgO[1~6], and revealed that these results strongly depend on pretreatment temperatures[7 and 8].

Furthermore, attempts to obtain various metal-modified MgO catalysts have been made as for other catalysts: it is well-known that MgO modified by several kinds of metal such as lithium or lanthanide (La, Sm, etc.) is active in the oxidative-coupling of methane[9~12], which is a very important reacton in so called C_1-Chemistry.

It has been reported that Ca^{2+} condenses onto MgO-crystal surfaces and renders them 'rumple'[13,14]. Tanabe et al.[15,16] studied surface properties of metal-ion-modified MgO by ESR spectroscopy.

We would like to present the effect of potassium, which is well-known as a prevailing promoter for many kinds of practical catalysts such as silver[17] or iron[18~23] etc., on the adsorption properties of CO_2 and H_2O by utilizing mainly TPD and IR spectroscopies.

2. Experimental Procedure

(1) *Preparation of the samples*

The MgO samples used in this study are from Merck Co., and the procedures

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to obtain these samples are as follows : 4 g–MgO was suspended in redistilled water of 75 ml and then dried on an electric heating-plate. It was then put in a oven at 90°C for 12 hrs and finally exposed to 600°C-air for 3 hrs, taking into account the experimental result that 600°C is the optimum pretreating temp. to get the most basicity of MgO.[24~26] We designate this sample, i. e., non-modified MgO, as MgO. Potassium was dosed with MgO as 0.02 N aqueous potassium-nitrate solution at room temp. The amount of potassium was 1 or 10% to MgO weight, respectively. We designate these samples as K(1)–MgO or K(10)–MgO. All other procedure for these samples was exactly the same as for MgO. Potassium-dosed α–Al_2O_3, which is acidic, was employed as a reference to examine the contribution of potassium to TPD profiles more clearly.

(2) *Equipment*

The IR spectra were obtained with an HITACHI 260-50 with an ordinary transmission spectroscopy. Thin disks of 20 mm in diameter and of 20 mg in weight were made for these measurements.

Our TPD experiments were done with a tubular-flow reactor made of a DAIKO-quartz glass tube of 0.8 cm in i. d. and a CHINO–KP temperature controller. Weight of the samples was 0.3 g, and length of the bed was about 3 cm. Total flow rate of the gases and rate of the rise in temperature was 90 ± 5 ml/min (NTP) and 5°C/min, respectively. Analysis of the effluent gases was done by two gas chromatographs : an HITACHI–164 equipped with a Porapak S column for CO_2 and a Shimazu-GC-3AH with a Porapak Q column for H_2O, respectively.

We also examined the crystallographic properties of the samples by measuring XRD (X-ray diffraction) patterns by the RIGAKU–DENKI produced equipment with an X-ray generator (A-41L–Cu) and a goniometer (SG-9), and their thermal properties by a DTA (differential thermal analyzer) (ULVAC TGD-7000).

3. Results and Discussion

3-1. XRD Patterns and DTA Spectra of MgO and K-modified MgO

It is obvious that the properties and nature of the product can be determined by the crystal structure of the parent.[28] So we should first look at the crystallographic properties of the samples before and after calcination.

(1) *Before Calcination*

As is well-known, water-suspended MgO easily forms magnesium hydroxide {$Mg(OH)_2$}[27]. We also reconfirmed that the original material of all the samples in this report was $Mg(OH)_2$ by XRD patterns of (a)s in Figs. 1 and 2 and observed no big differences between their XRD patterns.

Furthermore, dehydration of (0001)-face of $Mg(OH)_2$ leads to the formation of (111)-rich face of MgO[28 and 29], whose face has such active sites as O^- ion in H_2–O_2 exchange reaction[30] and Mg^{2+} ion in hydrogenation of 1.3-butadiene[31]. The procedure for our samples must be, therefore, advantageous to obtain active MgO catalysts.
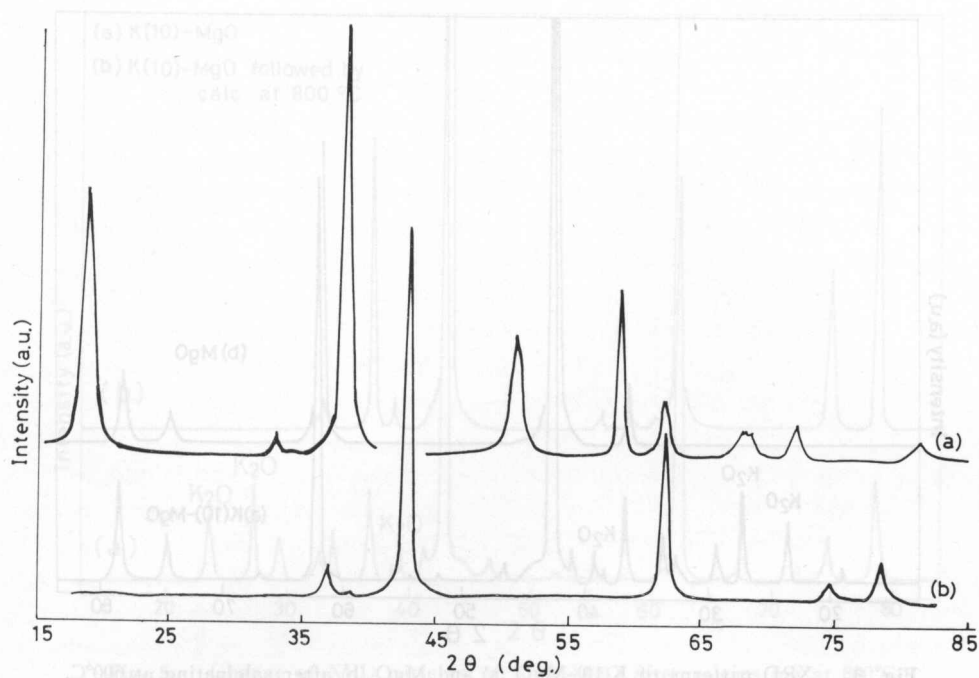
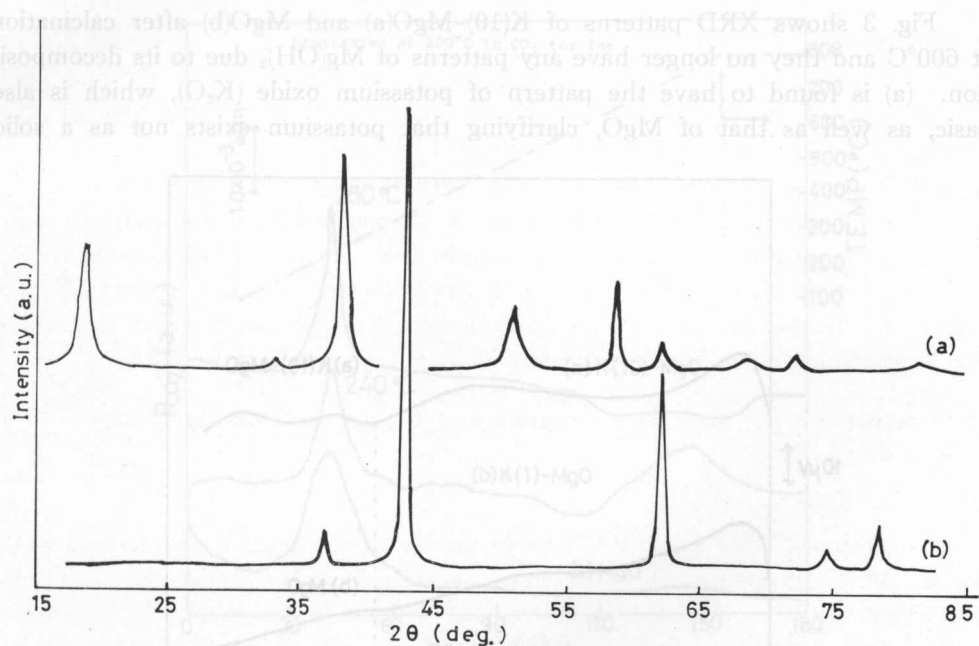**Fig. 1.** XRD patterns of MgO before (a) and after (b) calcinating at 600°C.

Fig. 3 shows XRD patterns of K(10)-MgO(a) and MgO(b) after calcination at 600°C and they no longer have any patterns of Mg(OH)₂ due to its decomposition. (a) is found to have the pattern of potassium oxide (K_2O), which is also basic, as well as that of MgO, clarifying that potassium exists not as a solid

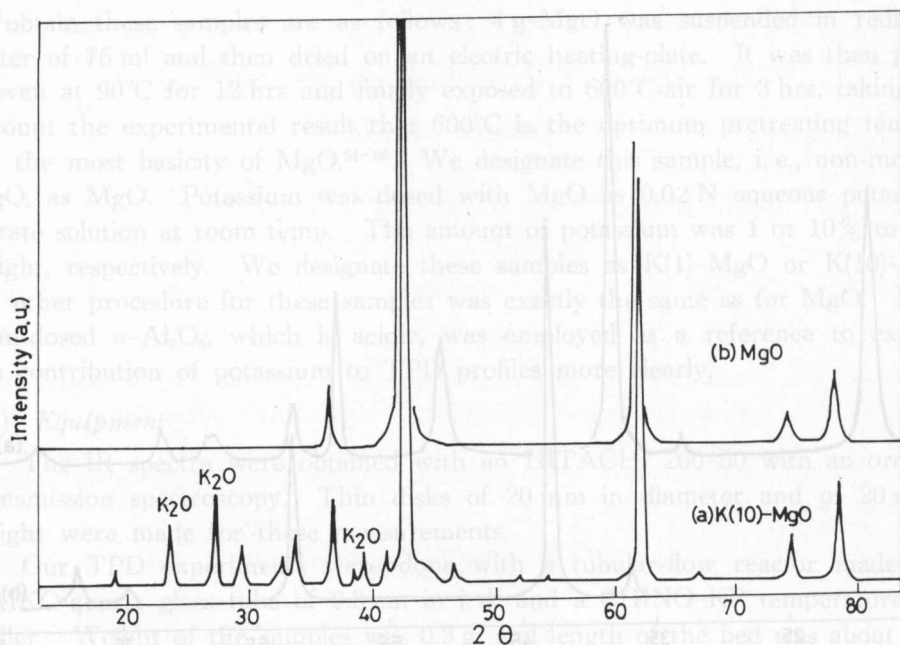**Fig. 2.** XRD patterns of K(1)-MgO before (a) and after (b) calcinating at 600°C.

Fig. 3. XRD patterns of K(10)–MgO (a) and MgO (b) after calcinating at 600°C.

(2) *After Calcination*

Fig. 3 shows XRD patterns of K(10)–MgO(a) and MgO(b) after calcination at 600°C and they no longer have any patterns of $Mg(OH)_2$ due to its decomposition. (a) is found to have the pattern of potassium oxide (K_2O), which is also basic, as well as that of MgO, clarifying that potassium exists not as a solid
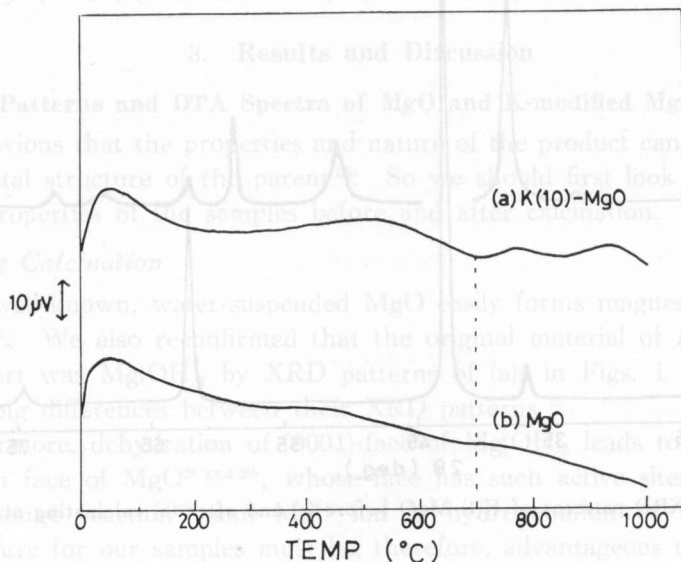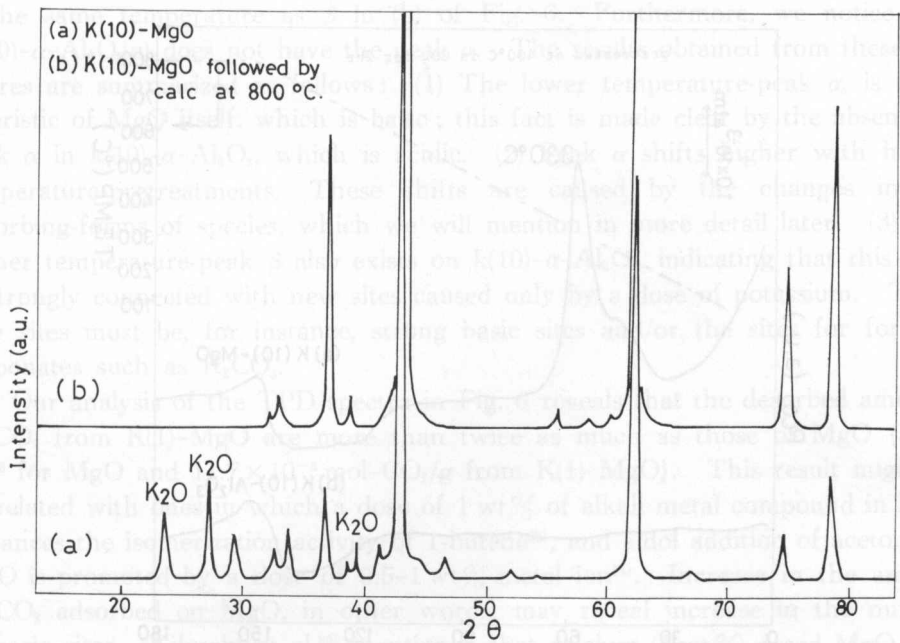

Fig. 4. DTA spectra of K(10)–MgO (a) and MgO (b).

Fig. 5.   Change of XRD patterns of K(10)–MgO after calcinating at 800°C.
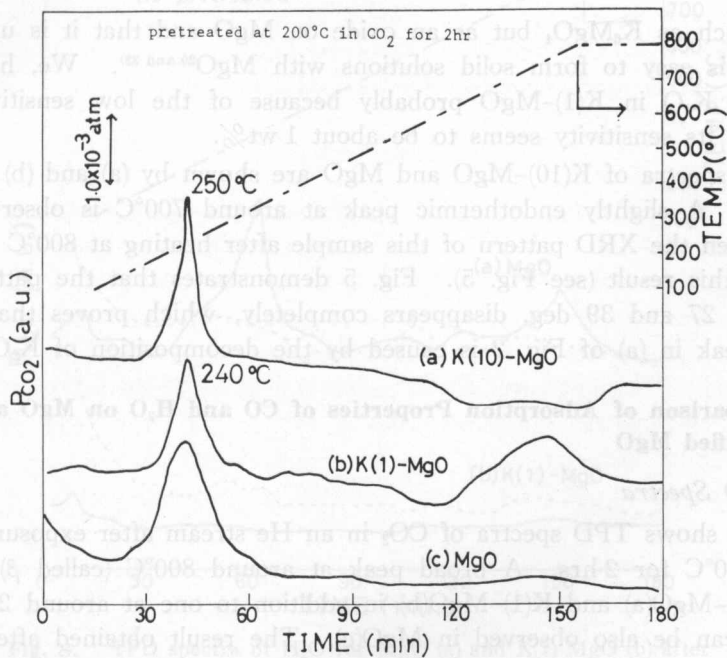(a); K(10)–MgO, (b); after calcinating at 800°C.

Fig. 6.   TPD spectra of CO_2 for MgO and K-dosed MgO after
pretreating in CO_2 stream at 200°C for 2hrs.
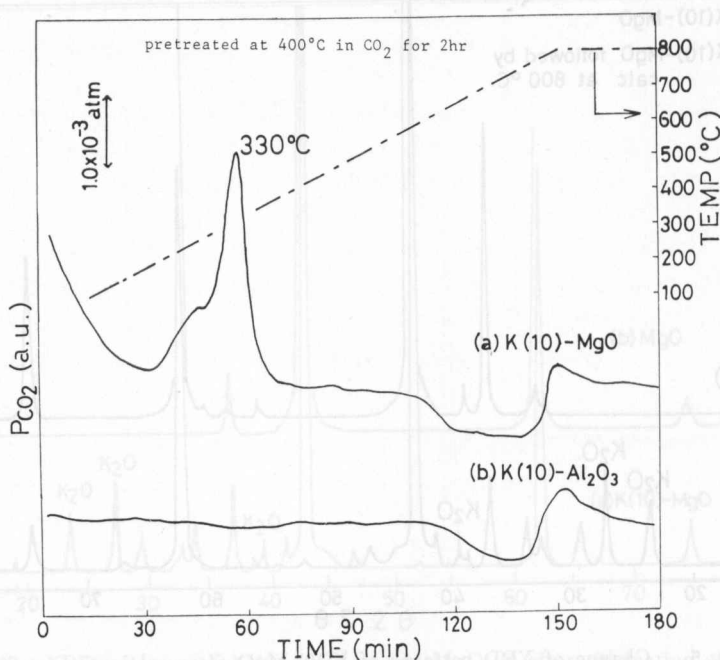(a); K(10)–MgO, (b); K(1)–MgO, (c); MgO.

Fig. 7.   TPD spectra of CO_2 for K(10)–MgO (a) and K(10)–Al$_2$O$_3$ (b)
after pretreating in CO_2 stream at 400°C for 2 hrs.

solution such as K$_6$MgO$_4$ but as an oxide on MgO and that it is unlike Co or Ni which is easy to form solid solutions with MgO[29 and 32].   We, however, did not detect K$_2$O in K(1)–MgO probably because of the low sensitivity of this technique ; Its sensitivity seems to be about 1 wt%.

DTA spectra of K(10)–MgO and MgO are shown by (a) and (b) respectively in Fig. 4.   A slightly endothermic peak at around 700°C is observed in only (a), and then the XRD pattern of this sample after heating at 800°C is measured to clarify this result (see Fig. 5).   Fig. 5 demonstrates that the pattern of K$_2$O at $2\theta = 24$, 27 and 39 deg. disappears completely, which proves that the endothermic peak in (a) of Fig. 2 is caused by the decomposition of K$_2$O.

3–2. Comparison of Adsorption Properties of CO and H$_2$O on MgO and K-modified MgO

(1) *TPD Spectra*

Fig. 6 shows TPD spectra of CO_2 in an He stream after exposure to a CO_2-flow at 200°C for 2 hrs.   A broad peak at around 800°C (called β) appears in both K(10)–MgO(a) and K(1)–MgO(b) in addition to one at around 250°C (called α) which can be also observed in MgO(c).   The result obtained after treatment at 400°C for K(10)–MgO is shown by (a) in Fig. 7.   We observe two peaks in this spectrum : one is at around 330°C which is higher than the peak temperature of α in (a) of Fig. 6 by about 80°C, and the other is at around 800°C which

is the same temperature as β in (b) of Fig. 6. Furthermore, we notice that K(10)-α-Al$_2$O$_3$(c) does not have the peak α. The results obtained from these two figures are summarized as follows: (1) The lower temperature-peak α, is characteristic of MgO itself, which is basic; this fact is made clear by the absence of peak α in k(10)-α-Al$_2$O$_3$, which is acidic. (2) Peak α shifts higher with higher temperature-pretreatments. These shifts are caused by the changes in the adsorbing-forms of species, which we will mention in more detail later. (3) The higher temperature-peak β also exists on k(10)-α-Al$_2$O$_3$, indicating that this peak is strongly connected with new sites caused only by a dose of potassium. These new sites must be, for instance, strong basic sites and/or the sites for forming carbonates such as K$_2$CO$_3$.

Our analysis of the TPD spectra in Fig. 6 reveals that the desorbed amounts of CO$_2$ from K(1)-MgO are more than twice as much as those of MgO $\{5.1 \times 10^{-3}$ for MgO and 11.7×10^{-3} mol-CO$_2$/g from K(1)-MgO$\}$. This result might be correlated with ones in which a dose of 1 wt% of alkali metal compound in MgO enhances the isomerization activity of 1-butene[33], and aldol addition of acetone on MgO is promoted by a dose of 0.5-1 wt%-metal ion[34]. Increase in the amount of CO$_2$ adsorbed on MgO, in other words, may reveal increase in the number of basic sites. Kikuchi et al.[35] mentioned that calcium (1 wt%)-dosed MgO gave
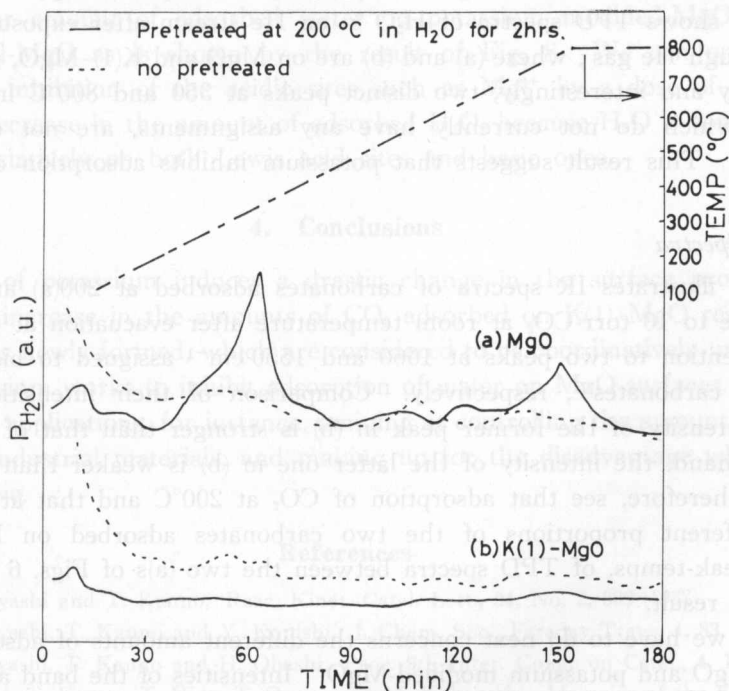

Fig. 8. TPD spectra of H$_2$O for MgO (a) and K(1)-MgO (b) after pretreating in H$_2$O stream at 200°C for 2 hrs.
——; pretreated at 200°C in H$_2$O for 2 hrs.
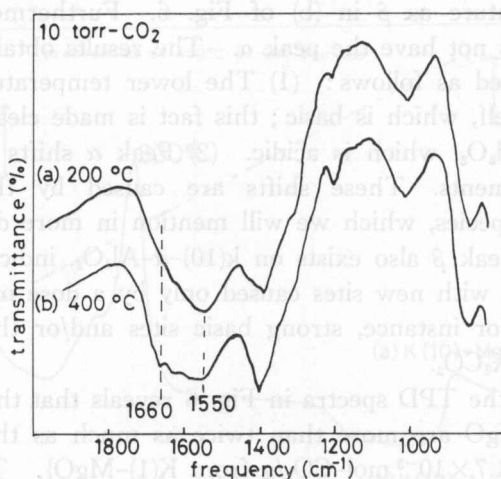– – –; not pretreated.

Fig. 9.   IR spectra of carbonates at 200°C (a) and 400°C (b) on MgO.

rise to the strong basic sites where CO_2 desorbs at higher than 673 K, and they ascribed them to coordinatively-unsaturated sites newly formed. Furthermore, Tanabe et al.[36] found that a dose of metal ions onto MgO increased the amount of coordinatively-unsaturated Mg^{2+}-O^{2-} pairs by ESR spectroscopy.

Fig. 8 shows TPD spectra of H_2O in an He stream after exposure to water vapor through He gas; where (a) and (b) are on MgO and K(1)-MgO, respectively. Surprisingly and interestingly, two disinct peaks at 350 and 800°C in MgO, the peaks of which do not currently have any assignments, are not observed in K(1)-MgO. This result suggests that potassium inhibits adsorption of water on MgO.

(2) *IR Spectra*

Fig. 9 illustrates IR spectra of carbonates adsorbed at 200(a) and 400°C(b) in exposure to 10 torr-CO_2 at room temperature after evacuation at 800°C. Let us pay attention to two peaks at 1660 and 1550 cm^{-1} assigned to bidentate and unidentate carbonates[37], respectively. Comparison of their intensities indicates that the intensity of the former peak in (b) is stronger than that of (a) and, on the other hand, the intensity of the latter one in (b) is weaker than that of (a). One can, therefore, see that adsorption of CO_2 at 200°C and that at 400°C lead to the different proportions of the two carbonates adsorbed on MgO. The different peak-temps. of TPD spectra between the two (a)s of Figs. 6 and 7 must reflect this result.

What we have to do next concerns the different amounts of adsorbed water between MgO and potassium modified-MgO. Intensities of the band at 1220 cm^{-1} assigned to bicarbonate[37], which is formed by CO_2 and H_2O, are compared in Fig. 10, where (a) and (b) are for MgO and K(1)-MgO, respectively. We could not obtain IR spectra of K(10)-MgO because of the difficulty in making the disks transparent enough to be comparable to the other two samples. The intensity
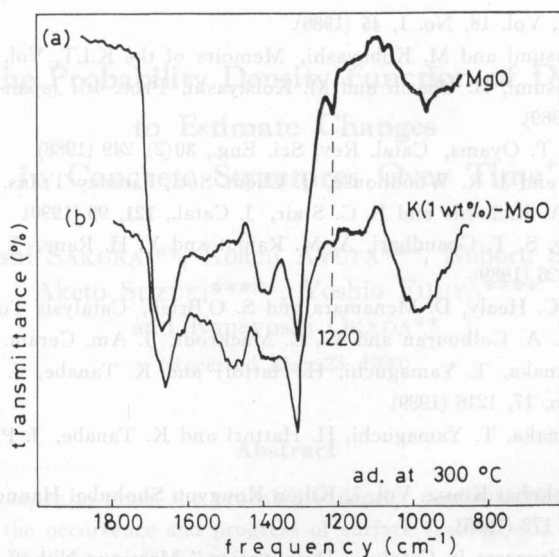
Fig. 10. Comparison of IR spectra of MgO (a) and K(1)–MgO (b) after exposure to H_2O followed by CO_2.

of (b) is found to be much weaker than that of (a), reconfirming that there is much smaller amount of adsorbed water on potassium modified-MgO than on non modified-MgO as is shown by the result of Fig. 8. We can only say at present that inhibition of the acidic sites such as Mg^{2+} by a dose of potassium causes the decrease in the amount of adsorbed H_2O, because H_2O is considered to adsorb dissociatively on both Lewis acid sites and basic ones.

4. Conclusions

A dose of potassium induces a drastic change in the surface properties of MgO. The increase in the amounts of CO_2 adsorbed on K(1)–MgO results from the basic sites newly formed, which are considered to be coordinatively-unsaturated ones. Potassium works to inhibit adsorption of water on MgO surfaces. It could have various applications, for instance, amining at controlling the amount of water-sorption in industrial materials, and making up for the disadvantage which basic materials have.

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