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Acid-Base Bifunctional Behavior of ZrO_2 in Dual Adsorption of CO_2 and NH_3

Bo-Qing XU, Tsutomu YAMAGUCHI,* and Kozo TANABE
Department of Chemistry, Faculty of Science,
Hokkaido University, Sapporo 060

Temperature-programmed-desorption(TPD) profiles of NH_3 and CO_2 coadsorbed on ZrO_2 revealed a progress of a new peak at around 553 K, which was not found when NH_3 and CO_2 were adsorbed individually. It was concluded that, though the most of the sites responsible to the adsorption of NH_3 and CO_2 were located independently, a part of them were located closely, where the pre-adsorbed NH_3 molecule enhanced the adsorption of post-adsorbing CO_2 molecules. This type of interaction was not found on either typical solid acid (SiO_2-Al_2O_3 ; SA) or solid base (MgO).

It has been reported that zirconium dioxide shows specific catalytic actions for the cleavage of a C-H bond1) and the hydrogenation of buta-1,3-diene by a molecular hydrogen and hydrogen donor molecules such as cyclohexadiene2-4) and high selectivities for the formation of 1-olefins from secondary alcohols5) and of isobutane in CO + H_2 reaction.6) Recently decomposition of triethylamine to yield acetonitrile, in which both dealkylation and dehydrogenation processes were involved, was reported.7) These characteristic behaviors of ZrO_2 are considered due to the acid-base bifunctional catalysis, since the catalysis by a cooperation of weak acid and weak base is known to be superior sometimes to the catalysis by a simply strong acid or base.8,9)

Zirconium dioxide is not only an interesting oxide catalyst, but is becoming even more important as a catalyst support. For instance, the Rh supported on ZrO_2 exhibits higher catalytic activitiy for the hydrogenation of CO and CO_2 compared with that supported on Al_2O_3, SiO_2, etc.10,11) In particular, the Rh/ZrO_2 catalyst shows the highest activity for the hydrogenation of CO_2.10)

In this article, we wish to report on the adsorption-desorption behavior of acidic and basic substances on ZrO_2 by means of IR spectroscopy and temperature-programmed-desorption (TPD) technique.

Zirconium dioxide was prepared by hydrolysis of zirconium oxynitrate ($ZrO(NO_3)_2\ H_2O$) with concentrated ammnonia water. ZrO_2 used for IR experiments was prepared by hydrolysis of benzene solution of zirconium propoxide. The precipitate was dried at 393 K and calcined in air at 873 K for 24 h. XRD examination revealed that both ZrO_2 samples were almost pure monoclinic crystal, and no difference was found in the TPD profiles of NH_3 and CO_2 on their surfaces. SiO_2-Al_2O_3 was N631(L) SA of Nikki Co. Ltd., which was calcined at 773 K for 5 h. Magnesium oxide was MgO of Merck Co. Ltd., which was evacuated at 1073 K for 2 h before use. BET surface areas of ZrO_2, MgO, and SA were 30, 93, and 396 m^2 g^{-1}, respectively.

TPD experiments were performed as follows.[7,12] A 0.1 g of sample was exposed to 1.33 kPa of corresponding gas for 30 min, followed by the evacuation for 1 h and then TPD procedure was started. A dual adsorption of NH_3 and CO_2 was carried out as follows. NH_3 was first adsorbed at room temperature for 30 min and was evacuated at the same temperature, then CO_2 was admitted in a similar way, which was followed by the evacuation and TPD experiments. At each evacuation step, evacuation was continued until the base pressure was reached around $1x10^{-5}$ Torr (1 Torr=0.133 kPa). The desorbed gas was analyzed by a NEVA NAG-515 quadrapole mass spectrometer at an ionization voltage of 90 eV. Peak intensities of desorbed gases were normalized by using Ar (ca. 0.1 Pa) as an internal standard.

Pyridine (Py), NH_3, and CO_2 were purified under vaccuum by repeated freeze-thaw cycles before use. Sample pretreatments and IR measurement are described in our preceding papers.[7,12]

Figures 1-a, -b, and -c show the TPD profiles of NH_3 and CO_2 on SA, MgO, and ZrO_2, respectively. SA adsorbed NH_3 but not CO_2, while MgO adsorbed CO_2 but not NH_3 so much. This means that SA and MgO are basically a single functional substance which adsorbs solely either basic or acidic molecule. ZrO_2 adsorbs comparable amounts of both CO_2 and NH_3, which suggests that both acidic and basic sites are present. Thus an attempt was made to distiguish whether the sites responsible to adsorb each substance are located closely or independently on the surface of ZrO_2 by using a dual adsorption technique.

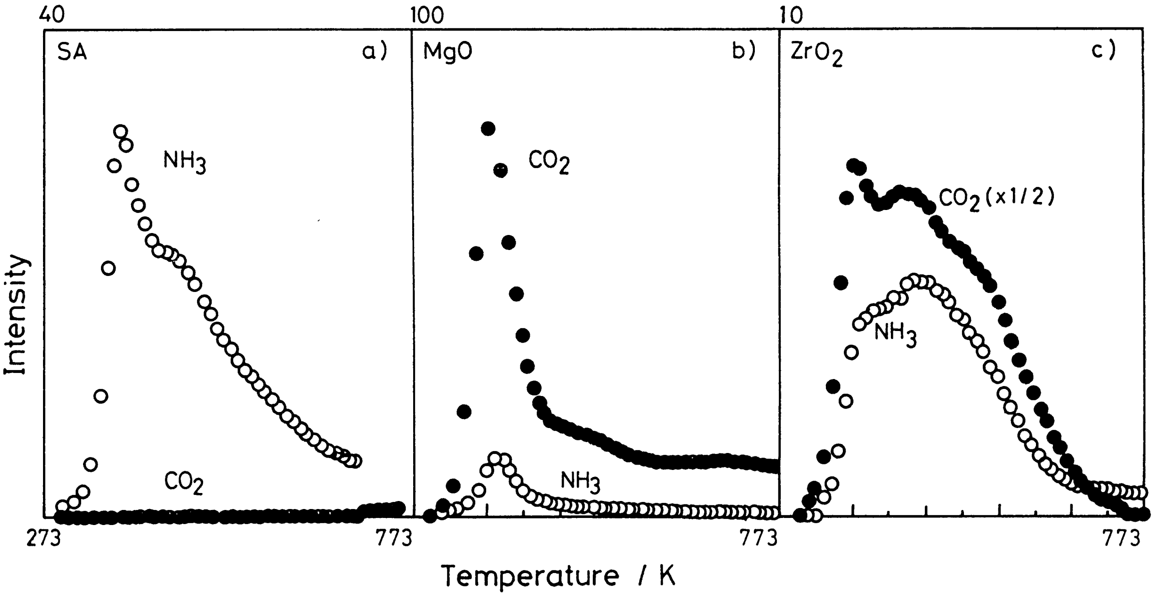

Fig. 1. TPD profiles of NH_3 and CO_2 on SA(a), MgO(b), and ZrO_2(c).
[○]:NH_3, [●]:CO_2

TPD profiles of NH_3 and CO_2 in the dual adsorption which were obtained after CO_2 and NH_3 pre-adsorption, respectively, are shown in Fig. 2. Single component TPD profiles of both substances are also shown in the same figures.

Results clearly indicates that both pre-adsorbed CO_2 and NH_3 did not disturb the adsorption of the post-adsorbing substances. The post-adsorbing materials did not replace the pre-adsorbed substances, though TPD profiles of the pre-adsorbed materials showed a slight change at lower temperature range. This suggests that most of the sites responsible to the adsorption of these materials on ZrO_2 are located independently.

It can be seen that a new peak appeared at around 553 K in the TPD profiles of both NH_3 (Fig. 2-a) and CO_2 (Fig. 2-b). It seems unlikely to conclude that the appearence of a new peak at 553 K could be assigned to the formation of chemical substances such as urea, since a fragment pattern analysis has revealed that no material other than NH_3 and CO_2 was found during TPD processes. These results clearly indicate that the amount of post-adsorbed materials was increased by the pre-adsorbed substances. These phenomena were not observed on either typical solid acid (SiO_2-Al_2O_3) or solid base (MgO).

Thus, it can be concluded that the pre-adsorbed materials promoted the adsorption of the post-adsorbing materials and that, though ZrO_2 possesses independent sites for the adsorption of NH_3 and CO_2, but a part of the sites responsible to adsorb NH_3 and CO_2 are located closely.

A TPD profile of Py from ZrO_2 was almost the same as that of NH_3. Pre-adsorbed NH_3 was completely replaced by post-adsorbing Py. Thus NH_3 and Py adsorb on the common sites and Py adsorbs more strongly than NH_3. This can be interpreted on the basis of the order of the gas phase basicity.

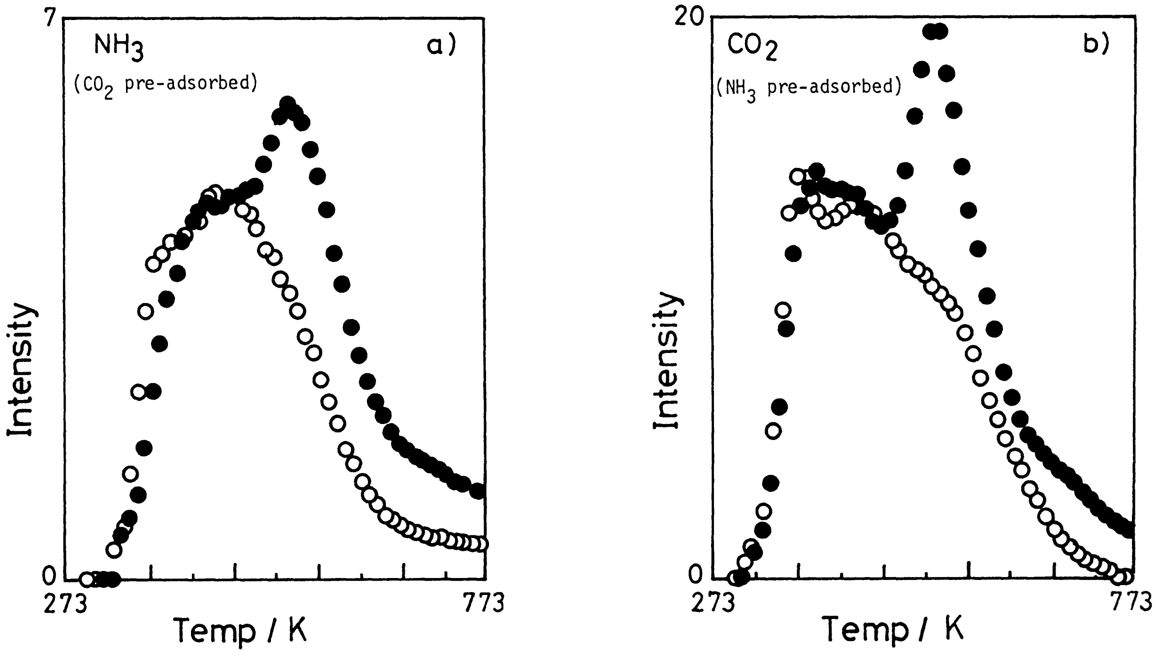

Fig. 2. TPD profiles of NH_3(a) and CO_2(b) in dual adsorption on ZrO_2. [○]:single adsorption, [●]:dual adsorption.

Influence of pre-adsorbed NH_3 on the adsorption of post-adsorbing CO_2 was also examined by IR spectroscopy. When CO_2 was admitted on the pre-adsorbed NH_3 on ZrO_2 at room temperature, a shift of a symmetric vibration of NH_3 (δ_s = 1168 cm^{-1}) to 1190 cm^{-1} was observed. This type of frequency shift was also observed on the sample which was evacuated at elevated temperature after the room temperature adsorption of NH_3. It is known that a symmetric vibration of NH_3 in metal-ammine complexes shifts to higher frequencies when the force constant of the bond between metal and nitrogen becomes higher.[13] A frequency shift of the symmetric vibration of NH_3 on ZrO_2 by the coadsorption of CO_2 thus reflects the change in the force constant of Zr-N bond. Hence, it can be pointed out that an adsorption of CO_2 increased the bond strength between ZrO_2 and NH_3. A change in the spectrum of adsorbed CO_2 was ambiguous.

Since NH_3 adsorbed on ZrO_2 was found to be solely a coordinated one and no dissociative adsorption was found by the IR investigations, the interaction between the pre-adsorbed NH_3 and the post-adsorbed CO_2 should be a through-bond interaction as illustrated in the following scheme.

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