June, 1985] © 1985 The Chemical Society of Japan NOTES Bull. Chem. Soc. Jpn., 58, 1827—1828 (1985) 1827

# The Promotion Effect of Surface Hydroxyl on the Oxygen Adsorption over NiO, $Fe_2O_3$, and CuO

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**Synopsis.** Oxygen TPD revealed that the adsorption of water vapor at 278 K promoted the desorption of the preadsorbed oxygen at 793→278 K over NiO and $Fe_2O_3$. Preadsorption of water vapor at 473 K brought about a marked enhancement over $Fe_2O_3$ and a slight increase over CuO in the adsorption of oxygen at 473→278 K.

It has been known that the addition of water vapor promoted the catalytic oxidations of methanol,[1] propene,[2] butene,[3] 2-butanone,[4] 2-methyl propenal (methacrolein),[5] toluene,[6] and the ammoxidation of propene.[7] It was proved that water or surface hydroxyl served as a reactant in the formation of alcoholic intermediate in several catalytic oxidations.[2,3,5] The promotion mechanism for other oxidations, however, is still not elucidated.

Water vapor is formed as by-product in almost all of catalytic oxidations of organic compounds and it will more or less affect the adsorption of reactants, products, and/or intermediates, so that it is of importance to know the behavior of oxygen adsorbate in the presence of water vapor for understanding of catalytic oxidations.

Recently, it has been reported that coadsorption of water vapor affected adsorption energy of oxygen on the metal oxide surfaces. $Co_3O_4$ gave a temperature programmed desorption (TPD) chromatogram of oxygen which composed of three kinds of oxygen adsorbate. The desorption peak with peak maximum temperature ($T_m$) at 365 K shifted to higher temperature by 50 K without loss of its amount when water vapor and oxygen were coadsorbed at 473→278 K.[8] Over $Ag^+$–$SnO_2$, a broad prateau above 610 K in oxygen TPD chromatogram was transformed into a sharp peak at 570 K by the coadsorption of water vapor.[9]

However it is still not known for other metal oxides. This paper deals with the behavior of oxygen adsorption in the presence of the adsorbate derived from water over the metal oxides.

The oxygen TPD chromatograms from NiO are shown in Fig. 1. The NiO sample after the treatment A (see Table 1) gave a chromatogram which consisted of a desorption peak with $T_m$=695 K and a shoulder peak at around 600 K (curve 1). This well agreed with that reported by Iwamoto *et al.*[10] Water adsorption at 294 K onto the NiO sample with oxygen adsorbate by the treatment A brought about drastic changes in its chromatogram of oxygen (curve 2): by the adsorption of 5.0 μmol/g water, a small $\alpha$ peak appeared at around 420 K and $\beta$ peak became larger but $\gamma$ peak decreased without shift of $T_m$. The amount of oxygen desorbed up to 793 K slightly increased from 7.92 to 8.89 μmol/g by the water coadsorption. Curve 3 is a chromatogram of water desorbed simultaneously with oxygen, which is composed of two peaks with $T_m$=490 K and >793 K. These peaks may arise from surface hydroxyl since the desorption temperatures are higher than the normal boiling point of water.

$Fe_2O_3$ showed two desorption peaks with $T_m$=620 K and 710 K (curve 1 in Fig. 2). Both $\alpha$ and $\beta$ peaks shifted to lower temperatures and the latter peak was much enlarged by the adsorption of water at 278 K onto the sample preadsorbed with oxygen. The total amount of desorbed oxygen increased to about 1.4 times of that of dry surface. Curve 3 in Fig. 2 revealed that all of the water vapor was chemisorbed onto $Fe_2O_3$. In these experiments, no oxygen was supplied from gas phase during the adsorption of water vapor at 294 K. Therefore the increment of desorbed oxygen probably came from the oxygen which should be desorbed at >793 K from the dry surface.

Figure 3 shows the results of oxygen chemisorption onto the $Fe_2O_3$ surface preadsorbed with water vapor.

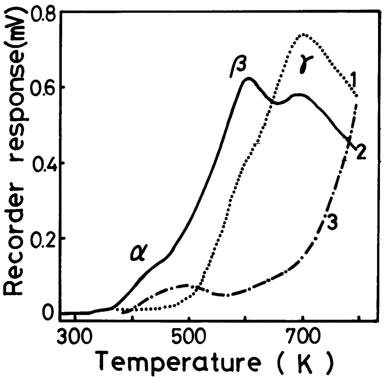

Fig. 1. TPD chromatograms from NiO.
1: Oxygen, treatment A, 2: oxygen, treatment B, 3: water, treatment B.

TABLE 1. TREATMENT OF OXIDES

| | | | | | |
|---|---|---|---|---|---|
| A: | Adsorption of oxygen<br>(100 Torr*, 793 K, 30 min) | → | Cooling to r.t.<br>(10 K/min) | → | Evacuation<br>(r.t., 15 min) |
| B: | Treatment A | → | Adsorption of water vapor<br>(2 Torr, 293 K, 30 min) | → | Evacuation<br>(r.t., 15 min) |
| C: | Adsorption of oxygen<br>(100 Torr, 473 K, 30 min) | → | Cooling to r.t.<br>(10 K/min) | → | Evacuation<br>(r.t., 15 min) |
| D: | Adsorption of water vapor<br>(2 Torr, 473 K, 30 min) | → | Evacuation<br>(473 K, 15 min) | → | Treatment C |

* 1 Torr=133.322 Pa.

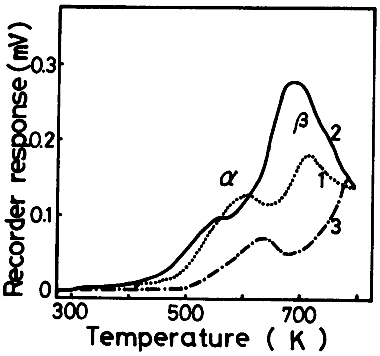

Fig. 2. TPD chromatograms from $Fe_2O_3$.
1: Oxygen, treatment A, 2: oxygen, treatment B, 3: water, treatment B.

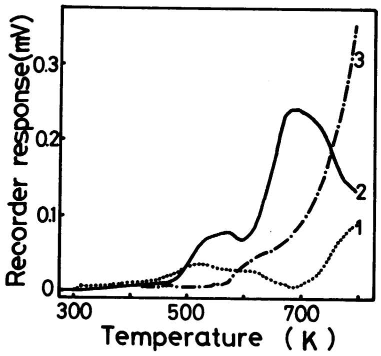

Fig. 3. TPD chromatograms from $Fe_2O_3$.
1: Oxygen, treatment C, 2: oxygen, treatment D, 3: water, treatment D.

In the oxygen adsorption on the dry surface at 473 K (the treatment C), only a small amount of oxygen could be chemisorbed and the chromatogram was composed of three desorption peaks with $T_m$=430 K, 610 K, and >793 K. The second peak ($T_m$=610 K) well coincided with that of α peak in curve 1 in Fig. 2. However, preadsorption of water at 473 K much promoted the adsorption of oxygen. The shape of curve 2 in Fig. 3 was much similar to that of curve 2 in Fig. 2, despite the differences in the adsorption temperature and procedure for water adsorption. The amount of desorbed oxygen was determined to be 2.35 μmol/g, which was 3.5 times larger than that of curve 1. It is noteworthy that this value exceeded the 2.06 μmol/g of oxygen adsorption at 793 K.

Assuming that surface concentration of iron(III) ion was about $10^{19}$ atom/m$^2$, surface coverages of adsorbed water and oxygen (tentatively presumed as dissociative adsorption) on the $Fe_2O_3$ sample after the treatment D were calculated to be 3.5 and 6.0%, respectively. Similarly, those for the NiO sample after the treatment B were 1.4 and 5.0%. Provided that all of the adsorbates are dispersed uniformly on the oxide surface, these values are too small for each adsorbate to interact with a neighboring another kind of adsorbate. So that it seems more likely that both species are adsorbed together onto some surface defects.

In the case of CuO, chromatogram of oxygen changed slightly by the preadsorption of water vapor with broadning of peak and shift of $T_m$ to higher temperature by 25 K (curve 2 in Fig. 4).

Although most of surface hydroxyl may be desorbed at higher reaction temperatures, a significant amount of surface hydroxyl may remain on the surface and modify the activity of oxygen adsorbate in the catalytic oxidation performed at moderate reaction temperatures. These phenomena may partly explain the promotion effect of water vapor in the catalytic oxidation of organic compounds.

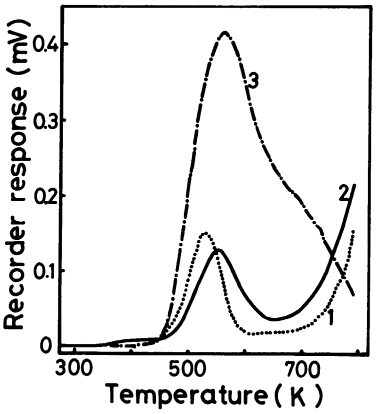

Fig. 4. TPD chromatograms from CuO.
1: Oxygen, treatment C, 2: oxygen, treatment D, 3: water, treatment D.

## Experimental

NiO, $Fe_2O_3$, and CuO were prepared by the thermal decomposition of $NiCO_3 \cdot 2Ni(OH)_2$, $Fe(NO_3)_2 \cdot 9H_2O$, and $CuCO_3 \cdot Cu(OH)_2 \cdot H_2O$ (Wako Pure Chem. Ind.) at 673 K for 4 h, followed by calcination at 823 K for 4 h in air. TPD apparatus used here was basically the same as that described in the literature.[11] Desorption chromatograms of water were obtained from the difference of the chromatograms recorded with two thermal conductivity detectors located at upper and at lower stream of the cold trap at 77 K for the removal of water vapor. The detector downstream gave chromatograms of oxygen.

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