Gaseous Molecular Sieving Property of a Microporous Hollandite-type Hydrous Manganese Oxide

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A microporous hollandite-type manganese oxide having protons as counter ions (H-Hol) was prepared by hydrothermal reaction and adsorption of various molecules from gas phase was examined. It is found that only H_2O and NH_3 can be adsorbed in the intra-pores; NH_3 is inserted as NH_4^+ as a result of reacting with lattice protons. Chemisorption of NH_3 is available even under co-existence of water, indicating that H-Hol can be an excellent selective trapper toward odor NH_3.

As one of microporous manganese oxide groups, hollandite-type manganese oxide (H-Hol) has a (2×2) tunnel structure whose pore opening can be estimated as 0.46 nm from crystalline data.[1,2] Although its structural specificity leads to hopeful application as rechargeable batteries[2–5] and as an ion-sieving sorbent towards cations from liquid phase,[6–9] its adsorption property toward gaseous molecules has not been sufficiently studied. Recently, we found that NH_3 having an effective diameter of 0.26 nm can be inserted into the tunnel structure of H-Hol from gaseous phase.[10] However, this property was not compared with those of other molecules with pore diameters below 0.46 nm. In this letter, we report the adsorption results using typical adsorbates of nitrogen, oxygen, water, and ammonia, and selective adsorption toward ammonia under co-existence of water, from which the gaseous molecular sieving property of H-Hol will be elucidated.

H-Hol was synthesized by a hydrothermal reaction of an Li_2MnO_3 precursor in a 3 M sulfuric acid solution at 363 K for 48 h.[10,11] The Li_2MnO_3 precursor was prepared by calcining the mixture of MnOOH and Li_2CO_3 at 1073 K for 48 h. The crystal structure of the prepared H-Hol was confirmed by powder X-ray diffraction (XRD) technique using a Rigaku RINT1200 diffractometer, as having a tetragonal unit cell with size of a = b = 0.981 nm and c = 0.286 nm, similar as that of natural cryptomelane (KMn_8O_{16}).[12] Adsorption isotherms of N_2 and O_2 were measured at 77 K while those of H_2O and NH_3 at 298 K using volumetric methods (Belsorp 18 of Japan Bell Co. and Autosorb-1 of Quanta-Chrom Co.). Before adsorption, samples were pre-evacuated under 1 mPa for 2 h at 573 K for N_2 and O_2 and at 393 K for H_2O and NH_3. After completely obtaining an adsorption isotherm (first run adsorption), a second run adsorption of H_2O or NH_3 was carried out at 298 K after evacuating the sample at the same temperature for 2h in case of H_2O and for 30 min in case of NH_3. IR absorbance on NH_3 adsorption under atmosphere or co-existence of H_2O was in-situ recorded using a Nicolet NEXUS 470 spectrometer in a resolution of 2 cm^{-1} and with 32 scans.

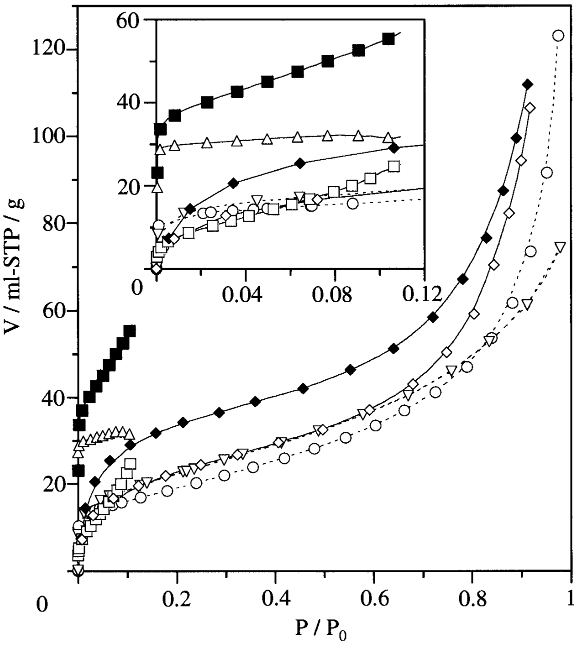

Figure 1. Adsorption isotherms of N_2 (○) and O_2 (▽) at 77 K, NH_3 of the first run (■), the second run (□), and the difference of the first and the second runs (△) at 298 K, H_2O of the first (◆) and the second (◇) runs at 298 K.

Figure 1 shows adsorption isotherms of N_2, O_2, H_2O, and NH_3. All the isotherms are of the shape of typical type IV,[13,14] which is characteristic of multi-layer adsorption. The NH_3 adsorption amount at the first run is around two or three-fold more than those of the other adsorbates. The second run adsorptions of H_2O and NH_3 overlap with each other, indicating that their physical adsorptions are exactly the same. Existence of irreversible adsorption (the difference of first and second run adsorption) of H_2O and NH_3 indicates the presence of stronger interaction between protons on H-Hol and the two adsorbates. As the molecular diameter is different from one another among the used adsorbates, the sequence of adsorption could not necessarily reflects whether an adsorbate is inserted or not into the micropores. For this reason, the specific surface areas (S_{BET}) are calculated by Brunauer-Emmett-Teller (BET) method from N_2, O_2, H_2O and NH_3 adsorption isotherms with data on molecular cross-sectional areas recommended by previous contributors (N_2: 0.162 nm^2, O_2: 0.143 nm^2, H_2O: 0.125 nm^2, NH_3: 0.129 nm^2).[13,15,16] The irreversible adsorption areas for NH_3 and H_2O are obtained by the difference between those from the first and second runs. In addition, the total ($S_{t,\ total}$), internal ($S_{t,\ int}$), and external ($S_{t,\ ext}$) surface areas based on N_2 adsorption are calculated by De-Boer's t-plot method using a non-porous alumina's data as a reference.[17] Table 1 shows the values of specific surface areas. From this table, the S_{BET} values from N_2 and O_2 adsorption are much less than those from H_2O and NH_3 adsorption. Since the value of $S_{t,\ ext}$ is comparable with that of $S_{t,\ total}$, N_2 together with O_2 having a

Table 1. Specific surface area of H-Hol calculated from each gas adsorption

Adsorbate	Molecular Diameter[19] / nm	Adsorption Temperature / K	S_{BET} / m^2/g	$S_{t, total}$ / m^2/g	$S_{t, ext}$ / m^2/g	$S_{t, int}$ / m^2/g
N_2	0.364	77	73	68	56	12
O_2	0.346	77	71			
NH_3 - 1st run	0.26	298	161			
NH_3 - 2nd run		298	90			
NH_3 - irreversible		298	71			
H_2O - 1st run	0.265	298	95			
H_2O - 2nd run		298	63			
H_2O - irreversible		298	32			

similar molecular diameter should mainly be adsorbed onto the external surface of H-Hol irrespective of a greater crystalline pore opening (about 0.46 nm). As the effective pore opening width can be approximated as 0.22 nm after subtracting the contribution of two lattice O^{2-} ionic radium (~ 0.122 nm for three coordination number[20]) from the crystalline pore opening value (~ 0.46 nm), exclusion of N_2 and O_2 from the micropores can be attributed to the blockade effect of lattice oxygen near the tunnel entrance. On the other hand, H_2O and NH_3 could be inserted into the intra-pores because their surface areas from the first run adsorptions are greater by 1.7 and 2.9 fold, respectively, than $S_{t, ext}$. Especially, the highest S_{BET} from the first run NH_3 adsorption reveals that NH_3 possibly intrudes into proton barrier inside the tunnel structure.

Figure 2 (a) shows the FT-IR absorbance after NH_3 adsorption. The band at 1402 cm^{-1} is assigned to an adsorbed NH_4^+ species,[18] indicating that NH_3 is chemisorbed via a reaction with protons on H-Hol. Another adsorption experiment shows that pre-evacuation at 473 K decreases NH_3 adsorption in agreement with a smaller IR absorbance due to NH_4^+ species as shown by Figure 2 (b). It is interesting to observe that the presence of water disturbs nothing but slightly enhances NH_3 adsorption after pre-evacuation at 473 K (Figure 2 (c) and (d)). Further researches indicate that there exist two kinds of hydroxyl groups on H-Hol; the weaker one, most possibly existing on the external surface, is lost above 393 K. Weak hydroxyl groups can be recovered under a condition of water exposure, which have relationship with the enhancement in NH_3 adsorption. Thus, the above results show that only water and ammonia can be inserted into the micropores of H-Hol while NH_3 is inserted as NH_4^+. H-Hol can be an excellent selective trapper toward odor NH_3 molecules.

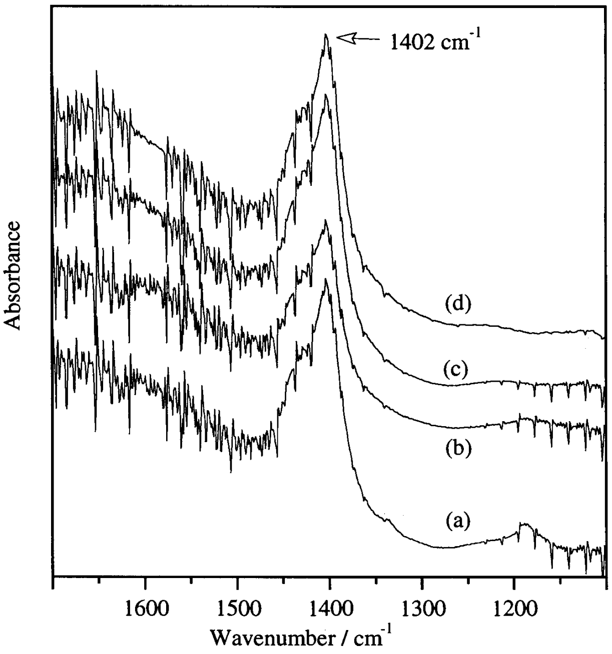

Figure 2. Change in NH_3 adspecies (NH_4^+) under co-existence of water.
(a)15 min in 27 torr NH_3 at RT after pre-evacuation at 298 K,
(b)15 min in 24 torr NH_3 at RT after pre-evacuation at 473 K,
(c)15 min in the mixture of 24 torr NH_3 + 3.8 torr H_2O at RT after pre-evacuation at 473 K,
(d) 2 h exposure to saturated water after evacuation at RT for 15 min following operation (b).

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