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Adsorption of Organic Halides on Amine-Impregnated Silica Gels

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The adsorption behaviors of methyl and propyl iodides, propyl chloride and chlorobenzene were examined on silica gels impregnated with 1,4-diazabicyclo[2.2.2]octane (DABCO), pyperazine (PPZ), hexamethylene tetramine (HMTA), and modified with (3-aminopropyl)triethoxysilane (ATS) and dimethoxybis[3-(methylamino)-propyl]silane (DAS). The irreversibly adsorbed amount of these halides except chlorobenzene was proportional to the amount of impregnated amines. The molar ratios of irreversible adsorption of the halides to the impregnated amine were less than 2 and in the order of DABCO>PPZ>HMTA>ATS>DAS. The former three amine compounds are less stable than the last two materials against thermal pretreatment.

Organic halides such as trichloromethane in city water, organic chlorides from waste plastics and solvents, 2,3,7,8-tetrachlorodibenzo[*b,e*][1,4]dioxin (dioxin) in insecticides and methyl iodide from nuclear reactors are serious environmental pollutants. Therefore, it is very important to find effective ways of removing these pollutants. From this point of view, silver-impregnated silica gels were found to adsorb organic halides effectively.[1)] Silver-impregnated molecular sieves are used to remove organic iodides in waste gases from nuclear reactors.[2)] However, in order to expect a good performance, a rather careful procedure of pretreatment of these materials seems to be necessary. Also, activated carbons impregnated with 1,4-diazabicyclo[2.2.2]octane triethylene diamine (DABCO) are used as an adsorbent to analyze atmospheric alkyl iodides.[3)]

In the present paper, the adsorption behaviors of methyl and propyl iodides, propyl chloride and chlorobenzene were described in detail on well-characterized mesoporous silica gels impregnated with DABCO, piperazine (PPZ), hexamethylene tetramine (HMTA) and modified with (3-aminopropyl)triethoxysilane (ATS) and dimethoxybis[3-(methylamino)propyl]silane (DAS). The mechanism of adsorption is clarified in view of thermodynamic properties and ir spectra.

Experimental

Materials. Thin and transparent plates of mesoporous silica gels suitable for spectroscopic measurement were synthesized by hydrolyzing tetraethoxysilane according to the method mentioned elsewhere.[4)] The BET specific surface area, pore volume and mean pore radius of this material obtained from the N_2 adsorption isotherm are 705 $m^2 g^{-1}$, 0.60 $ml g^{-1}$ and 1.7 nm respectively. These gels were impregnated with DABCO, PPZ, and HMTA by immersing them in methanol solutions of each of these amines of various concentrations at 298 K for 10 h and then evaporating methanol in the samples in vacuo at room temperature. The impregnated amounts were determined by CN elemental analysis. Free silanol groups on silica surface were modified with ATS and DAS by immersing gels in toluene solutions of ATS and DAS of various concentrations at 323 K for 5 h and washing with acetone and then drying at room temperature. The amounts of ATS and DAS reacted were determined

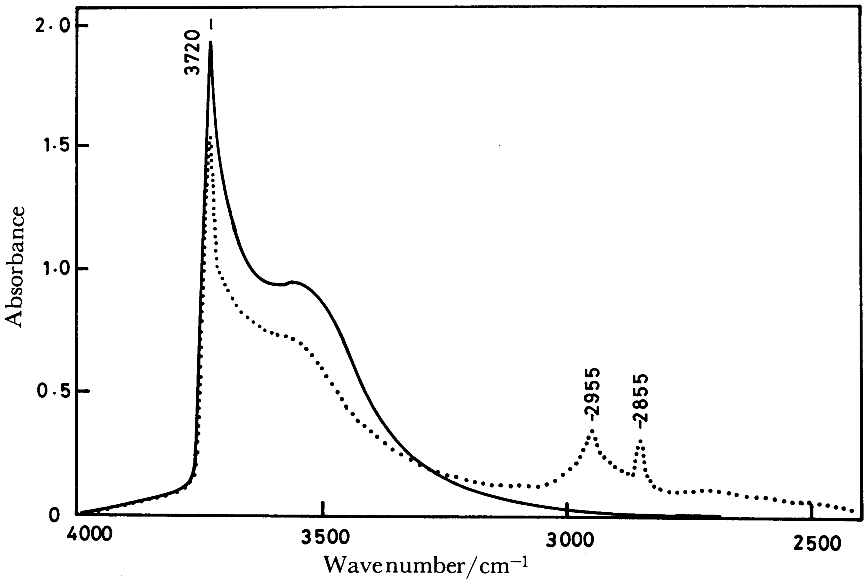

Fig. 1. IR spectra of silica gels before and after impregnating DABCO of 0.331 mmol g^{-1}. The full line, before impregnation; the dotted line, after impregnation.

by CN elemental analysis.

Methods of Measurements. The adsorption isotherms of methyl and propyl iodides, propyl chloride and chlorobenzene were measured at 298 K by means of a computer-operated quartz spring balance using a diaphragm manometer (BARATRON, 170M-6C). These samples were pretreated at desired temperatures under 10^{-3} Pa for 2 h. The adsorbates were dried with molecular sieves 3A and then distilled into a reservoir of the adsorption apparatus in the same vacuum system without exposing to air.

IR spectra were measured with a dispersion-type IR spectrophotometer (Hitachi-Perkin Elmer) and a FT-NIR spectrometer (Digilab, FTS-15E). A vacuum and high-temperature cell5) was used to measure spectra at room temperature after pretreating the sample at 423 K unless otherwise stated.

Results and Discussion

In Fig. 1, the IR spectrum of silica gels before impregnating DABCO (a full line) has a sharp 3720 cm^{-1} and a broad 3500 cm^{-1} absorption bands which are assigned to the stretching vibration of free and hydrogen-bonded silanol groups respectively. After impregnating 0.331 DABCO mmol g^{-1} SiO_2 (about 0.3 DABCO molecules nm^{-2} of the original surface), the intensity of 3720 cm^{-1} band decreased to about 80% and two bands assigned to assymmetric and symmetric C-H vibrations of methylene groups of DABCO appeared at 2955 and 2855 cm^{-1} as is shown by a dotted line in this figure. Since there are about three free silanol groups per nm^2 on this mesoporous silica gels6) and 0.6 free silanol groups (about 20% of total silanol groups) adsorbed DABCO, one DABCO molecule seems to be adsorbed on two free silanol groups by hydrogen bond.

The adsorption isotherms of methyl iodide on pure silica gels at 288 K (a full line) and on silica gels impregnated with 1.00 DABCO mmol g^{-1} SiO_2 and pretreated at 303 K for 2 h in vacuo (a dotted line) are shown in Fig. 2. No hysteresis was observed in the former isotherm, but the latter material shows a remarkable irreversible desorption in the low pressure range after evacuation at the temperature of adsorption, the amount of which at $P/P_0=0$ is shown by W_{ir} molecules nm^{-2} in Table 1. The same kind of hysteresis was observed on the adsorption isotherms of methyl iodide to the PPZ- and HMTA-impregnated samples pretreated at 303 K in vacuo. The monolayer adsorption capacities, W_m molecules nm^{-2} obtained by applying BET equation to the isotherms of the halides except chlorobenzene increased on impregnating these amines as is shown in Table 1. The adsorption behav-

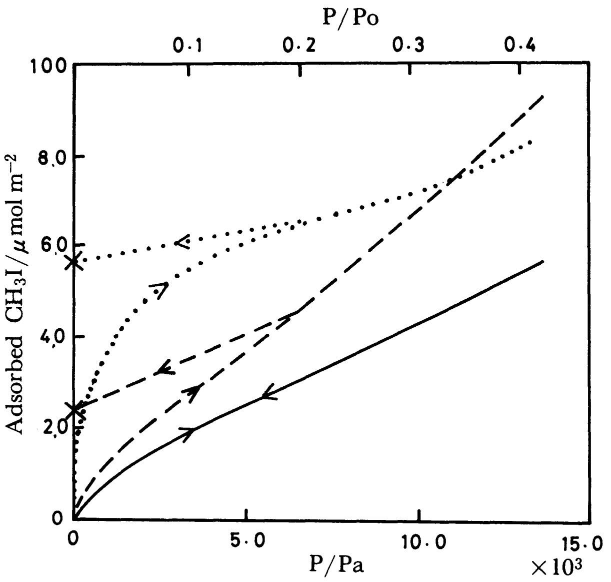

Fig. 2. The adsorption isotherms of methyl iodide on DABCO and ATS-impregnated samples which were pretreated at 303 and 373 K in vacuo for 2 h respectively. The impregnated amounts of DABCO and ATS are 1.00 and 1.21 mmol g^{-1} respectively. The full line, pure silica gels; the dotted line, DABCO-impregnated sample; the broken line, ATS-impregnated sample; X, the amount of irreversible adsorption.

Table 1. The Monolayer Adsorption Capacity (W_m) and the Amount of Irreversible Adsorption (W_{ir}) of Organic Halides on Silica Gels Impregnated with 1,4-Diazabicyclo[2,2,2]octan (DABCO), Pyperazine (PPZ), Hexamethylene Tetramine (HMTA), and (3-Aminopropyl)-triethoxysilane (ATS). DABCO-, PPZ-, and HMTA-Impregnated Samples were Pretreated at 303 K in vacuo for 2 h. ATS-Impregated Sample was Pretreated at 373 K

Impregnated		Pure	DABCO	PPZ	HMTA	ATS
Surface area ($m^2 g^{-1}$)		705	360	430	378	377
Impregnated amount (mmol $^{-1}$)		—	1.00	1.31	1.06	1.21
W_m (molecules nm^{-2})	CH_3I	2.34	3.18	3.40	3.53	3.87
	n-C_3H_7I	2.42	2.89	2.92	2.56	3.62
	n-C_3H_7Cl	2.20	4.64	2.20	2.26	3.07
	C_6H_5Cl	3.71	3.63	2.49	3.08	2.81
W_{ir} (molecules nm^{-2})	CH_3I	0	3.44	2.40	1.77	1.52
	n-C_3H_7I	0	1.20	0.07	1.25	0.44
	n-C_3H_7Cl	0	0.69	0.03	0	0.16
	C_6H_5Cl	0	0	0	0	0

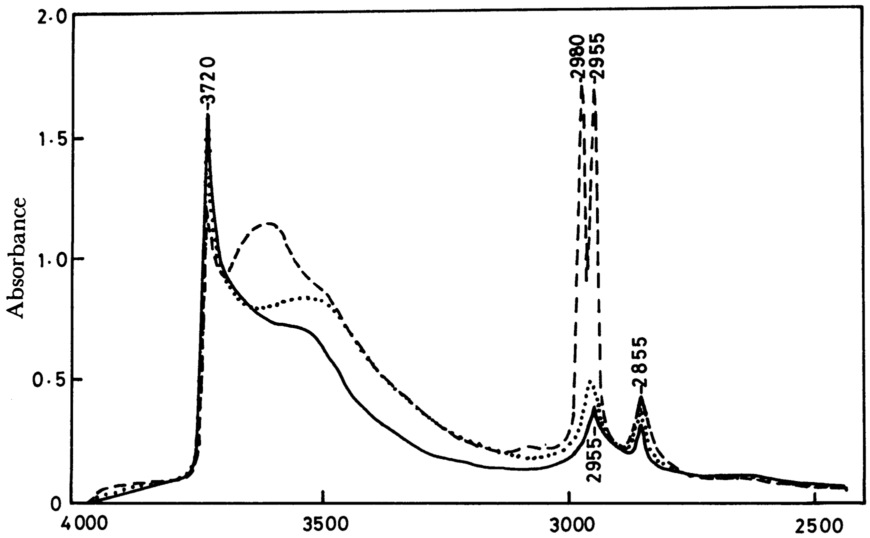

Fig. 3. The influence of adsorption and desorption of methyl iodide on the IR spectrum of DABCO-impregnated silica gels. The full line, before adsorption; the broken line, after adsorption; the dotted line, after desorption.

iors of propyl iodile and propyl chloride were similar to that of methyl iodide. On the other hand, the adsorption and desorption of chlorobenzene was reversible on pure and amine-impregnated samples. W_m in this case was larger for pure material than these with amines.

A full, a broken and a dotted lines in Fig. 3 show the IR spectrum of original DABCO-impregnated sample, that after the adsorption of methyl iodide at 1.3×10^4 Pa, and that after desorption by evacuation at room temperature respectively. After methyl iodide adsorption, the intensity of the 3720 cm^{-1} band decreased by the hydrogen-bond adsorption of methyl iodide, and the 2980 and 2955 cm^{-1} bands assigned to C-H vibrations of methyl groups of the adsorbate appeared. When evacuating this sample at 298 K, these C-H bands disappeared and the 3720 cm^{-1} band revived. These changes indicate the reversible desorption of most of methyl iodide molecules adsorbed. There is no positive evidence of irreversible adsorption in these spectra because the amount of irreversible adsorption was very small. However, there may exist an irreversible adsorption as follows. Methyl iodide is known to react easily with DABCO at room temperature by the reaction.[7]

$$N(CH_2CH_2)_3N + 2CH_3I \rightarrow I^-[H_3CN^+(CH_2CH_2)_3N^+CH_3]I^- \quad (1)$$

The IR spectrum of this resultant compound shown in Fig. 4 has two bands at 2945 and 2871 cm^{-1} which may be assigned to assymmetric and symmetric C-H vibrations of the methyl radicals of the resultants in Eq. 1. The bands mentioned above are different from those of methyl groups of methyl iodide molecules, because the molecular orbitals of these radicals would be different from sp^3 hybrid orbitals of methyl groups by the Reaction (1). Since the irreversible amount of adsorption is rather small and the wave numbers of the bands of radicals are close to those of impregnated amines, it was not possible to identify the existence of the bands of methyl radicals in the spectrum after desorption in Fig. 3 under the present experimental error. Therefore, it may be plausible to postulated Reaction (1) for the present irreversible adsorption.

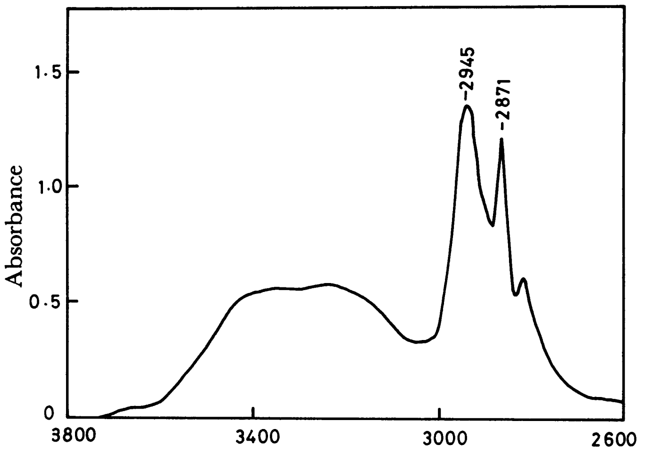

Fig. 4. The IR spectrum of the resultant of reaction of methyl iodide with DABCO in tetrachloromethane at room temperature.

The amount of irreversible adsorption, W_{ir}, in Table 1 is in the order of methyl iodide>propyl iodide >propyl chloride>chlorobenzene for each amine impregnated. This is because the Reaction (1) can take place more easily for larger ionicity of carbon-halogen bonds which can be estimated from the nuclear quad-

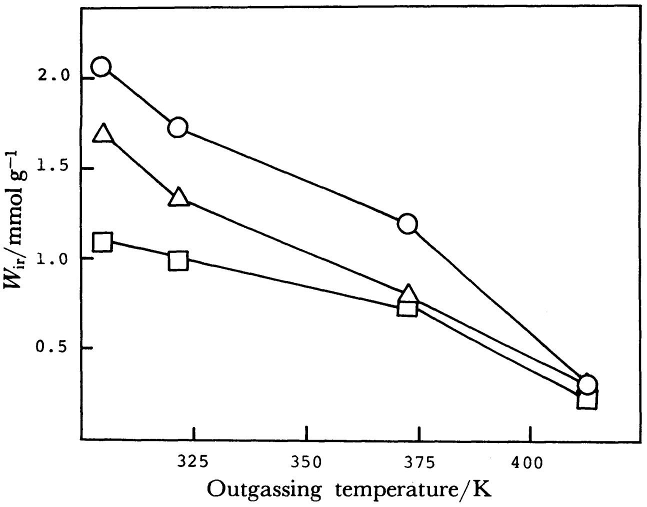

Fig. 5. The relations between the amount of irreversible adsorption of methyl iodide and pretreatment temperature. ○: DABCO-impregnated sample, △: PPZ-impregnated sample, □: HMTA-impregnated sample.

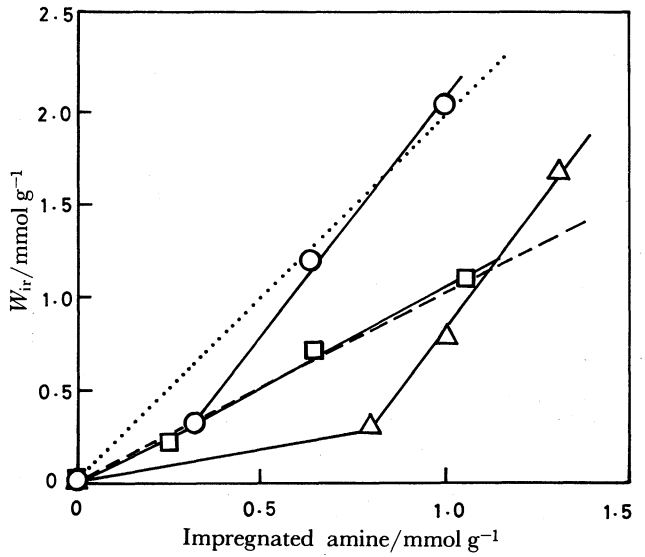

Fig. 6. The relations between the amount of irreversible adsorption of methyl iodide and the amount of amines impregnated. The dotted and broken lines show that the molal ratios of adsorbed methyl iodide to impregnated amine are 2 and 1 respectively. ○: DABCO, △: PPZ, □: HMTA.

rupole moments.[8] In Fig. 5, W_{ir} of all the amine impregnated samples decreased as the pretreatment temperature was raised. This is because the impregnated amines are removed by evacuating samples above 303 K as confirmed by CN elemental analysis.

Figure 6 shows the relations between W_{ir} of methyl iodide and the amount of impregnated amines. The molar ratios of adsorbed methyl iodide to impregnated DABCO and that to HMTA are 2 and 1 respectively as is shown by the dotted and broken lines in Fig. 6 respectively, suggesting that two nitrogen atoms of a DABCO molecule react with two methyl iodide molecules. This result supports the postulated Reaction (1). On the other hand, only one nitrogen atom of HMTA molecule having four nitrogen atoms reacts with one methyl iodide molecule, the reason for which lies perhaps in the lower basicity of HMTA than that of DABCO. The molar ratio of PPZ-impregnated sample is 2 above 0.8 PPZ mmol g^{-1} SiO_2, and, below this amount, this molar ratio is very small as is seen in Fig. 6. The reason for this difference can be interpreted as follows. Below 0.8 PPZ mmol g^{-1}, molecules are likely to lie on the surface with their molecular plane parallel to the surface and with two nitrogen atoms in the molecule are hydrogen-bonded to the surface silanol groups. This impregnated amount corresponds to the monolayer adsorption capacity estimated with the cross sectional area of PPZ molecules as equal to that of molecular plane. Therefore, these nitrogen atoms may not react with methyl iodide. The steep increase of W_{ir} above this amount can be interpreted as that both nitrogen atoms of PPZ molecules on the second layer may be free to capture methyl iodide molecules. The molar ratios of adsorbed propyl iodide to impregnated DABCO, PPZ, and HMTA are always less than unity, probably because C–I bond of propyl iodide has less ionicity than that of methyl iodide.

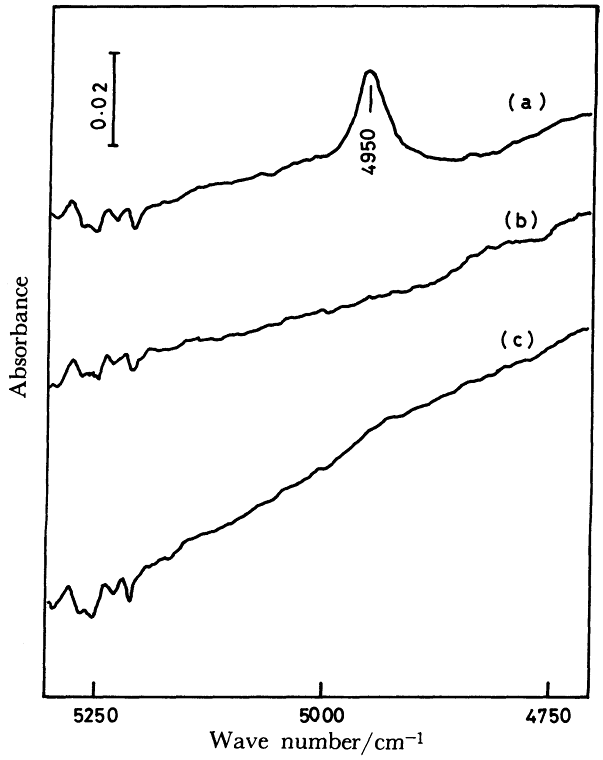

Fig. 7. The influence of adsorption and desorption of methyl iodide on NIR spectra of ATS modified sample. (a): Before adsorption, (b): after adsorption, (c): after desorption.

Most of impregnated amines are removed by outgassing at 423 K and hence W_{ir} decreases by heating as is seen in Fig. 5. In order to increase W_{ir}, amino groups were fixed on the surface of mesoporous silica gels by substituting free silanol groups to ethoxy and methoxy groups of ATS and DAS, and thus the surface density of substituted amino groups was about $1/\mathrm{nm}^2$. CN elemental analysis indicated more thermal stability of ATS than the above mentioned amines till 673 K. The adsorption isotherm of methyl iodide on ATS-modified sample shown by a broken line in Fig. 2 is irreversible like these of amine-impregnated samples. W_{ir} in this case did not decrease on heating, and was in the order of methyl iodide>propyl iodide> propyl chloride>chlorobenzene. One methyl iodide molecule is adsorbed to about one nitrogen atom of ATS. NIR spectra of this sample before methyl iodide adsorption in Fig. 7 has a combination vibration band of N-H bond of ATS molecule at 4950 cm^{-1}. This band diminished after methyl iodide adsorption and did not recover on heating in vacuo, suggesting the irreversible adsorption of methyl iodide by amino groups. The 4950 cm^{-1} band diminished after propyl chloride adsorption, but revived almost after desorption. W_{ir} of DAS-modified sample was very little, perhaps because dimethylamino groups interact with free silanol groups on the surface as will be reported soon.

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