CHEMISTRY LETTERS, pp. 415-418, 1983.

THE ADSORPTION OF METHYL IODIDE ON SILVER-IMPREGNATED SILICA GELS

Tatsuo ISHIKAWA*, Eiichi AMANO, Masaaki MUROYA+, and Seiichi KONDO
Osaka University of Education, Minamikawahoricho, Tennojiku, Osaka 543
+ Osaka Electrocommunication University, Neyagawa, Osaka 572

Both the reversible and irreversible adsorption sites for methyl iodide molecules are found on the silver-impregnated silica gel surface. The former sites are the free silanol groups, while the latter sites are the silver ions for which the protons of free silanol groups are ion-exchanged.

Radioactive isotopes of iodine are one of the hazardous elements exhausted from nuclear reactors in the form of alkyl iodide gases. The silver-impregnated porous adsorbents such as silica gels and zeolites are known to be useful for the removal of these compounds by selective adsorption. However, the details of the mechanism of the adsorption are not clear yet. This report describes the mechanism of adsorption of methyl iodide and the state of silver by the analysis of the adsorption behavior of these compounds on the silver-impregnated silica gels, so as to improve the removal efficiency of these compounds.

Silica gels were prepared by the method mentioned elsewhere.1) Hydrosols were obtained by the hydrolysis of redistilled silicium tetraethoxide adjusted to pH 2 and at 70 °C for about 100 min. These sols were gelled, washed to remove ethanol and hydrochloric acid, and hydrothermally aged at the conditions mentioned below. These hydrogels were dried carefully at room temperature. The materials thus obtained have the shape of thin transparent films, 0.03 - 0.05 mm thick and more than 1 cm^2 wide, which are suitable for IR spectroscopy. The xerogels being obtained by aging of hydrogels at pH 7 for 8 h at 100 °C are mesoporous and hydrophilic2) and the ones obtained by aging at pH 11 for 110 h at 100 °C are macroporous and hydrophobic.3) The surface areas and pore structures of these xerogels, determined from the nitrogen adsorption isotherms, are shown in Table 1.

Table 1 The surface and adsorption properties of pure and silver-impregnated meso- and macroporous silica gels. S_n: the surface area, V_p: the pore volume, $\bar{r}_p$: the mean pore radius, A: the amount of supported silver, A_m: the monolayer adsorption capacity, A_i: the amount of irreversible adsorption

Sample	S_n $m^2\ g^{-1}$	V_p $ml\ g^{-1}$	$\bar{r}_p$ nm	A ions nm^{-2}	A_m molecules nm^{-2}	A_i molecules nm^{-2}
Mesoporous silica gels (pH 7, 8 h)	750	0.60	1.6	0	2.3	0
Macroporous silica gels (pH 11, 110 h)	130	0.67	10.3	0	1.6	0
Ag-silica gels (0.5 M $AgNO_3$)	702	-	-	0.22	2.7	0.080
Ag-silica gels (1.0 M $AgNO_3$)	407	0.32	1.6	0.68	3.0	0.400

Silver was impregnated by immersing the mesoporous xerogels into 0.5 and 1.0 M silver nitrate solution at 50 °C for 20 h and by drying these gels carefully. The content of silver was analysed by dissolving the impregnated silver by immersing the materials into 1.0 M nitric acid and by measuring the silver ion in the solution by the atomic absorption spectroscopy. The amount of silver contained in these materials are listed in Table 1. These samples were pretreated at 150 °C for 2 h under 10^{-3} Pa. Nitrogen compounds were not detected in these samples after this pretreatment by CHN microanalysis. The adsorption isotherms of methyl iodide were measured by means of an automatic gravimetric instrument consisting of a quartz spring balance and a DATAMETRICS manometer[4] in the pressure range from 1.33×10^{-2} to 1.33×10^{4} Pa. The transmission IR spectra were measured with the methods mentioned elsewhere.[5,6]

The adsorption isotherms of methyl iodide on the pure mesoporous and macroporous gels are reversible as shown in Fig.1. The hydrophilic xerogels which are covered with free OH groups[2] adsorb more methyl iodide molecules than the hydrophobic gels which have more hydrogen-bonded OH groups than free OH groups.[3] Since the number of free OH groups per unit surface area is about 3/nm^2 in case of mesoporous gels,[7] one methyl iodide molecule seems to be adsorbed approximately on one free OH group, as seen in Table 1. The isosteric heats of adsorption (Q_{iso}) of methyl iodide on these gels being calculated from the

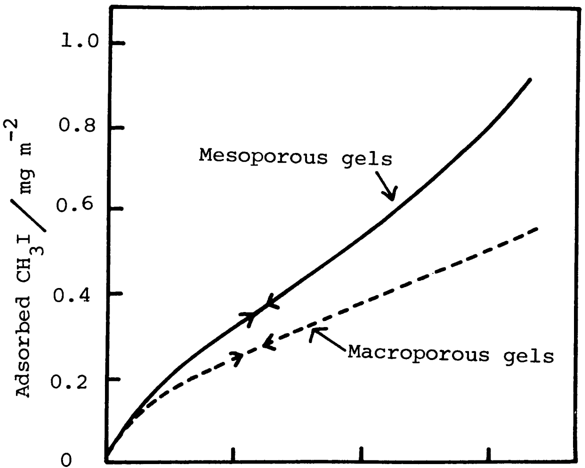

Fig.1 The adsorption isotherms of methyl iodide on pure silica gels at 15 °C.

adsorption isotherms at 15, 25, and 35 °C by using the Clausius-Clapeyron equation are shown in Fig.2 against the adsorbed amount of methyl iodide. The Q_{iso} of methyl iodide on mesoporous gels at low coverage is higher than that of macroporous gels in this figure, which reflects the hydrophobic nature of the latter gels. The monolayer adsorption capacity of methyl iodide molecules (A_m) of the hydrophobic silica surface is lower than that of hydrophilic surface as shown in Table 1. This result, together with the low value of Q_{iso} of the latter surface, indicates that the methyl iodide molecules are not specifically adsorbed on the surface OH groups. The mechanism of the adsorption interaction between the methyl iodide molecules and the surface free OH groups of mesoporous gels is more clearly shown in the IR spectra being illustrated in Fig.3. The sharp OH band before adsorption (full line) shows that this surface consists of the free OH groups. After the adsorption of methyl iodide at 2.98×10^3 Pa, this free OH band becomes smaller than before, and a new perturbed OH band appears at about 3600 cm^{-1} (broken line) accompanying the C-H symmetric and assymmetric streching absorption bands of the adsorbed methyl iodide molecules at about 2900 cm^{-1}. The number of free OH groups which adsorbed these molecules, can be estimated from the intensity ratio of free OH band before and after adsorption, multiplied by the free OH density of $3/nm^2$. This number is almost equal to the number of adsorbed methyl iodide molecules.

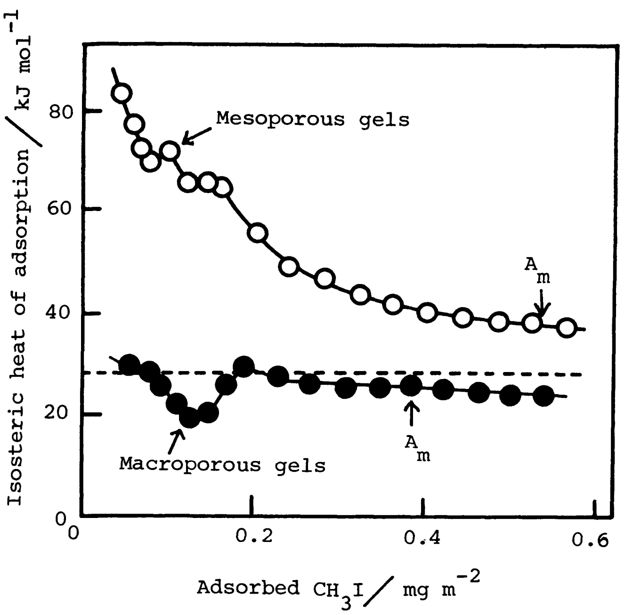

Fig.2 The isosteric heats of adsorption of methyl iodide on pure silica gels.
A_m: the monolayer adsorption capacity. The broken line: the heat of vaporization of methyl iodide.

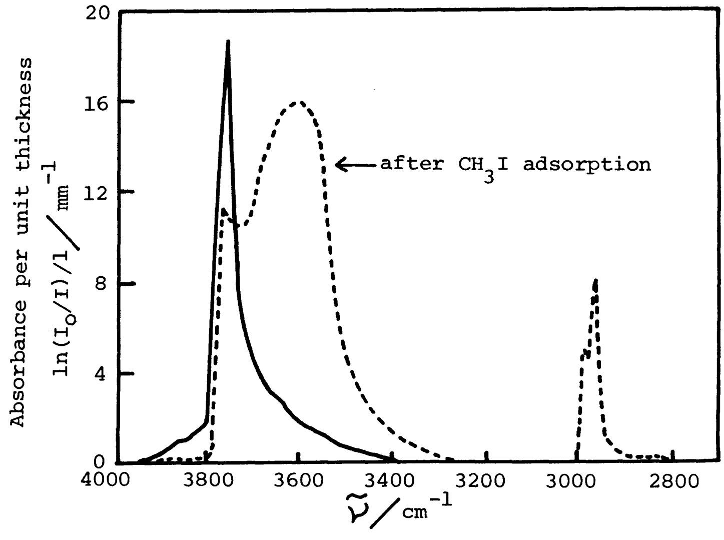

Fig.3 The influence of methyl iodide adsorption on IR spectrum of mesoporous silica gels.

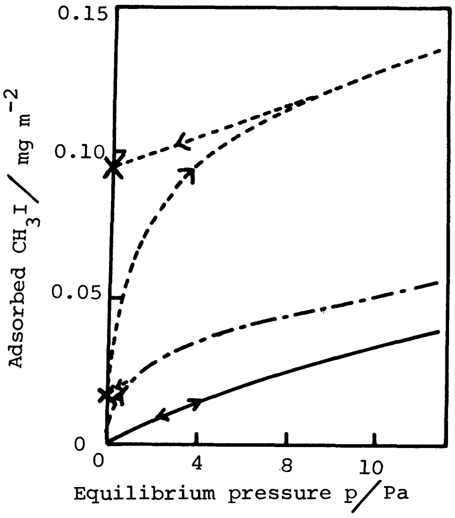

Fig.4 The adsorption isotherms of methyl iodide on Ag-supported silica gels at 15 ^{o}C.

—·—: Ag-silica gels (0.5 M $AgNO_3$).

----: Ag-silica gels (1.0 M $AgNO_3$).

——: pure mesoporous silica gels.

X : the amount of irreversible adsorption.

The intensity of the free OH band decreases by the impregnation of silver to the mesoporous gels, which indicates that the silver ions are ion-exchanged for the protons of free OH groups by this preparation. The methyl iodide molecules are adsorbed on these gels irreversibly, in contrast to the pure gels, as is clear from Fig.4. The amount of irreversibly adsorbed methyl iodide which remained on the surface after evacuation (marked by X in Fig.4: A_i in Table 1) is proportional to the amount of supported silver as is listed in Table 1. This result shows that there are two kinds of adsorption sites such as the ion-exchanged silver ions as the irreversible adsorption sites and the free OH groups as the reversible adsorption sites. As is seen from Table 1, the number of silver ions is roughly twice the number of the adsorbed molecules. This is probably because the silver ions would have been reduced partially to form aggregates in the reductive atmosphere of the pretreatment. Since the transparent silver-impregnated silica gels turn light yellow after the adsorption of methyl iodide, silver ions seem to react with methyl iodide to form silver iodide. These adsorption behaviors suggest the possibility of characterization of surface metal atoms such as silver by this sort of adsorption reaction. The more details of the mechanism of adsorption reaction of organic halides with metal-impregnated silica gels are now under investigation, and will be reported soon.

This work was partly supported by a Grant in Aid for Scientific Research from the Ministry of Education (Special Research Project on Environmental Science R32-5).

References

1) S. Kondo, K. Tomoi, and C. Pak, Bull. Chem. Soc. Jpn., 52, 2046 (1979). 2) S. Kondo, H. Fujiwara, T. Ichii, and I. Tsuboi, J. Chem. Soc. Faraday Trans. I, 75, 646 (1979). 3) S. Kondo, Y. Saito, T. Ishikawa, and H. Yamauchi, Stud. Surf. Sci. Cat., 10, 245 (1982). 4) K. Naoki, E. Amano, and S. Kondo, Memoirs of Osaka Univ. of Education III, 27, 1 (1977). 5) S. Kondo, M. Muroya, and K. Fujii, Bull. Chem. Soc. Jpn., 47, 553 (1974). 6) M. Muroya and S. Kondo, J. Japan Soc. Color Materials, 55, 374 (1982). 7) S. Kondo, H. Fujiwara, E.Okazaki, and T. Ichii, J. Colloid Interface Sci., 75, 328 (1980).

(Received January 10, 1983)