Capture of Chromate and Arsenate by Amino Groups in Functionalised SBA-1

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Mono-, di-, and triamino ligands fixed on SBA-1 mesoporous silica capture chromate and arsenate effectively in a fashion where the saturation stoichiometries (Cr/N and As/N) depend on the type of ligand. Extraordinary adsorption capacities were achieved: 211 and 263 mg/g-adsorbent for chromate and arsenate, respectively.

The pollution of oxyanions such as chromate and arsenate has recently been issued in redevelopment of the lands in industrial areas or in drinking water supplies from the groundwater. Effective and low-cost removal of the pollutants has been strongly desired and the adsorption method is one of the promising methods.[1,2] The high surface area and large pore size is necessary in addition to the high density of adsorption site. The porous silicas with highly ordered mesopores and BET surface area more than 1000 $m^2 \cdot g^{-1}$ have been developed with novel preparation recipes by using micellar templates as structure directing agents.[3,4] Unlike zeolite, the pore size is large where many of the chemical reactions are free from diffusion control. In addition the high density of silanol is beneficial to introducing functional groups with high coverage.[5] Actually, several kinds of silylations have been conducted for providing new functions to the surfaces.[6] Those functionalised mesoporous silica can be used for adsorbing heavy metal cations.[7–9] The aminosilanes are considered to interact with oxyanions just as the cationated amino groups in soil will do in nature. Because of their physical and chemical properties, mesoporous silicas will promise to be an ideal framework for the adsorption site. We report here excellent adsorption properties of SBA-1 functionalised with silanes containing mono-, di- and triamino groups.

Mesoporous silicas were synthesized with tetraethyl orthosilicate (TEOS) as a silica source. It was mixed with cetyltriethylammonium bromide + HCl in a teflon container. The precipitates were filtrated and calcined according to the literature.[11] The structure was analysed by X-ray diffraction and nitrogen adsorptions. The BET surface area was 1221 $m^2 \cdot g^{-1}$ and the most probable pore diameter was 3.0 nm. These mesoporous silicas were stirred vigorously in toluene containing one monolayer equivalent amount of 3-aminopropyltrimethoxysilane ($H_2NCH_2CH_2CH_2Si(OCH_3)_3$), [1-(2-aminoethyl)-3-amino-propyl]trimethoxysilane ($H_2NCH_2CH_2NHCH_2CH_2CH_2Si(OCH_3)_3$) or (trimethoxysilyl)-propyldi ethylenetriamine ($H_2NCH_2CH_2NHCH_2CH_2NHCH_2CH_2CH_2Si(OCH_3)_3$) and heated to 383 K under dry nitrogen for 6 h. The powder was collected and dried at 373 K. We denote these functionized silicas as *N*-, *NN*- and *NNN*-SBA-1.

The elemental analyses showed that the surface density of silane was almost independent of the kind of silane: 1.5 ± 0.2 nm^{-2}. The C/N ratio after functionalisation was 2.9, 2.6 and 2.1 for *N*-, *NN*- and *NNN*-SBA-1, respectively. They agreed well with those of the parent silanes (= 3.0, 2.5 and 2.3), suggesting no decomposition of the alkyl chains. Figure 1 shows the ^{29}Si-NMR spectrum of *NN*-SBA-1. The peaks appeared at −58, −67, −100 (*sh*) and −111 ppm which are assigned to $Si(OH)R(OSi)_2$, $SiR(OSi)_3$, $Si(OH)(OSi)_3$ and $Si(OSi)_4$.[7] Isolated species, $Si(OH)R(OCH_3)(OSi)$, was not observed. $Si(OH)R(OSi)_2$ and $SiR(OSi)_3$ are almost equally populated. The population of the Si species bounding with −OH suggests that the surface remains hydrophilic.

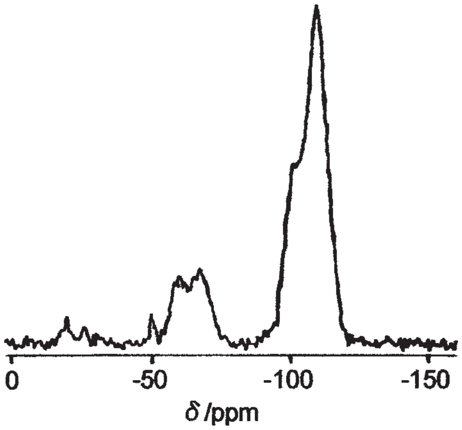

Figure 1. ^{29}Si-NMR spectra of SBA-1 functionalised with $H_2NCH_2CH_2NHCH_2CH_2CH_2Si(OCH_3)_3$.

The functionalised SBA-1 prepared by the procedures described above was impregnated with 0.1 N hydrochloric acid, filtrated and then dried. The anion adsorptions were carried out with 50 mg of functionalised silica stirred in 100 ml of aqueous solutions of K_2CrO_4 and K_2HAsO_4 at room temperature for 10 h. After removing the solid, the concentrations of the oxyanion were determined by ICP-AES. The detection limit was 1×10^{-6} g/L. Typical pH value of the solution at the beginning was between 5 and 6 and, after the adsorption, it decreased or increased by less than 1.

Table 1 shows the data of adsorptions of the oxyanions showing the initial and final concentrations in the liquid phase, *w*/*w* specific adsorption and distribution coefficient. The adsorption as well as the distribution coefficient increased with the number of N. For the adsorptions of the oxyanions below 30 ppm on *NNN*-SBA-1, the final concentration was below detection limit and K_d became more than 200000.

The maximum adsorptions were deduced from the adsorption isotherms, i.e. adsorptions of oxyanions plotted against the equilibrium anion concentrations of the liquid phase. The results are summarized in Table 2. From the charge balance, Cr/N and As/N would be 0.50. All the stoichiometries agreed with this ratio, independent of the number of N and kind of anions. The agreements of oxyanion/N ratio in *N*-SBA-1 with macroscopic charge balancing implies that the heads ($-NH_3^+$) of two silanes interact with one anion at the same time. Considering the surface density of

Table 1. Adsorptions of chromate and arsenate on functionalised mesoporous silicas

absorbent	C(Chromate)/ppm initial	 final	specific ads. mg/g-ads (θ^a)	K_d[b]	C(Arsenate)/ppm initial	 final	specific ads. mg/g-ads (θ^a)	K_d[b]
N-SBA-1	10.8	0.78	2.01 (0.02)	2.59×10^3	10.6	0.16	2.08 (0.02)	1.28×10^4
	30.4	4.66	5.15 (0.05)	1.11×10^3	30.3	0.57	5.95 (0.04)	1.04×10^4
	151.3	46.7	20.9 (0.22)	448	204.1	28.4	35.1 (0.26)	1.23×10^3
NN-SBA-1	10.8	0.00	2.17 (0.01)	$>2.0 \times 10^5$	10.6	0.00	2.11 (0.01)	$>2.0 \times 10^5$
	30.4	0.06	6.07 (0.03)	9.79×10^4	30.3	0.26	6.01 (0.03)	2.29×10^4
	163.82	5.90	31.6 (0.17)	5.35×10^3	213.7	14.6	39.8 (0.19)	2.73×10^3
NNN-SBA-1	10.8	0.00	2.17 (0.01)	$>2.0 \times 10^5$	10.6	0.00	2.11 (0.008)	$>2.0 \times 10^5$
	30.4	0.00	6.08 (0.03)	$>2.0 \times 10^5$	30.3	0.00	6.07 (0.02)	$>2.0 \times 10^5$
	317.16	3.02	62.8 (0.29)	2.08×10^4	254.8	0.65	50.9 (0.19)	7.85×10^4

[a]Coverage = (oxygen/N)/(oxyanion/N)$_{\text{saturation}}$. See text. [b]Distributioin coefficient between solid and water phase.

silane (1.5 nm^{-2}), the proximity of the head groups is necessary for this mode of interaction.

The parallel experiments were carried out for *N*-, *NN*- and *NNN*-MCM-41. The adsorption capacities were 50–70% of those of corresponding results of *N*-, *NN*- and *NNN*-SBA-1 while the K_d was comparable in low adsorption regions.

Chromate and arsenate were not adsorbed on unfunctionalised SBA-1. The positively charged amino group is indispensable to the adsorption of these anions.

Distribution coefficient depends on the number of vacant sites in the adsorption equilibrium; it increases with the number of unoccupied sites. In contrast, the aqueous solution is dilute enough to neglect the effect of concentration. Thus the comparison of K_d between *N*-, *NN*- and *NNN*- groups should be made at the same coverage, $\theta = (\text{Cr/N})/(\text{Cr/N})_{\text{saturation}}$ and $(\text{As/N})/(\text{As/N})_{\text{saturation}}$. Comparing the arsenate adsorptions between *NN*- and *NNN*-SBA-1, the K_d for the latter is much larger than that of the former. This is probably caused by the enhancement of adsorption entropy by the number of N. Since this mode of interaction does not work near the saturation coverage, the molar ratio, As/N, becomes independent of the number of N in the functional group.

Today the environmental regulation for Cr and As in a drinking water is 50 and 10 ppb in many countries. The precise experiments around several ten ppb are difficult and were not done. Since the oxyanions with much larger concentrations than the environmental regulations were removed completely (under the detection limit) in Table 1, the adsorbing of the environmental oxyanions will involve less problems. Several kinds of anions in the hydrosphere should be considered in the adsorptive removal of the oxyanions. We carried out experiments in the presence of sulphate and chlorate in order to investigate the inhibition effect on the adsorption capacities of arsenate for *NN*-SBA-1. The suppression by 7 and 1% was obtained for 20 ppm SO_4^{2-} and Cl^-, respectively, which implies that *NN*-SBA-1 will remove arsenate effectively in a real environment. For chromate adsorptions, the suppressions by these anions were smaller than those in arsenate adsorptions.

Recently, Fryxell et al. reported that copper coordinated *NN*-MCM-41 (in our notation) removes chromate and arsenate effectively.[10] The phenomena in this paper are similar to their observations in the terms of cation-anion interactions occurring in the mesopores. w/w specific adsorption at the adsorption saturation is 120 (chromate)–140 (arsenate) mg/g-adsorbent, which is less than the results in Table 2. Our study additionally shows that simple amine groups on the solid surfaces remove these anions in the acidic conditions without help of other metal cations. And, to the best of our knowledge, the adsorption capacities for chromate (211 mg/g) and arsenate (263 mg/g) are the largest ever reported. The former is almost comparable to the achievement in the absorption of hexavalent chromium by a condensed-tannin gel (287 mg/g-dry tannin gel).[11] Without using the toxic cations, amine functionalised SBA-1 can be an environmentally friendly adsorber of polluting oxyanions.

Table 2. Molar ratio of anion/N and specific adsorption at saturation

	Chromate Cr/N	 mg/g-ads	Arsenate As/N	 mg/g-ads
N-SBA-1	0.47	94.2	0.55	133
NN-SBA-1	0.50	178	0.50	214
NNN-SBA-1	0.46	211	0.48	263

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