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Short communication

Sequestration of Cu(II), Ni(II), and Co(II) by ethyleneimine immobilized on silica

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Abstract

Thermodynamic data on interaction of Cu(II), Ni(II), and Co(II) with silica modified with ethyleneimine are obtained by calorimetric titration. The amount of ethyleneimine anchored on silica surface was estimated to be 0.70 mmol g^{-1}. The enthalpies of binding Ni(II), Cu(II) and Co(II), are -3.59 ± 0.001, -4.88 ± 0.001, and -7.75 ± 0.003 kJ mol^{-1}, respectively.

Keywords: Chelating centers; Silica gel; Adsorption; Calorimetry; Thermochemical data

1. Introduction

Many studies concerning the synthesis and characterization of modified surface systems have been reported in the last half-century [1–3]. Materials derived from grafting organic compounds on the surface of inorganic oxides have several types of applications, in gas chromatography [4–6], in catalysis [7], for treatment of waste and toxic effluents [1,8], and in ion exchange [9].

As a continuation of research on silica gel, modified with ethyleneimine (etn) and the adsorption of metals [10,11], this work describes chemisorption of Cu(II), Ni(II), and Co(II) on etn grafted silica.

2. Materials and methods

The silica gel (Aldrich) with particle size 70–230 mesh, average diameter 60 Å and pore volume 0.75 m^3 g^{-1}, was modified with ethyleneimine and characterized as previously described [10–12]. The solution of divalent metals was prepared in double distilled water from reagent grade materials.

The amount of attached ethyleneimine was assessed from the nitrogen content determined by the Kjeldhal method.

Activated silica gel and functionalized silica were characterized by estimation of the surface area with the BET method [13] through nitrogen sorption isotherms at 77 K, by a Flowsorb II 2300 Micrometrics apparatus [10].

For solid samples, ^{13}C NMR spectra were obtained on an AC/300P Bruker spectrometer with cross-polarization and magic-angle spinning (CPMAS) at a frequency of 75.47 MHz with acquisition time 0.156 s, pulse delay at 4 s, contact time 1 ms and in the range of 13,663–25,600 scans [10].

The adsorption capacity of the modified silica was estimated in duplicate, using a batch process with divalent Cu, Ni, and Co nitrates, as follows: about 50 mg of the modified silica was suspended in 20.0 cm^3 of an aqueous solution of the metal ion with concentration varying from 0.05 to 5.5 mmol dm^{-3}. The suspension was mechanically stirred for 3 h at room temperature and separated by centrifugation for 10 min at 1813 × *g*. Aliquots of the supernatant were pipetted and the cations estimated by EDTA complexometric titration.

Adsorption isotherm data were fitted to the modified Langmuir model,

$$\frac{C_s}{n_f} = \frac{C_s}{n^s} + \frac{1}{n^s b} \qquad (1)$$

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where C_s is the remaining cation concentration (mol dm^{-1}) in solution after equilibrium, n_f is the number of moles adsorbed (mol g^{-1}), n^s is the maximum amount of adsorbed cation per gram of the silica (mol g^{-1}), and b is a parameter associated with the equilibrium constant for the reaction. The n^s and b values for each adsorption process were obtained from the slope and intercept, of the linearized form of the adsorption isotherm, by the method of least squares.

The thermal effect evolved from the reaction was measured in an LKB 2277 calorimeter [14,15]. A sample of functionalized silica, varying from 15.0 to 50.0 mg, was suspended in 2.0 cm^3 of water in a steel ampoule under stirring at 298.15 ± 0.02 K. Thermostated solutions of the cations, in the 0.054–0.199 mol dm^{-3} range, were incrementally added into the calorimetric vessel [14,15]. The corresponding thermal effect of dilution of the cation solution was obtained in the absence of the silica (Q_d). The thermal effect of the hydration of the immobilized silica in water was evaluated as before [14,15]. The net thermal effect of adsorption ($\sum Q_r$) was obtained as

$$\sum Q_r = \sum Q_t - \sum Q_d. \tag{2}$$

3. Results and discussion

Reaction of etn, generated 3.40 mmol of etn per gram of the support [10,11], Based on the estimated amount of nitrogen bonded to the organic chain and in the ^{13}C NMR in solid state [10], each new pendant group on the surface has, on average, five nitrogen atoms in the organic chain, generating approximately 0.70 mmol of grafted chain per gram of silica.

The initial specific surface area of 484 ± 2 m^2 g^{-1} decreases as the reaction with etn takes place, to give 121 ± 3 m^2 g^{-1} for the modified silica.

The results of cation adsorption are presented in Table 1. The adsorption isotherms showed a very similar profile in adsorbing the cations. The isotherms are very similar to that proposed for L2 type, as stated by Giles' classification [16,17]. However, the isotherms are well-fitted by a modified Langmuir model. Fig. 1 shows the linearized isotherms.

The inorganic framework, $\equiv$Sil–O($CH_2CH_2NH)_4CH_2CH_2NH_2$, containing five basic nitrogen centers, is a typical hard base [18,19], the three divalent metal ions are borderline acids, according to Pearson [18,19]. These cations show nearly the same maximum adsorption capacity (n^s), even though they have different degree of hardness [20]. This indicates that adsorption is not governed only by hardness, but also by other factors in opposition.

Table 1

Amount of adsorbed cations (n_f), maximum adsorption capacity (n^s), constant (b), and correlation coefficient (r^2) for the adsorption of divalent cations (MX_2), by direct immobilization of ethyleneimine on silica at 298 ± 1 K

MX_2	n_f (mmol g^{-1})	n^s (mmol g^{-1})	b (dm^3 mol^{-1})	r^2
$Ni(NO_3)_2$	0.55	0.57 ± 0.02	4.975	0.9993
$Co(NO_3)_2$	0.45	0.58 ± 0.03	2.390	0.9945
$Cu(NO_3)_2$	0.44	0.55 ± 0.05	1.371	0.9996

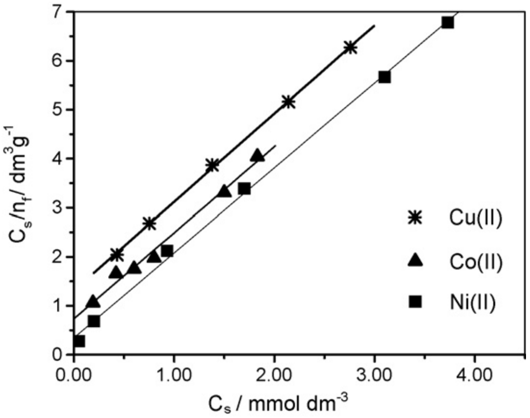

Fig. 1. The linearized forms of the isotherms of adsorption on $\equiv$Sil($CH_2CH_2NH)_4CH_2CH_2NH_2$.

The thermal effect of the hydration of the support was null, so the resultant thermal effect from the reaction was calculated by considering the thermal effects of titration and dilution, Eq. (2).

These values were adjusted to a modified Langmuir equation, Eq. (3), to calculate the integral enthalpy for formation of a monolayer per unit mass of adsorbent Δ_{mon}:

$$\frac{\sum X}{\sum \Delta_r H} = \frac{1}{(k-1)\Delta_{mon} H} + \frac{\sum X}{\Delta_{mon} H} \tag{3}$$

where $\sum X$ is the sum of the mole fractions of the cation in solution after each injection, and X is obtained for each point of the titration from the batch experiments; $\Delta_r H$ is the integral enthalpy of adsorption (J g^{-1}) obtained by dividing the thermal effect of adsorption (Q_r) by the number of moles of the adsorbate; k is a constant of proportionality that also includes the equilibrium constant and $\Delta_{mon}H$ is the thermal effect of formation of the metal ion monolayer on the surface. $\Delta_{mon}H$ and k values were obtained from the slope and intercept of the $\sum X/\Delta_r H$ versus $\sum X$ plot. The calorimetric curve obtained for cobalt nitrate was fitted to the above Langmuir modified equation as shown in Fig. 2. From these values ΔG° and ΔS° values calculated are shown in Table 2.

The enthalpy changes corresponding to one monolayer formation are in inverse order to the ionic hydration numbers

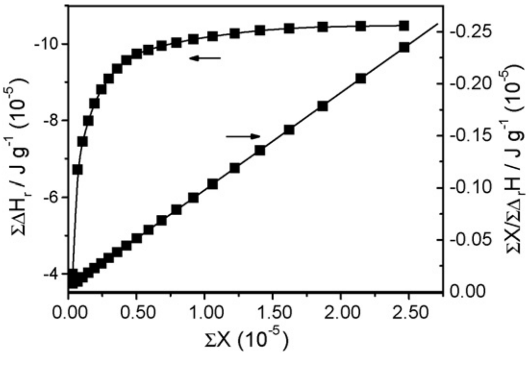

Fig. 2. Isotherm of calorimetric titration of modified silica surface, $\equiv$Sil($CH_2CH_2NH)_4CH_2CH_2NH_2$, with cobalt nitrate at 298.15 ± 0.02 K. The straight line is a linearized form of the isotherm.

Table 2
Thermodynamic data for the interaction of divalent metal ions on surface $\equiv\mathrm{Sil(CH_2CH_2NH)_4CH_2CH_2NH_2}$ at 298.15 ± 0.02 K

MX_2	$-\Delta_{\mathrm{mon}}H$ ($\mathrm{J\,g^{-1}}$)	$-\Delta_{\mathrm{ads}}H$ ($\mathrm{kJ\,mol^{-1}}$)	$-\Delta G^{\circ}$ ($\mathrm{kJ\,mol^{-1}}$)	ΔS° ($\mathrm{J\,mol^{-1}\,K^{-1}}$)	r^2
$Ni(NO_3)_2$	3.59 ± 0.001	6.13 ± 0.01	11.06 ± 0.001	17 ± 1	1.0000
$Co(NO_3)_2$	7.75 ± 0.001	13.95 ± 0.01	19.47 ± 0.002	19 ± 1	1.0000
$Cu(NO_3)_2$	4.88 ± 0.003	8.78 ± 0.03	11.49 ± 0.010	09 ± 2	0.9989

obtained from apparent molal isothermal compressibilities [20], which are 8.8, 9.4, and 9.2, for Co(II), Ni(II), and Cu(II), respectively.

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