Journal of Thermal Analysis and Calorimetry, Vol. 86 (2006) 2, 371–377

THERMAL EVOLUTION OF MICROPOROUS NITROPRUSSIDES ON THEIR DEHYDRATION PROCESS

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Divalent transition metal nitroprussides form a family of microporous materials which lose their crystallization water (coordinated and zeolitic) below 100ºC and then remain stable up to above 150ºC. The dehydration process of representative samples in their stable phases was studied by thermo-gravimetry (TG) and differential scanning calorimetry (DSC). The copper complex dehydrates in a single step through a practically irreversible process. For cadmium and cobalt complexes the water evolution on heating takes place in two stages. The first one, where only zeolitic waters are removed, is dominated by a diffusion mechanism while, during the loss of the strongly bonded waters (second stage) the material framework effect is added. The involved activation energy and its dependence on the conversion degree were estimated evaluating the thermo-gravimetric data according to an isoconversion model.

Keywords: *dehydration kinetics, Hi-Res TGA, nitroprussides, thermal analysis, TMDSC*

Introduction

Insoluble transition metal nitroprussides can be considered as a tridimensional assembling of the pentacyanonitrosylferrate(II) anion, $[Fe(CN)_5NO]^{2-}$, through an appropriate cation of transition metal (Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} or Cd^{2+}). They can be obtained as single crystals [1–3] or as polycrystalline powders [4–7] with a crystal structure and hydration degree which depend on the preparation method. However, when both polycrystalline and single-crystal samples are aged in air at room temperature, they adopt, with the exception of the copper complex, the same crystal structure [5, 8]. These stable phases have an open framework with a system of channels suitable for small molecules storage [9] and/or separation [10]. In this sense, cobalt and nickel nitroprussides have showed relatively high hydrogen adsorption capacity [11]. These nitroprussides have a channel topology and specific adsorption sites similar to those found in hexacyanocobaltates where hydrogen storage has also been studied [12]. The adsorption of molecules on channels modifies the electronic structure of the host solid and this can be used to introduce changes in its electronic structure and as modulation way for the material properties and functionality. The studied complexes show interesting properties as holographic information storage materials [13] and for the nickel compound, a photo-induced magnetic order has been reported [14]. The framework outgassing is an essential step in the applications of porous materials and nitroprussides are not an exception in that sense. However, the dehydration process of these porous molecular materials remains poorly documented [1–4, 8, 9]. Thermal analysis has been widely used to study solid-state reactions [13, 14] and particularly the dehydration reactions [15–19]. The aim of this paper is to shed light on thermo-kinetic aspects of the water desorption process in polycrystalline nitroprussides by means of thermogravimetric and calorimetric experiments. The copper, cadmium and cobalt complexes were studied. They are representative of all the reported stable phases in this family of compounds.

Experimental

Sodium nitroprusside, $Na_2[Fe(CN)_5NO]\cdot 2H_2O$, was used as source of the molecular block, $[Fe(CN)_5NO]^{2-}$. The assembling metal was provided by a soluble salt, in this case chloride, of divalent transition metals (Co^{2+}, Cu^{2+} and Cd^{2+}). The assembling process was carried out mixing aqueous solutions (0.01 M) of sodium nitroprusside and metal chloride. The formed precipitate was isolated and washed several times with distilled water to obtain a filtrate free of the starting anions and cations. The resulting solids were air-dried at room temperature until reaching constant mass. The chemical nature and

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1388–6150/$20.00

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phase compositions of the obtained samples were established in a previous report [9]. A TA Instrument's high resolution (Hi-Res^{TM}) thermogravimetric analyzer TGA 2950 and the instrument control software Thermal Advantage version 1.1A were used to obtain the mass loss profile of the studied samples. The TGA 2950 was used in dynamic rate mode. In this mode the heating rate is varied dynamically during the heating ramp in response to the derivative of mass change (as derivative increases, the heating rate is decreased and vice versa). The heating rates were constrained to the range 0.001°C min^{-1} to the maxima: 5, 10 and 20°C min^{-1} with an instrumental resolution of 5. The furnace purge was nitrogen using flow rates of 830 mL min^{-1}.

The data of temperature modulated differential scanning calorimetry (TMDSC) were obtained with a DSC (TA Instruments, MDSC-2910 model), from an initial temperature of 25°C (stabilized during 5 min), to final temperature of 300°C, a modulation of ±0.318°C each 60 s and a ramp of 2°C min^{-1} under a N_2 atmosphere and hermetic pans.

Results and discussion

Hi-Res TGA curves were used to obtain information on the amount and nature of the crystal water and to estimate the activation energy involved in the dehydration process of the samples and its dependence on the degree of reaction extent (α). TMDSC technique provided the total heat flow, its heat capacity and kinetic components (reversible and nonreversible fraction, respectively, from now on) during the dehydration process, which help to understand the nature of the thermal processes involved in the sample dehydration. The nominal (expected) hydration degree (number of water molecules per formula unit) was taken from the water vapor adsorption isotherm [9], as the amount of adsorbed water molecules per mole of adsorbent at a relative pressure of 0.8, equivalent to 80% of relative humidity.

Dehydration process according to Hi-Res TGA and TMDSC

Dehydration of $Cu[Fe(CN)_5NO]\cdot 2H_2O$

Figure 1A shows the Hi-Res TGA curve, the heating program and the corresponding derivatives for copper nitroprusside (Amm2 phase). The mass loss (10.56%) corresponds to a dihydrate (expected value 11.41%). The two water molecules per formula unit evolve in a single step at around 60°C, in correspondence with their nature as coordinated waters to the copper atom. Their small structural difference, related to the Jahn–Teller effect in copper(II) ion [7], cannot be resolved by the TG curve even using the high resolution mode. Both the heating program and the derivative of the TG curve only show two inflections in the dehydration region corresponding to a single stage of mass loss. In the region from 50 to 70°C the heating rate falls to a relatively low value, below 4°C min^{-1} and then remains stable up to the end of the dehydration

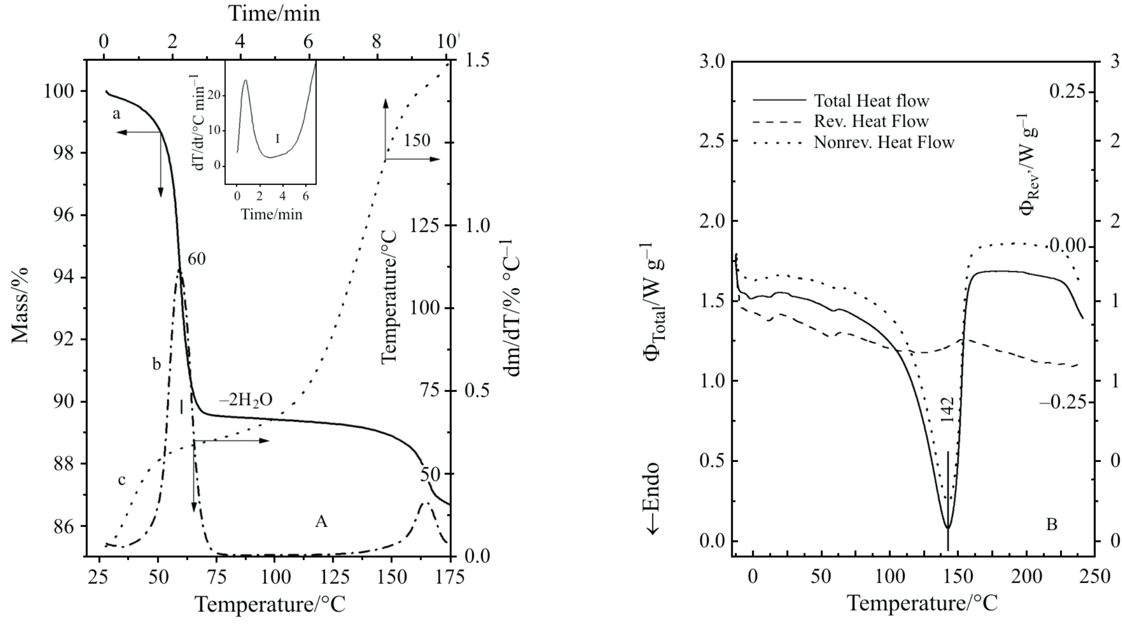

Fig. 1 A – HRTGA and B – TMDSC curves of copper nitroprusside (orthorhombic Amm2 dihydrate). A – a – TG, b – DTG curve, c – the heating program and its derivative (inset). B – Total, reversible and non-reversible flow of heat

Table 1 Total, reversible and irreversible heats involved in dehydration process of the studied materials according to TMDSC experiments. The total heat per water molecule to be liberated is also reported*

Composition	Q_r, reversible/ kJ mol^{-1}	Q_i, irreversible/ kJ mol^{-1}	Q_t, total/ kJ mol^{-1}	$Q_t$water molecule/ kJ mol^{-1}
$Cu[Fe(CN)_5NO]\cdot 2H_2O$	6	82	88	44
$Cd[Fe(CN)_5NO]\cdot 2H_2O$	2	94	96	48
$Co[Fe(CN)_5NO]\cdot 5H_2O$	6	265	271	54

*Errors in heats are less than 5%

process (Fig. 1A, inset). This suggests that the activation energy does not change during the water release. It seems that the reaction proceeds in sites energetically equivalent. On dehydration, the orthorhombic (Amm2) dihydrate transforms into the anhydrous tetragonal (I4mm) phase [7]. The formation of the tetragonal phase requires the loss of all the coordinated water without formation of an intermediate hydrate or a transition state. This could explain the large energetic homogeneity of the dehydration process in this complex (discussed below). The anhydrous complex, once formed, remains stable up to above 150°C where its decomposition begins with the loss of the NO group according to the sample mass loss.

Figure 1B shows the TMDSC curves for the region of dehydration. The endothermic peak around 140°C corresponds to the same thermal effect detected by Hi-Res TGA at 60°C, but now it appears at a higher temperature due to the TMDSC experiment conditions (essentially due to the closed sample holder). In hermetic pans, the evolution of the first water molecules creates a relatively large local pressure of water vapor which retards the dehydration process. The total heat flow associated to the dehydration is dominated by the nonreversible component (82 *vs*. 6 kJ mol^{-1}) (Table 1), which suggests that this thermal effect, and the related structural transformation, are essentially irreversible processes, within the time scale of this experiment. The initial orthorhombic structure (Amm2 dihydrate) is restored, from the anhydrous phase, after at least a week of the sample immersion in water. The small reversible fraction of the flow of heat is related to that behavior. The observed change in the base-line on 150°C for the reversible heat curve was attributed to a variation in the sample heat capacity due to the related structural transformation and composition change.

Dehydration of $Cd[Fe(CN)_5NO]\cdot 2H_2O$

This compound is representative of orthorhombic (Pnma) nitroprussides (Mn^{2+} [4], Fe^{2+} [6], Zn^{2+} [5] and Cd^{2+} [5] complexes). Its Hi-Res TG curve shows a set of inflections which appear partially resolved in the derivative curve (Fig. 2A). A similar TGA curve has been reported for the Mn^{2+} analog [4]. The derivative curve can be fitted as the sum of two Gaussian peaks. The total mass loss (8%) corresponds to a dihydrate (expected value 9.9%). The partial dehydration related to the first peak (at 50°C) is equivalent to the evolution of 0.7 water molecule per formula unit. At a higher temperature (around 64°C), the coordinated water evolves. A fraction of the zeolitic water could have been removed under the N_2 flow during the experimental setting before running the TG experiment explaining the observed difference between estimated and expected mass loss (1.9%). Once the two water molecules have evolved the complex remains stable up to above 200°C. The two peaks observed in the TG derivative curve are also detected in the derivative of the heating program (Fig. 2A, inset). The variation in the d*T*/d*t* curve is slightly more pronounced for the region of the zeolitic water removal. This fact could be related to a variation in the activation energy during the release of that weakly bonded water molecule. Desorption of hydrogen bonded water molecules involves a cooperative process because initially all the porous framework, the release way of the evolved molecules, remains saturated of adsorbed water. Such situation changes once the channels are partially liberated from zeolitic water, facilitating the diffusion process of the remaining water molecules.

Figure 2B shows the TMDSC curves for this orthorhombic complex. The two minima at 84 and 137°C correspond to the two peaks observed in the TG derivative curve due to the release of both, zeolitic and coordinated waters. The total heat flow is dominated by the irreversible component which agrees with the relatively large equilibrium time (at least one hour per point) required in the water adsorption experiment, particularly in the region of zeolitic waters [9]. A higher reversible component of the heat flow is observed in the region of coordinated waters, which agrees with the framework nature that provides a highly polar surface to interact with these last removed water molecules and also with the availability of free space around the polar sites to accommodate polar species.

Dehydration of $Co[Fe(CN)_5NO]\cdot 5H_2O$

This composition is representative of cubic (Fm3m) nitroprussides (complexes of Fe^{2+} [6], Co^{2+} [3] and

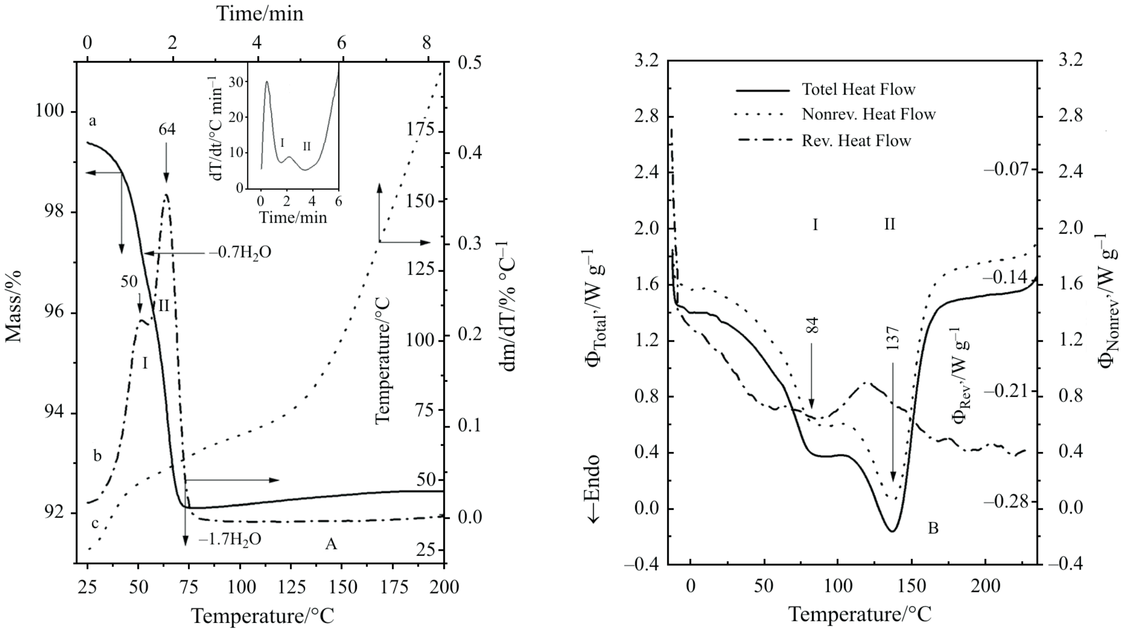

Fig. 2 A – HRTGA and B – TMDSC curves of cadmium nitroprusside (orthorhombic Pnma dihydrate). A – a – TG, b – DTG curve, c – the heating program and its derivative (inset); B – Total, reversible and non-reversible flow of heat

Ni^{2+} [9]). The observed mass loss (25.5%) corresponds to a pentahydrate (expected value 25%) (Fig. 3A). The first three water molecules (zeolitic) are lost at relatively low temperature (below 50°C) resulting in a dihydrate. The remaining two waters are liberated at a higher temperature, around 65°C. These two dehydration steps are observed as two well resolved peaks in the TG derivative curve. An analogous behavior was observed in the adsorption experiment; the first two water molecules are rapidly absorbed leaving a very low relative pressure, then the adsorption of the remaining ones (zeolitic) takes place [9].

Once the complex has been thoroughly dehydrated, it remains stable up to above 150°C where its decomposition through the evolution of the NO group begins. In ferrous nitroprusside (cubic modification) the loss of the NO group has been reported at 200°C in vacuum and then, at 350°C a CN is liberated to form a tetracyano complex [20].

According to the Mössbauer spectra of ferrous nitroprusside, in the cubic structure there are three structural sites for the assembling metal (Fe, Co or Ni), particularly, $M(NC)_5(H_2O)$, $M(NC)_4(H_2O)_2$ and $M(NC)_6$ in a relative population of 72:18:10 [9]. This leads to the existence of 1.1 coordinated water molecules per formula unit, a value close to that found (1 molecule) for the orthorhombic complexes.

However, the second dehydration step corresponds to the loss of two water molecules. This suggests that the most strongly hydrogen bonded water and the coordinated ones (1.1) evolve practically together. A similar effect but less pronounced was observed in the Hi-Res TGA curve of the cadmium complex where both, zeolitic and the coordinated waters evolve with a relatively small temperature difference. In cobalt complex that difference must be smaller because the framework is more open and the coordinated and first hydrogen bonded water molecules stabilized the crystal structure. This supposes a stabilization of a zeolitic water once the compound has been partially dehydrated, which explains the observed behavior during the water vapor adsorption process in cubic nitroprussides [9]. The coordinated and first zeolitic waters are rapidly adsorbed giving a low residual pressure and requiring short equilibrium times. The heating program (d*T*/d*t*) curve also provides information on the processes involved in the dehydration of cubic nitroprussides. A narrow valley in the d*T*/d*t* curve (Fig. 3A, inset) corresponds to the first dehydration step which suggests that this process takes place in a relatively short time and with variable activation energy. The second dehydration step consumes more time, and has a higher and more stable heating rate.

Figure 3B shows the TMDSC curves of cobalt nitroprusside. The thermal effects observed at 98 and 150°C correspond to those detected in the Hi-Res TGA curve at 30 and 65°C, respectively. According to the TMDSC data, the water loss is characterized by a small but significant contribution of the reversible fraction to the total heat flow (Table 1) which is in correspondence with the reversibility of the dehydration process in this material [9]. The total heat flow continues being dominated by the nonreversible contribution. This could be interpreted as a kinetic effect: the modulation time of the DSC heating ramp results insufficient to allow the

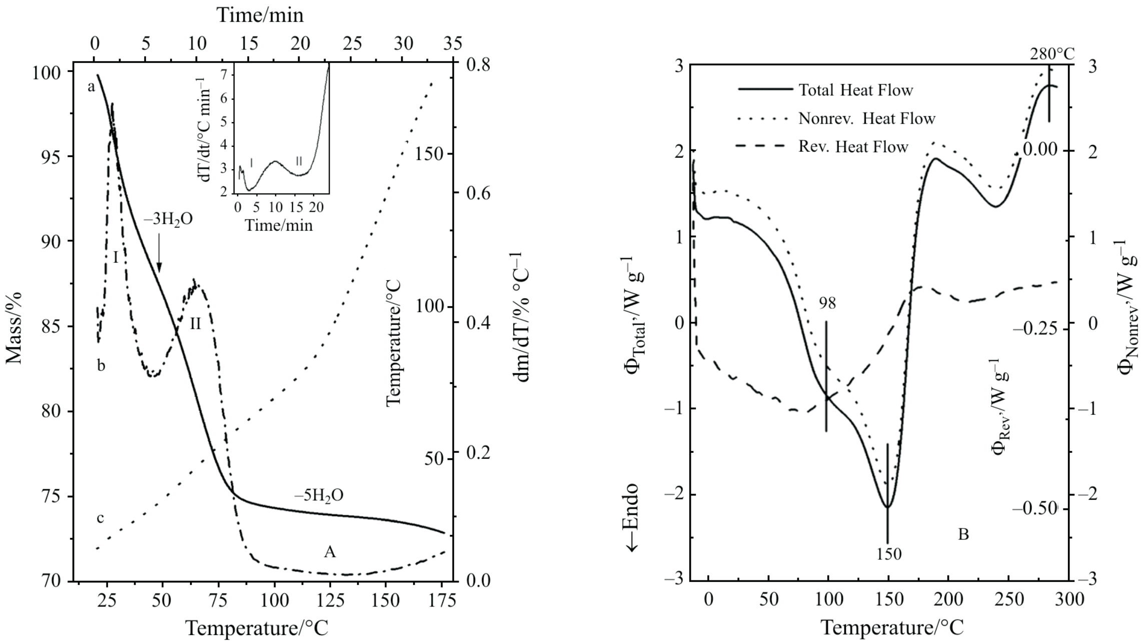

Fig. 3 A – HRTGA and B – TMDSC curves of cobalt nitroprusside (cubic Fm3m pentahydrate). A – a – TG, b – DTG curve, c – the heating program and its derivative (inset); B – Total, reversible and non-reversible flow of heat

re-adsorption of a large fraction of the removed water molecules. In addition, cubic nitroprussides have relatively large pores, of about 8.5 Å in diameter but communicated by smaller windows, c. a. 4 Å of effective cross section, and the diffusion through these small windows could be the limiting factor for a fast dehydration or re-hydration process. The estimated reversible fraction of the heat flow results 2.2% which is similar to that found for the cadmium complex (2.1%). Probably this is related to the window size in these two materials which is also similar [3, 5].

Kinetic study

The Hi-Res TGA data collected at different heating rates were processed according to the isoconversion principle in order to obtain the dependence of the activation energy $(E_a)_\alpha$ as a function of the transformation degree (α), using a reported methodology [21].

Figure 4 shows the obtained results for the copper complex. The activation energy $(E_a)_\alpha$ appears to be independent of the conversion degree (α), with a value of (48.3±0.4 kJ mol^{-1}). This suggests that all the dehydration process of this material is controlled by a same reaction mechanism, i.e. the reaction limiting step does not change. This is an expected result since the dehydration process and the related structural transformation in copper nitroprusside take place without formation, for instance, of a monohydrate as intermediate phase, and the formed anhydrous phase has a hydrophobic framework facilitating the water release through the material framework. The estimated value of $(E_a)_\alpha$ is equal to those reported for other hydrated copper salts (for instance, $Cu(HCO_2)_2{\cdot}4H_2O$, E_a = 47 kJ mol^{-1}) [22], which is a typical value for the activation energy of many thermal dehydration processes [23]. The energy required to overcome the van der Waals forces typically falls from 20 to 40 kJ mol^{-1} [24]. This suggests that there is a low energy barrier related to the rupture of the Cu–OH$_2$ bond.

From the two partially resolved dehydration steps of cadmium nitroprusside the dependence of $(E_a)_\alpha$ on α was estimated. These overlapped contributions were separated fitting the DTG curve with two gaussian peaks and then they were integrated. Figure 5 shows such dependence for the loss of both, the hydrogen bonded and the coordinated waters. For zeolitic water the value of $(E_a)_\alpha$ decreases from about 120 kJ mol^{-1} in the region of low conversion until an average of 57 kJ mol^{-1} for α>0.6. This dependence of $(E_a)_\alpha$ on α is typical of a multiple-steps reaction ini-

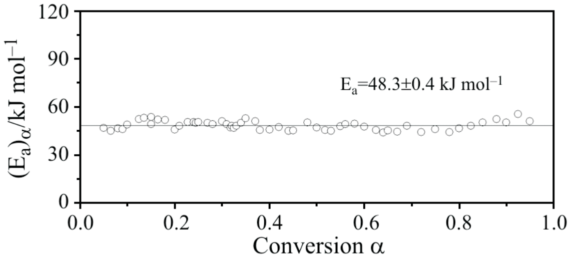

Fig. 4 Dependence of the activation energy $(E_a)_\alpha$ on the transformation degree (α) for the dehydration of copper nitroprusside

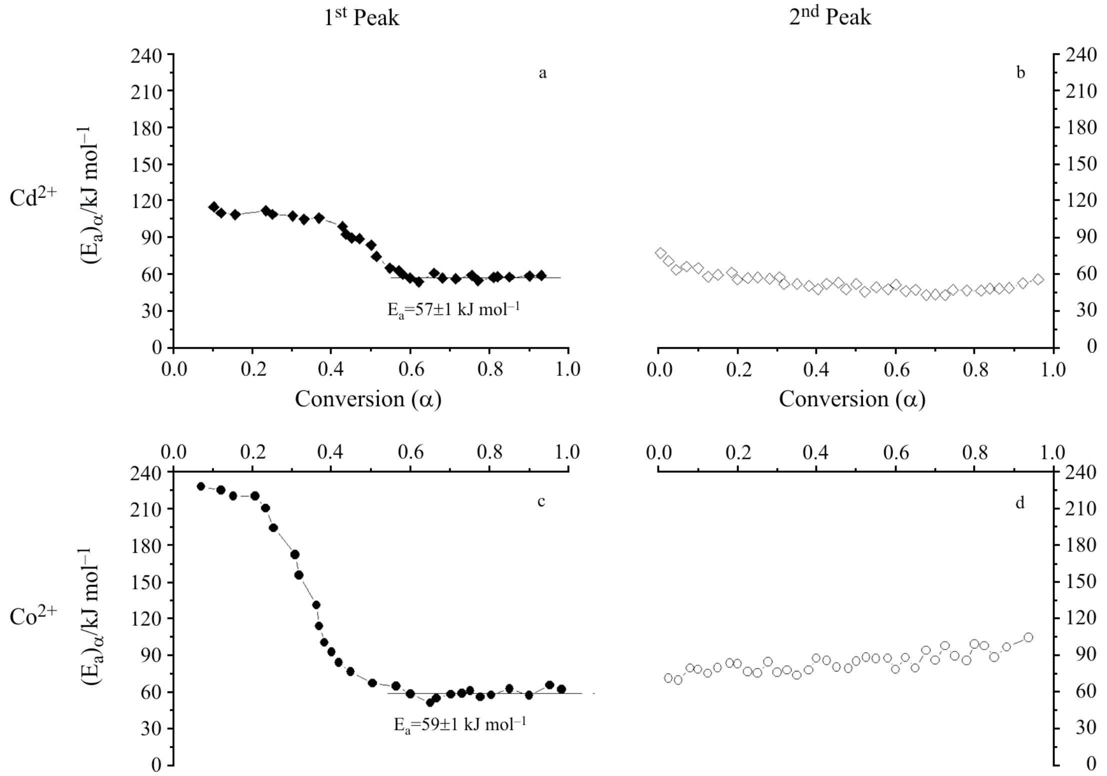

Fig. 5 Dependence of the activation energy $(E_a)_\alpha$ on the transformation degree (α) for the dehydration of: $Cd[Fe(CN)_5NO]\cdot 2H_2O$ a – zeolitic water, b – coordinated water; $Co[Fe(CN)_5NO]\cdot 5H_2O$, c – loss of three zeolitic waters molecules, d – loss of coordinated and strongly hydrogen bonded water molecules

tially limited by a diffusion mechanism (in the region $0.1\leq \alpha\leq 0.6$) [21, 25]. The second dehydration step also shows a variation of $(E_a)_\alpha$ with α but now from about 78 kJ mol^{-1} at low conversion degree until 47 kJ mol^{-1} at $\alpha = 0.9$. This last behavior of $(E_a)_\alpha$ on the reaction extent has been reported as typical of a kinetic scheme of a reversible reaction [21, 26]. Such prediction agrees with the reversible character of the dehydration process in this compound which was observed during the acquisition of its water vapor adsorption isotherm [9]. An analog dependence of $(E_a)_\alpha$ on α has been reported for dehydration processes involving a reversible step, for instance, dehydration of $KNbWO_6\cdot H_2O$ [27].

For cobalt nitroprusside ($Co[Fe(CN)_5NO]\cdot\cdot 5H_2O$) the dehydration process proceeds in two well-resolved steps (Fig. 3). The loss of the first three zeolitic waters corresponds to a large variation in $(E_a)_\alpha$ with α (Fig. 5c), from above 200 kJ mol^{-1} for $\alpha<0.2$, induction period, until an average value of 59 kJ mol^{-1} for $0.5<\alpha<1$. As already mentioned, such dependence of $(E_a)_\alpha$ on α is characteristic of a reaction dominated by diffusive mechanism, in this case of water molecules from the large pores of the cubic structure through their relatively small windows. Once a large fraction of these water molecules has evolved the remaining ones diffuse more easily and their activation energy falls down to 59 kJ mol^{-1}. For the second dehydration step, corresponding to the loss of a mixture of coordinated and strongly hydrogen bonded water molecules, the value of $(E_a)_\alpha$ also depends on α but with a smaller range of variation, from 73 kJ mol^{-1} for $\alpha<0.1$ until 90 kJ mol^{-1} at $\alpha \sim 0.9$ (Fig. 5d). This increase in the value of $(E_a)_\alpha$ as the compound loses its more firmly bonded waters could be related to a cell contraction resulting in a decrease in the effective window cross section affecting the diffusion rate. The cell contraction on dehydration has been reported for other cubic microporous cyanometallates [28]. In the orthorhombic structure this effect could not be observed because it has regular prismatic channels without a significant reduction of their entrance windows on dehydration.

According to the values of total heat involved in the dehydration process, as estimated from TMDSC experiments, the most favored dehydration reaction takes place in the copper complex (Table 1). Considering that in copper nitroprusside the two water molecules are coordinated, its relatively easy dehydration could be related to the bond distance $Cu–OH_2$ and to the structural transformation to form a tetragonal anhydrous phase with an open framework of interconnected hydrophobic pores. Consequently, the interaction of water molecules with copper atoms in the tetragonal structure is strongly hindered not only by a structural factor but also by the electronic configuration of the NO group which is sited within the channels system. The re-hydration reaction is kinetically limited by the reverse structural transformation from tetragonal to orthorhombic phases with simultaneous diffusion and interaction of water molecules with copper ions. The smaller and more stable value of the activation energy, $(E_a)_\alpha$ also corresponds to this compound. The dehydration of the cobalt compound represents the opposite case. It involves a high value of total heat per water molecule (Table 1) while $(E_a)_\alpha$ shows a large variation, particularly pronounced during the loss of the first three water molecules. Probably this correlation reveals details on the water diffusion through the network of relatively small windows of this microporous material.

Conclusions

The dehydration kinetics of divalent transition metal nitroprussides is dominated by the material framework features. In orthorhombic (Amm2) copper complex the structure of stacked layers that remain together by van der Waals forces and the hydrophobic character of the anhydrous phase facilitate the water release from the material bulk on heating. The water removal from the cadmium complex appears as two partially resolved events. In the first one, a zeolitic water is released and then, at a higher temperature, also the coordinated one evolves. In this case, the relatively rigid framework of this material is related to its minor effect on the dehydration kinetics. For the cobalt complex, the existence of a large amount of zeolitic water and a less rigid material framework impose certain special features to the dehydration process. The evolution of both zeolitic and coordinated waters is strongly controlled by their diffusion through a network of small windows that interconnect the larger structural pores where these water molecules are sited. This effect is more pronounced for the evolution of the weakest bonded water molecules which are filling the releasing ways from the material bulk. Then, for the removal process of the strongly bonded waters that effect is minimized but certain additional windows size reduction appears due to the material framework contraction caused by the dehydration process.

Acknowledgements

The authors thank to DGAPA project IN-119606, CONACYT project sep-2004-C0l-47070 and C. Vázquez Ramos from IIM-UNAM the Hi-Res TGA data collection.

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Received: October 5, 2005
Accepted: June 6, 2006

DOI: 10.1007/s10973-005-7385-1