

Effect of Framework and Layer Substitution in Manganese Dioxide Related Phases on the Energetics

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The energetics of a set of MnO₂-related phases having a framework or a layer structure were determined by high-temperature drop solution calorimetry at 977 K using sodium molybdate as a solvent. Enthalpies of formation were calculated from the measured enthalpies of drop solution. In these materials, different metal cations can be incorporated through framework, tunnel, and interlayer substitution. The stability of the structure depends mostly on the nature and the amount of the tunnel (or interlayer) cations. The enthalpy of formation of small-OL-1(Na_{0.04}) is more exothermic than that of large-OL-1(Na_{0.26}). However, framework substitution of Ni or Cu destabilizes the structure; [doped]-OL-1 or [doped]-OMS-1 materials are less stable in enthalpy than OL-1 or OMS-1. The energetics are more sensitive to the cations incorporated into the tunnels than to the cations substituting in the framework. A trend has been observed between the enthalpy of formation of the doped materials from the oxides and the ionic radius of the dopant. The average oxidation state of the manganese does not correlate directly with the energetics. These results confirm and extend previous work on manganese dioxide. The similarity of energetics of many different structures shows that the synthesis of these metastable microporous materials is not limited by energetic constraints.

Introduction

Manganese oxide mixed-valence materials have interesting electrical, magnetic, photocatalytic, surface, and catalytic properties, because of their particular structure and the various oxidation states of manganese.^{1–4} The conducting nature of these layer and tunnel structure materials sets them apart from most other molecular sieves. They also occur in soils and other surficial geological environments.

Mixed-valent manganese oxide octahedral molecular sieves (OMS) have recently been the subject of several studies.^{5–7} Such materials consist of MnO₆ octahedra, which are linked at vertexes and edges. The structure of the compound is generally defined by the number of octahedra forming each side of a tunnel. When two

octahedra comprise each side of a tunnel, the hollandite structure results, whose synthetic form is called OMS-2 in the literature.⁶ If there are three octahedra on each side of the tunnel, the todorokite structure (synthetic OMS-1) is formed.⁵ The pore sizes of OMS-1 and OMS-2 are 6.9 and 4.6 Å, respectively.^{8–11} They can absorb many organic molecules inside the tunnels.¹² These materials also have cation exchange properties and most metal ions can diffuse in the tunnels.^{9,10} When extraframework cations are present, some of the Mn⁴⁺ is replaced by Mn³⁺ to maintain electroneutrality. Countercations and water are also present in the tunnels of mixed-valent hollandite and todorokite to provide charge balance and stabilize the structure.^{13,14}

A related phase is birnessite, which has an octahedral layer structure (OL-1) and is the synthetic precursor to OMS-1. This structure consists of layers of edge- and corner-linked MnO₆ octahedra with water molecules and metal cations in the interlayer voids and an interlayer

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Table 1. Structure and Composition of Studied Samples

reference	phase	structure	composition
large-OL-1	birnessite	layer structure	Mg _{0.14} Na _{0.26} MnO ₂ ·0.19H ₂ O
small-OL-1	birnessite	layer structure	Mg _{0.13} Na _{0.04} MnO ₂ ·0.19H ₂ O
[Ni]-OL-1	birnessite	layer structure	Mg _{0.13} Na _{0.26} Ni _{0.16} MnO ₂ ·0.19H ₂ O
[Cu]-OL-1	birnessite	layer structure	Mg _{0.14} Na _{0.19} Cu _{0.007} MnO ₂ ·0.19H ₂ O
[Ni]-OMS-1	todorokite	octahedral framework, 3 × 3 tunnel	Mg _{0.20} Na _{0.013} Ni _{0.16} MnO ₂ ·0.75H ₂ O
[Cu]-OMS-1	todorokite	octahedral framework, 3 × 3 tunnel	Mg _{0.20} Na _{0.013} Ni _{0.16} MnO ₂ ·0.75H ₂ O

distance of 7–10 Å, depending on cation content and hydration. The compound that has the smallest inter-layer distance is called small-OL-1 while that with the largest one is designated as large-OL-1.

Numerous studies have been carried out on the synthesis and characterization of these OMS and OL materials using various methods.^{5–12} They can be synthesized by reflux, hydrothermal, precipitation, calcination, ion-exchange, isomorphous, and sol–gel methods.¹⁵ The different synthetic methods result in materials that have different physical and chemical properties. There are some interesting similarities between the syntheses of OMS and zeolites. As in the synthesis of zeolites, the template, pH, water, and temperature are important parameters that influence the formation of specific OMS structures.⁹ To understand the rich structural diversity of these systems, a thorough understanding of the influence of the different parameters, such as tunnel cations and water content, on the framework energetics and thermodynamic stability is essential.

The first calorimetric study of pure metastable manganese oxides (MnO₂) and oxyhydroxides (MnOOH) was made recently.¹⁶ Results from high-temperature calorimetric experiments indicate that the nature of the framework has only a minor effect on the energetics, as is the case for SiO₂ zeolites.¹⁷ The enthalpy difference between 1 × 1 and 1 × 2 tunnel structures is very small, less than 6 kJ/mol. The next calorimetric study was on a family of natural and synthetic framework and layer manganese dioxides.¹⁸ This work established that the enthalpy of formation of these oxides depends strongly on the nature and the amount of the cation located in the tunnel (or between the layers), but only weakly on the tunnel size or the average manganese oxidation state.

As a continuation of the work mentioned above, the stability of several framework substitutions of OMS and OL compounds has been examined to determine the influence of cations which substitute into the framework (rather than in the tunnels) on the enthalpy of formation. Using high-temperature solution calorimetry with sodium molybdate as a solvent, the enthalpy of formation of large-OL-1, small-OL-1 and [Cu]-OMS-1, [Ni]-OMS-1, [Cu]-OL-1, and [Ni]-OL-1 have been determined. This paper reports these results and discusses them in terms of structural variation, pore size, and the role of structure-directing agents in molecular sieve synthesis.

Table 2. Enthalpy of Drop Solution of Complex Manganese Dioxides in Na₂O·4MoO₃ at 977 K

composition	FW (g/mol O ₂)	ΔH drop solution in Na ₂ O·4MoO ₃ at 977 K	
		measured ^a	calculated ^b
large-OL-1	99.7	1.56 ± 0.04	155.7 ^c ± 3.9 ^d (7) ^e
small-OL-1	94.4	1.53 ± 0.02	144.3 ± 2.2 (6)
[Ni]-OL-1	108.9	1.30 ± 0.02	142.1 ± 1.5 (7)
[Cu]-OL-1	98.6	1.27 ± 0.02	125.2 ± 1.7 (9)
[Ni]-OMS-1	114.9	1.25 ± 0.02	143.2 ± 1.3 (10)
[Cu]-OMS-1	106.8	1.37 ± 0.01	146.3 ± 0.6 (9)

^a Enthalpy of drop solution (J/g), measured by drop solution calorimetry. ^b Enthalpy of drop solution (kJ/mol), calculated from drop solution calorimetry using molecular weight, *M*, based on chemical analysis. ^c Average based on *n* runs. ^d Number of run. ^e Uncertainty is two standard deviations of the mean.

Experimental Methods

Sample Preparation and Characterization. The studied materials have been synthesized at the University of Connecticut and their structure type and composition are summarized in Table 1. The layer structure birnessite (OL-1) was obtained by sol–gel synthesis from KMnO₄ and simple sugars.¹⁹ The framework substitution, [M]-OL-1, was achieved by adding metal dopants into the initial solution as described previously.¹⁵

The precursor of OMS-1, Na-OL-1, was prepared by reacting MnCl₂ with NaOH to form pyrochroite, Mn(OH)₂, followed by adding a solution of Mg(MnO₄)₂ to the suspension to form Na-OL-1.⁵ The framework substitution of OMS-1 was accomplished by adding metal dopants to the initial solution to form [M]-OL-1 followed by ion exchange with Mg²⁺. The sample was then converted to [M]-OMS-1 by hydrothermal treatment.¹⁵

All samples have been characterized by X-ray diffraction, thermogravimetry, SEM/EDX, and ICP analysis. The characterization details are given elsewhere.^{5,7,9–12,19,20}

Calorimetric Experiments. High-temperature drop solution calorimetry was performed in Calvet-type twin calorimeter.^{21–23} Samples were dropped from room temperature into sodium molybdate in a platinum crucible in the calorimeter at 977 K. Sodium molybdate was chosen as the solvent because it dissolves manganese oxides easily. A flow of oxygen (1.3 cm³/s) through the calorimeter ensured that all the Mn cations was in the 3+ valence state in the melt.¹⁶ The calibration factor of the calorimeter was obtained by dropping pellets of known mass (and heat content) of alumina (Aldrich, 99.99%) stabilized in the corundum phase by heating for 24 h at 1773 K. The total heat effect measured was a combination of the heat content, the enthalpy of solution, and the enthalpy of reaction (oxidation, or dehydroxylation). Calorimetric data for drop solution calorimetry of complex manganese dioxides in 3Na₂O·4MoO₃ at 977 K are presented in Table 2.

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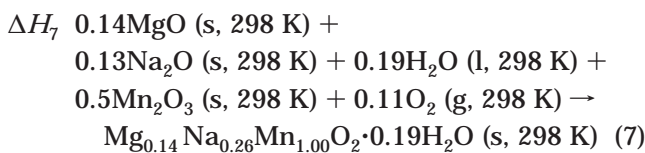
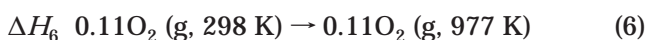
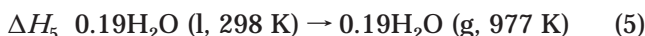
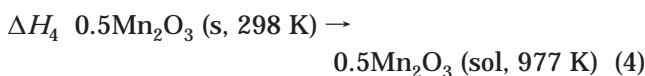
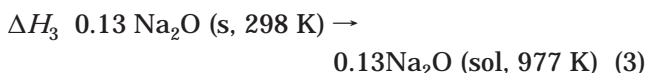
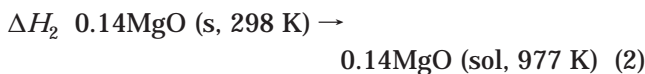
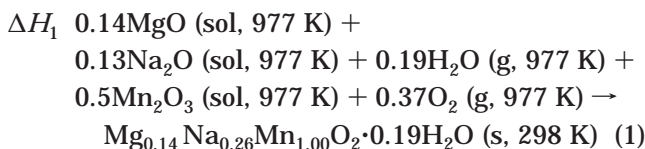
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Results and Discussion

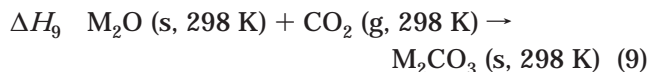
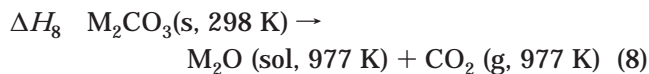
The enthalpy of formation from the oxides, at 298 K, of the MnO₂-based phases has been calculated from the measured values of the enthalpies of drop solution. An example of a thermodynamic cycle is shown for large-OL-1:



$$\Delta H_7 = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 + \Delta H_6$$

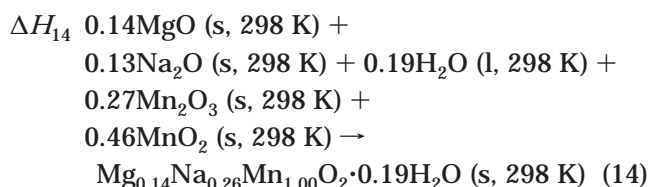
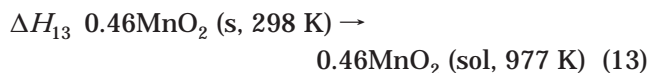
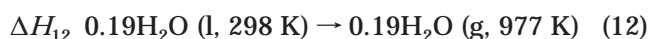
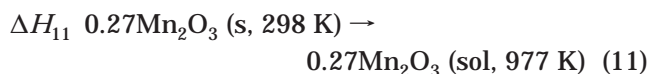
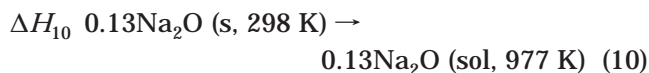
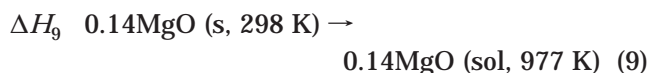
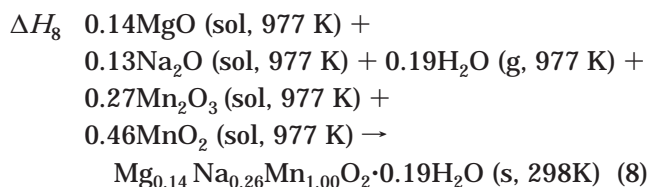
where ΔH_1 , ΔH_2 , ΔH_3 , and ΔH_4 are the measured enthalpies. ΔH_6 is the heat content of oxygen.²⁴ Previous thermochemical studies made on calcium zeolites²⁵ and clay minerals²⁶ have shown that the enthalpy of hydration of different tunnel or cage cations depends on their size and charge. Furthermore, water molecules are presumably bonded in different ways to the structure and consequently may show a variety of hydration energies. Since for the related manganese oxide phases there is insufficient information on how the water is located in the structure, it is impossible to attempt to predict the energy of hydration. Further work characterizing the hydration state and its thermal evolution is needed. However, for the related manganese oxides, it is likely that the water is weakly bound. As a first approximation, we assume that the heat of adsorption of the "extra" H₂O (the physisorbed surface water) is given by the heat of condensation of gaseous water, 70.09 kJ/mol (ΔH_5).

The enthalpy of drop solution of K₂O (ΔH_2), Na₂O (ΔH_3) had been determined from the measured drop solution enthalpy of the corresponding carbonates (Table 3), according to the following thermochemical cycle:



$$\Delta H_{11} = \Delta H_8 + \Delta H_9 + \Delta H_{10}$$

where ΔH_8 is the measured enthalpy, ΔH_9 is the enthalpy of formation of carbonates from the oxides at 298 K,²⁴ and ΔH_{10} is the heat content of CO₂.²⁴ The enthalpies of formation of the complex manganese dioxide based materials are reported in Table 4 and in Figure 1. According to a previous study of manganese dioxides, the oxidation state of the manganese cations strongly affects the energetics of the MnO₂-related materials.¹⁸ To separate effects of the reduction reaction (O₂ involved in the reaction, see reaction 7), the formation reaction of, for example, Mg_{0.14}Na_{0.26}Mn_{1.00}O₂·0.19H₂O is written considering Mn₂O₃ and MnO₂ rather than Mn₂O₃ and gaseous O₂ (eq 14). In this case, the thermodynamic cycle used is the following:



where ΔH_8 , ΔH_9 , ΔH_{10} , ΔH_{11} , and ΔH_{13} are the measured enthalpies. ΔH_{12} is the enthalpy change of eq 5. Therefore, $\Delta H_{14} = \Delta H_8 + \Delta H_9 + \Delta H_{10} + \Delta H_{11} + \Delta H_{12} + \Delta H_{13}$ represents the enthalpy of formation (from the oxides), at 298 K of Mg_{0.14}Na_{0.26}Mn_{1.00}O₂·0.19H₂O with no gas phase involved.

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Table 3. Measured and Calculated Enthalpies of Drop Solution of Carbonates and of Simple Oxides, in Na₂O·4MoO₃, at 977 K

composition	origin and purity	heat treatment before experiment	FW (g/mol)	$\Delta H_{\text{drop sol}}$ (kJ/mol) ^a
Na ₂ CO ₃	Fisher, 99.9%	24 h, 100 °C	-105.9	143.6 ^b ± 1.8 ^c (8) ^d
K ₂ CO ₃	Aldrich, 99.995%	24 h, 100 °C	138.2	134.7 ± 1.8 (8)
NiO	Aldrich, 99.99%		74.7	25.2 ± 1.8 (8)
CuO	Aldrich 99.99%		79.5	37.5 ± 1.2 (6)
MgO	Johnson Matthey, 99.95%		40.3	13.5 ± 1.4 (7)
Mn ₂ O ₃	Johnson Matthey, 99.95%		157.9	168.2 ± 2.6 (6)
MnO ₂	Johnson Matthey, 99.99%		86.94	126.3 ± 1.2 (6)
Na ₂ O ^e			61.98	-220.6 ± 1.4 (7)
K ₂ O ^e			94.20	-285.6 ± 2.7 (7)

^a Enthalpy of drop solution, measured by drop solution calorimetry. ^b Average based on *n* runs. ^c Uncertainty is two standard deviations of the mean. ^d Number of run. ^e Values calculated from measured enthalpies of the corresponding carbonates (see above).

Table 4. Enthalpy of Formation from the Oxides and from the Elements at 298 K of Complex Manganese Dioxides

phase	tunnel size	composition	FW (g/mol)	ΔH_f , 298 K (kJ/mol) ^a	ΔH_f , 298 K (kJ/mol) ^b	ΔH_f , 298 K (kJ/mol) ^c
large-OL-1	layer structure	Mg _{0.14} Na _{0.26} MnO ₂ ·0.19H ₂ O	99.74	-82.5 ± 1.3	-65.6 ± 4.0	-746.1 ± 2.3
small-OL-1	layer structure	Mg _{0.13} Na _{0.04} MnO ₂ ·0.19H ₂ O	94.44	-45.7 ± 1.3	-19.9 ± 2.4	-659.5 ± 2.8
[Ni]-OL-1	layer structure	Mg _{0.13} Na _{0.26} Ni _{0.16} MnO ₂ ·0.19H ₂ O	108.89	-53.4 ± 1.3	-60.8 ± 1.7	-763.1 ± 5.1
[Cu]-OL-1	layer structure	Mg _{0.14} Na _{0.19} Cu _{0.007} MnO ₂ ·0.19H ₂ O	98.58	-43.7 ± 1.3	-25.3 ± 1.9	-696.4 ± 3.5
[Ni]-OMS-1	3 × 3 tunnel	Mg _{0.20} Na _{0.013} Ni _{0.16} MnO ₂ ·0.75H ₂ O	114.99	0.2 ± 1.4	10.1 ± 1.7	-822.9 ± 1.2
[Cu]-OMS-1	3 × 3 tunnel	Mg _{0.23} Na _{0.014} Cu _{0.009} MnO ₂ ·0.75H ₂ O	106.77	-5.0 ± 1.3	13.7 ± 1.1	-810.4 ± 2.3

^a Enthalpy of formation of the complex manganese dioxide at 298 K from thermodynamic cycle involving Mn₂O₃ and O₂. ^b Enthalpy of formation of the complex manganese dioxide at 298 K from thermodynamic cycle involving Mn₂O₃ and MnO₂. ^c Enthalpy of formation of the complex manganese dioxide at 298 K from the elements.

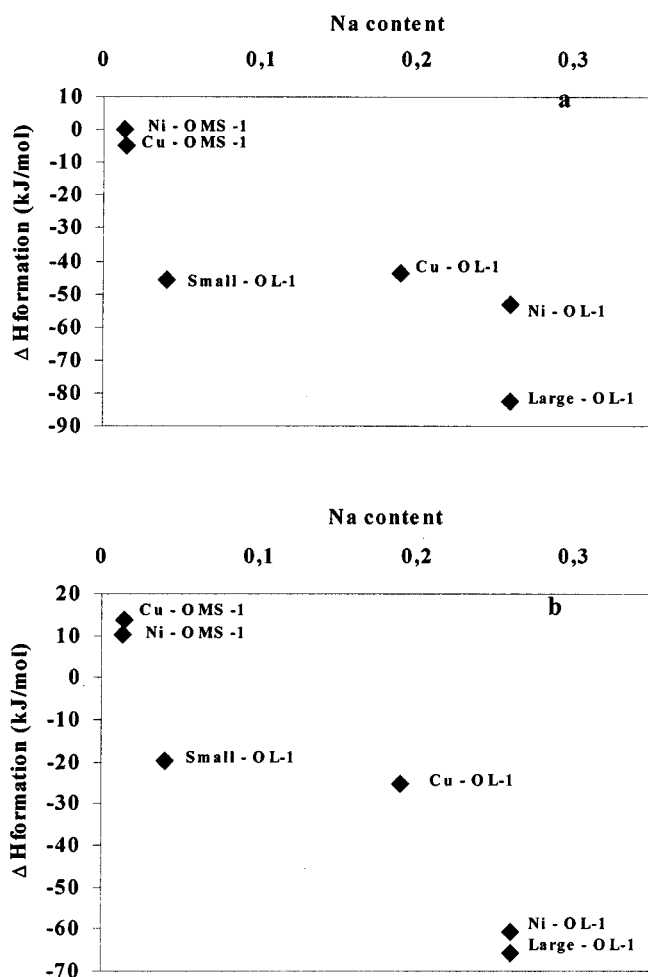


Figure 1. (a) Enthalpy of formation, at 298 K, of MnO₂-related phases from Mn₂O₃ and M₂O or MO (with M = Ni, Cu, Mg, Na) as a function of sodium content in the tunnel and (b) enthalpy of formation, at 298 K, of MnO₂-related phases from Mn₂O₃ and MnO₂, M₂O or MO (with M = Ni, Cu, Mg, Na) as a function of sodium content in the tunnel.

The corresponding enthalpies of formation are reported in Table 4. The enthalpies of formation of the manganese dioxide related phases from the elements have been reported in Table 4 as well. The enthalpies of formation are more endothermic if no oxidation is considered (reaction 14). However, the energetic trends are similar in both cases. Accordingly, for the following discussion, for the sake of simplicity, when we talk about the enthalpy of formation of MnO₂-related phase, we refer to the one calculated from the cycle involving Mn₂O₃ and MnO₂.

Figure 1b represents the evolution of the enthalpy of formation of MnO₂-related phase as a function of sodium content. A comparison of ΔH_f for small-OL-1 sample (-19.9 kJ/mol, Na: 0.04) with the one obtained for large-OL-1 sample (-65.6 kJ/mol, Na: 0.26) shows that the enthalpies of formation of birnessite (OL) become more negative with increasing sodium content in the structure. These samples differ from each other by the interlayer distance and the tunnel cation content. However, these two parameters are interconnected: the large-OL-1 sample which has the largest interlayer cation content and the largest interlayer distance. Accordingly, the difference in energy can be explained by the interlayer cation content and the openness of the structure. As pointed out by Fritsch,¹⁸ the contribution of the openness of the structure on the energetics is smaller than the effect of the tunnel cation in manganese dioxide polymorphs. Since the difference in enthalpy is about 40 kJ/mol, the framework stability can be explained by the tunnel cation content.

A comparison of ΔH_f for [Ni]-OL-1 and large-OL-1 samples shows that the sodium content is not the only factor influencing the energetic of MnO₂-related phase. To study the influence of the framework substitution on the enthalpy of formation of large birnessite samples, ΔH_f for [M]-OL-1 with M = Ni, Cu is plotted in Figure 2a as a function of the nature of cation. For comparison

Table 5. Enthalpy of Formation from the Oxides at 298 K of OL-1, OMS-1, and OMS-2 Samples

phase	tunnel size	composition	ΔH_f , 298 K (kJ/mol) ^a	ref
large-OL-1	layer structure	Mg _{0.14} Na _{0.26} MnO ₂ ·0.19H ₂ O	-65.6 ± 4.0	this work
small-OL-1	layer structure	Mg _{0.13} Na _{0.04} MnO ₂ ·0.19H ₂ O	-19.9 ± 2.4	this work
OL-1	layer structure	K _{0.29} MnO ₂ ·0.19H ₂ O	-69.6	18
OMS-1	3 × 3 tunnel	Mg _{0.19} MnO ₂ ·0.75H ₂ O	-22.8	18
OMS-2	2 × 2 tunnel	K _{0.3} MnO ₂ ·1.55H ₂ O	-11.5	18

^a Enthalpy of formation of the complex manganese dioxide at 298 K from thermodynamic cycle involving Mn₂O₃ and MnO₂.

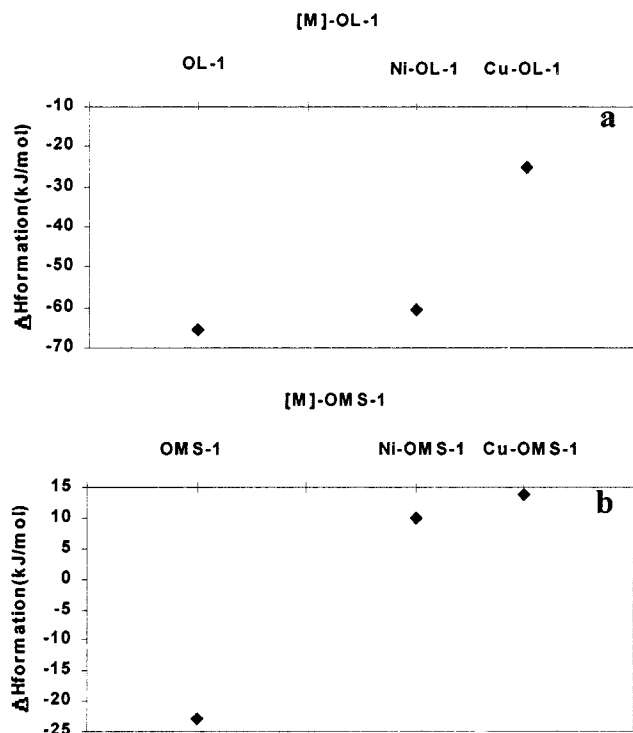


Figure 2. Enthalpy of formation at 298 K of MnO₂-related phases from Mn₂O₃ and MnO₂ as a function of framework substitution: (a) [M]-OL-1 sample and (b) [M]-OMS-1 sample.

purposes, the enthalpy of formation of Large-OL-1 sample is also reported in this figure. The OL-1 sample, without framework substitution, is 5–35 kJ/mol more stable in enthalpy than [Cu]-OL-1 and [Ni]-OL-1. The same trend has been observed in OMS samples. On Figure 2b is reported the enthalpy of formation of [M]-OMS-1 sample. The OMS sample without tunnel substitution is more stable in enthalpy than [Cu]-OMS-1 and [Ni]-OMS-1. Accordingly, framework substitution seems to destabilize the framework stability.

Figure 1b points out that the tunnel substitution stabilizes the structure while framework substitution destabilizing the framework stability (Figure 2). Thus, the effect of the substitution of cation in the framework or in the tunnel/interlayer on the energetics is opposite.

Studying the framework substitution on energetics (Figure 2), it appears that the energetics of MnO₂-related phase seems to be also influenced by the nature of the framework substituting cation. The enthalpy of formation of [Ni]-OL-1 is about -60.8 kJ/mol, while the one for [Cu]-OL-1 is -25.3 kJ/mol. The same trend is observed with framework doped OMS-1 sample (Figure 2b). For both systems (OL and OMS samples), the dependence of framework stability of MnO₂-related phases may be associated with the radius of framework

substituted cations. Therefore, the sample with the most negative enthalpy of formation is the one that has the lowest ionic radius ($r_{\text{Ni}^{2+}} = 0.83 \text{ \AA}$, $r_{\text{Cu}^{2+}} = 0.87 \text{ \AA}$). This characteristic is analogous to thermal stability studies on M-OMS-1 compounds. Results of TGA and XRD show that inorganic cations strongly affect the thermal behavior of the M-OMS-1 samples and that the thermal stability (temperature at which decomposition starts for a fixed heating rate) decreases as follows: Mg-OMS-1 > Ni-OMS-1 > Co-OMS-1 > Cu-OMS-1. This sequence indicates that the apparent thermal stability (kinetic stability against decomposition) of the M-OMS-1 samples decreases with increasing ionic radius of the tunnel cations. In addition, XRD and TGA made on framework-substituted [M]-OMS-1 with M = Zn, Co, Ni, and Cu reveal that the framework-substituted samples decompose at much higher temperatures than the tunnel-substituted M-OMS-1. However, their sequence of thermal stability is similar to the sequence of the M-OMS-1 sample, as described above. The sample with the highest thermal stability is the one that has the lowest ionic radius. However, no direct correlation can be made between the thermochemical trends we observed and the thermal stability seen in other work because the thermal decomposition reactions reflect the kinetics of decomposition, which are strongly affected by factors such as grain size and water content.

The substitution of framework cations by divalent inorganic cations such as Ni²⁺ and Cu²⁺ changes the average manganese oxidation state.¹² TGA analyses of M-OMS-1 samples have shown decreasing thermal stability with increasing average oxidation states of manganese.¹² In this case, the thermal stability and the thermodynamic stability parallel each other. The [Cu]-OMS-1 sample, which has the highest average manganese oxidation state is the least stable energetically. This linkage of kinetic and thermodynamic observations probably reflects the strong thermodynamic destabilization of the structure by framework substitution of Ni or Cu. In contrast, tunnel substitution by M⁺ or M²⁺ offers overall energetical stabilization though the framework may become more kinetically susceptible to breakdown when it contains mixed valence manganese.

A survey of hydrothermal reactions involving several OL-1 compounds shows that the synthesis of tunnel manganese oxides depends on the nature of the interlayer cation and the surrounding medium and on solution conditions (*T*, pH). For example, the synthesis of todorokite (OMS-1) involves hydrothermal treatment of OL-1 materials that contain Mg²⁺ interlayer divalent cations while, OMS-2 is formed when K⁺ and high temperatures are used. Table 5 reports the enthalpy of formation of OL-1, OMS-1, and OMS-2. OL-1 doped with Mg²⁺ is 3 kJ/mol more stable in enthalpy than OMS-1

while OL-1 doped with K^+ is 50 kJ/mol more stable than OMS-2. Thus, in all systems studied, layer or framework structures are allowed by energetics.

Are the substituted MnO_2 -related phases metastable? Previous work on pure MnO_2 phases shows that pyrolysis is the only thermodynamically stable polymorph.¹⁸ Incorporation of Ni or Cu in the framework is energetically destabilizing while substitution of extraframework cations is stabilizing. The latter effect often outweighs the former (see Figure 1b), with substantially negative enthalpies of formation from the binary oxides, even in reactions involving no oxidation (and small entropy changes). However, the fact that a given MnO_2 -related phase is thermodynamically stable with respect to a mixture of Mn_2O_3 , MnO_2 , Na_2O and CuO or NiO is not directly relevant to its thermodynamic stability under synthesis conditions. There, the question is one of stability with respect to ions in aqueous solution and to other multicomponent solid phases. Obviously, for spontaneous synthesis, the formation from aqueous solution must have a negative free-energy change. Our data suggest that at a given solid composition, several structures can be energetically similar. Thus, small changes in synthesis conditions (pH, aqueous ion concentrations, and temperature) could cause different MnO_2 -related phases to become thermodynamically stable, both by forming a different framework and by changing the cation composition. Whether the phase actually formed always represents the global free energy minimum for the given conditions, or whether metastable phases form as well is not yet clear. The appropriate choice of solution conditions and/or structure directing cations may select kinetic pathways to a given structure and composition in cases where several structures are thermodynamically very similar, as is the case for zeolites.¹⁷ The major difference between zeolites and MnO_2 -related materials is that in the latter, cation substitution is closely linked to manganese oxidation state (and framework charge) and that this redox reaction can happen in situ without varying the framework composition. In zeolites, in contrast, framework

charge is determined by Al/Si ratio, and strong bonds must be broken. Thus, the MnO_2 -based systems may respond even more strongly (in both kinetic and thermodynamic senses) to change in preparation conditions than the zeolites.

Conclusions

The crystal structure/stability relations in the series of octahedral molecular sieve samples have been studied by high-temperature solution calorimetry in sodium molybdate at 977 K. The enthalpies of formation of complex manganese dioxides have been evaluated.

The enthalpy of formation depends on the cations incorporated into the structures through framework or tunnel substitution. The stability of the complex manganese dioxides becomes more exothermic with the tunnel cation content while the structure is destabilized when cations are incorporated through the framework. However, the framework substitution has a smaller effect on the energetic than the tunnel one.

Substitution of cation inside the framework or the tunnel changes the manganese average oxidation state and the structure of complex manganese dioxides is destabilized with the increase of Mn^{4+} content.

The synthesis of different microporous materials should be possible by varying certain parameters, such as pH, metal dopants (Mg^{2+} , Na^{2+} , etc.). The trend observed for various structure suggests that for complex manganese dioxides, the synthesis of a given structure depends on finding an appropriate mechanistic pathway, rather than being limited by large energetic differences between different possible framework topologies.

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