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Magnesia formed on calcination of $Mg(OH)_2$ prepared from natural bischofite

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Abstract

Calcination of magnesium hydroxide, which was prepared from natural bischofite $MgCl_2{\cdot}6H_2O$, leading to dehydration $2(\equiv MgOH) \rightarrow \equiv Mg–O–Mg\equiv + H_2O$, is accompanied by transition of phase not only to MgO but also to MgO_x at $x < 1$ (assigned to Mg_4O_3) at moderate temperatures. At higher temperatures, MgO_x is completely transformed into MgO. Magnesium hydroxide and oxide heated at different temperatures were studied using the TEM, XRD, IR, PCS, TG-DTA, nitrogen and argon adsorption methods. The electronic structure of MgO and Mg_4O_3 was studied using the ab initio quantum chemical method with periodic conditions. According to TEM images, the morphology of particles changing from $Mg(OH)_2$ laminae to aggregates of interpenetrated MgO cubelets and foils depend strongly on the calcination temperature. Significant changes in surface area are observed mainly at 325–470 °C on desorption of a major portion of eliminated water corresponding to 28.4 wt.% at its total amount of 30.9 wt.%. Pore size distribution (PSD) is sensitive to treatment conditions and the main PSD peaks shift towards larger pore size with elevating temperature. The characteristics of the surface hydroxyls as well as of the bulk Mg–O bonds depend on heating conditions, as noticeable changes are observed in the XRD patterns and the IR spectra of the samples undergoing the mentioned transformation of phase $Mg(OH)_2 \rightarrow MgO_x \rightarrow MgO$.

Keywords: Bischofite; Magnesium hydroxide; Magnesia; MgO_x; TEM; XRD; IR; PCS; TG-DTA; Argon adsorption; Nitrogen adsorption; Periodic ab initio calculation; Water desorption; Transition of phase; Particle morphology; Surface hydroxyls

1. Introduction

Synthesis of nanomaterials with metal oxides possessing the particle morphology and the physicochemical properties strongly different from those of solid materials is of importance for many applications

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[1,2]. Magnesia (MgO) powders are widely used for preparation of heat-resistant ceramics and special cements [3]. MgO is also utilized as a heterogeneous catalyst in synthesis of organics [4]. Disperse magnesia can be also applied as a drug carrier, a filler of lacquer-paint and polymer materials as well as for many other purposes [1–6]. Roughly disperse magnesia can be produced on calcination of magnesite or dolomite or by treatment of MgS or other similar compounds [2–7]. Highly disperse magnesia can be prepared on calcination of natural compounds, such as $4MgCO_3{\cdot}Mg(OH)_2{\cdot}4H_2O$ or magnesium hydroxide $Mg(OH)_2$ [2–7]. Similar materials could be produced by treatment of brucite at 520–550 K in vacuo [7,11–15]. It should be noted that polycrystalline magnesia is useful as a model system because its morphological changes on heating are well documented [8–15]. The TEM and AFM methods were successfully applied to image the evolution of the morphology of polycrystalline MgO formed from $Mg(OH)_2$ on sintering procedures and compared with more regular MgO samples [7]. The ordered and periodic structure on surfaces of polycrystalline MgO powders were observed in air by means of the AFM method. The transformation $Mg(OH)_2 \rightarrow MgO$ is accompanied by fragmentation of the original laminae into parallel foils of MgO with 1–1.5 nm thickness, developed along (1 1 1) planes and by the appearance of aggregates of interpenetrated MgO cubelets of 1–1.5 to 2–3 nm. The resulting aggregates, formed by topotactic $Mg(OH)_2 \rightarrow MgO$ transformation, were maintaining the gross shape of the original $Mg(OH)_2$ microcrystals [7]. The effect of successive annealing at higher temperature causes an increment of the MgO terraces from 2–3 to 10 nm [7,11,14,15]. The average edge length of the MgO cubes corresponds to approximately 7 nm in agreement with the high value of surface area of 200 m^2/g [7]. The increased values of dimension and roughness as compared to $Mg(OH)_2$ can be explained with the transition to a new crystalline habitus, caused by the well known topotactic transformation $Mg(OH)_2 \rightarrow MgO$ with release of H_2O. Annealing at 800 °C results in a further enlargement of MgO aggregates with a decreased mean height and in lower values of surface average roughness [7]. Textural and acid–base properties of MgO depend, to a great extent, on the synthesis conditions, such as pH, gelifying agent, sequence of the addition of reagents, calcination temperature, etc. [16,17]. The modification of the acid–base properties of magnesia is usually carried out by mixing it with other oxides, metallic ions or noble metals, which has revealed as a very effective way of tailoring the activity towards many organic processes. Calcination of gel with $Mg(OH)_2$ at 372 °C gives the weight loss of 32.3%, higher than theoretical value of 30.9% [18]. Multidimensional magnesium oxide structures with cone-shaped branching were produced using a simple chemical vapour deposition method. The dominant structures in the product include two-dimensional assemblies and three-dimensional complex configurations [19]. Thus, the $Mg(OH)_2 \rightarrow MgO$ transformation can result in formation of materials of varied textures and surface physicochemical properties. However, the processes of preparation of highly disperse magnesia from row natural minerals utilized to form magnesium hydroxide as an intermediate compound to produce MgO are complex and have been studied only partially, e.g. on treatment of seawater [20]. Therefore, the aim of this work is to study changes in the morphology, the structural and adsorption properties of magnesia characterized by different phase composition ($MgO + MgO_x$) dependent on temperature of dehydration of $Mg(OH)_2$ produced from natural bischofite ($MgCl_2{\cdot}6H_2O$ plus such impurities as Br, Fe, Mn, Si, Al, Ti, Cu, Ba, B, Au and Ca).

2. Experimental

2.1. Materials

Natural bischofite $MgCl_2{\cdot}6H_2O$ (Poltava Deposit, Ukraine) was used as the raw material. It was mixed with distilled water to concentration of 200 g/dm^3. This solution includes also 1.0 g $MgCO_3$ and 0.16 g/dm^3 of Br and such impurities as Fe, Mn, Si, Al, Ti, Cu, Ba, B, Au and Ca at the total content lower than 0.0185%. $Mg(OH)_2$ was prepared using a mixture of the bischofite solution with NaOH at pH 10.5–11.0 and room temperature. The precipitated product was washed-off by distilled water and dried at 110 °C for 5 h. The structural characteristics of the product were studied after its heating at different temperatures.