Preparation of Mg/Al layered double hydroxide (LDH) with structurally embedded molybdate ions and application as a catalyst for the synthesis of 2-adamantylidene(phenyl)amine Schiff base

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\textbf{Article info}

Article history:
Received 5 August 2013
Accepted 10 November 2013
Available online 19 November 2013

\textbf{Keywords:}
Layered double hydroxides
Molybdate
Co-precipitation
Schiff base
2-Adamantylidene(phenyl)amine

\textbf{Abstract}

Preparation of MoO\textsubscript{4}\textsuperscript{2−}-containing Mg/Al layered double hydroxide (LDH) using co-precipitation method has been suggested. The possibility of introduction of molybdate ions from solutions with different concentrations of molybdate to the structure of LDH has been investigated. For this purpose, the mixture of magnesium and aluminium nitrates was added to the solution of molybdate or vice versa. The XRD patterns of obtained specimens showed formation of layered double hydroxide phases without any impurities. The basal spacing of formed LDH was not affected when concentration of molybdate used in the synthesis process was low. However, at higher concentration of molybdate an increase of cell parameter c was observed. The determined Mg/Al ratio and the amount of Mo in LDH were found to be dependent on the preparation conditions. Molybdate-containing LDH was tested as a catalyst in solvent free synthesis of 2-adamantylidene(phenyl)amine. It was demonstrated, that the addition of molybdenum in LDH improved the yield of Schiff base.

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1. Introduction

Layered double hydroxides (LDH) also known as hydrotalcite type materials (HT) or ionic clays are based upon the brucite (Mg(OH)\textsubscript{2}) structure with general formula of \[\text{M}^{\text{II}}_{\text{x}} \text{M}^{\text{III}}_{\text{1-x}} (\text{OH})_{\text{x}}\text{M}^{\text{III}}_{\text{1-x}}(\text{A}^{\text{n-}})_{\text{n}}\cdot \text{nH}_{\text{2}}\text{O},\] where \(\text{M}^{\text{II}}\) and \(\text{M}^{\text{III}}\) are the di- and trivalent cations with similar radii, and \text{A}\ is almost any anion, which does not form stable complexes with the above cations. The structure of LDH is formed by positively charged metal hydroxide layers \([\text{M}^{\text{II}}_{\text{x}} \text{M}^{\text{III}}_{\text{1-x}}(\text{OH})_{\text{x}}]_{\text{n}}^{-}\) and negatively charged anions in the interlayer space [1]. As a rule, \(\text{H}_{\text{2}}\text{O}\) molecules are also present in the interlayer space. A large number of LDH can be synthesized by varying either the nature of the cations or anions. Consequently, new materials can be obtained with specific properties. Recently, it was reported on the preparation, characterization and catalytic performance of molybdenum containing layered double hydroxides [2]. It was concluded that these LDH do not act as a simple support. Moreover, the specific features, such as the nature of the cations in the brucite-like layers, specific surface area and the method used for the preparation of polyoxometalates-LDH have enormous effect on their final catalytic properties.

The simplest method to obtain modified LDH is to replace the cations in the brucite-type layer with others which have a similar ionic radius to \(\text{M}^{\text{II}}\) or \(\text{M}^{\text{III}}\) and can adopt the same octahedral arrangement. Metals those are not compatible with the octahedral sites of the brucite-type sheet, such as molybdenum, may be introduced in the interlayer space of these solids in their anionic form [3]. Hydrotalcites with various Mg/Al ratios were synthesized using co-precipitation method to investigate inclusion of molybdate ions into the structure of LDH. Two step mechanisms were proposed for intercalation of the molybdate anions. Firstly, carbonate ions intercalate into the structure, and then molybdate ions interpose between the layers [4]. The most advantageous preparation procedure for the preparation of hydrotalcite with \(\text{MoO}_{4}^{\text{2−}}\), which could be used as catalysts for selective oxidation of cyclohexene, was proved to be co-precipitation at pH 10 under high supersaturation conditions [5]. The preparation of LDH samples with molybdate by ionic exchange requires initial synthesis of LDH with other anions, such as carbonate, nitrate or chloride, and then the obtained specimen should be placed to ionic exchanger with solution containing \(\text{Na}_{2}\text{MoO}_{4}\) [5,6]. Besides, it was shown that in situ absorption of molybdate is complicated process and...