Synthesis of $Cr_2(MoO_4)_3$ from Mechanically Activated Precursors

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Abstract

The effect of mechanical activation on the synthesis of $Cr_2(MoO_4)_3$ is studied. Its formation was monitored by X-ray diffraction (XRD) and infrared spectroscopy (IR). Shape and size of the product particles were studied by scanning electron microscopy (SEM). The compound studied presents a special interest as a catalyst for mild oxidation of alcohols. A stoichiometric mixture of $Cr(OH)_3$ and MoO_3 in a 2 : 3 molar ratio was subjected to intense mechanical treatment in a planetary ball mill (Fritsch-7) for different periods of time, followed by calcination at various temperatures. The 2.5 h milling produced broadening and decrease in the intensity of the MoO_3 XRD peaks, while the principle peaks of Cr_2O_3 appeared. Further milling (5 h) resulted in complete amorphization of the reagent mixture. IR spectroscopic analysis indicated occurrence of structural transformation in the mixture of solid reagents during the mechanical activation. These phase and structural changes are a precondition for a drastic decrease in the temperature of classical solid state synthesis of $Cr_2(MoO_4)_3$ from 700 to 400 °C.

INTRODUCTION

Many compounds of $A_2(MoO_4)_3$ and $A_2(WO_4)_3$ types are known and have been the subject of scientific and practical interest. Chromium molybdate $Cr_2(MoO_4)_3$, has special magnetic, electrical and catalytic properties [1–3] and is interesting as a catalyst for mild oxidation of alcohols. The $Sc_2(MoO_4)_3$ structure type consisting of corner shared MO_6 octahedra and MoO_4 tetrahedra is characteristic of $Cr_2(MoO_4)_3$ [4, 5]. There is a low-temperature monoclinic modification of $Cr_2(MoO_4)_3$ which is transformed into orthorhombic one at 385 °C. It is established that chromium molybdate melts incongruently at 800–810 °C [6].

$Cr_2(MoO_4)_3$ is usually obtained by several methods: solid state synthesis [7–9], precipitation method [3, 6] or thermal decomposition of chromate and molybdate sols [10]. The synthesis methods of the compound strongly affect its properties. One of the promising approaches is the mechanical activation of the reagents [11].

The aim of the present study is to obtain crystalline $Cr_2(MoO_4)_3$ by mechanochemically assisted synthesis, in order to prevent the processes of sintering and aggregation of the product particles.

EXPERIMENTAL

One of the starting compounds was amorphous $Cr(OH)_3$ prepared from a $Cr(NO_3)_3$ solution, precipitated with NH_4OH (0.6 M) at a final pH 9. The precipitate was washed with distilled water and dried at 100 °C for 10 h. A mixture of $Cr(OH)_3$ and MoO_3 (Merck) in a 2 : 3 molar ratio was subjected to intense mechanical treatment using a planetary ball mill (Fritsch Pulverisette-7) for different periods of time (2.5, 5 and 7.5 h). After mechanical activation, the reagents were subjected to calcination at different temperatures (350, 400, 450 °C). The synthesis was carried out in air. Both the mechanically activated reagent mixtures and the thermally treated were ones analysed by X-ray diffraction (XRD) (TYP G2M CoK_α radiation). The changes of the structural units of the mechanically and termally treated samples were investigated by infrared spectroscopy in the 1200–400 cm^{-1} region using the KBr pellet technique (Nicolet-320 FTIR spectrometer). The granule size and morphology of the obtained samples were analysed by SEM photography (Jeol-357).

RESULTS AND DISCUSSION

X-ray diffraction analysis

X-ray diffraction patterns of the initial mixtures before and after different times of mechanical treatment are shown in Fig. 1, *a*–*c*. The XRD data on the sample not subjected to mechanical activation exhibit the main peaks of MoO_3 (35-0609 JCPDS). After a milling time of 2.5 h, partial amorphisation takes place, the

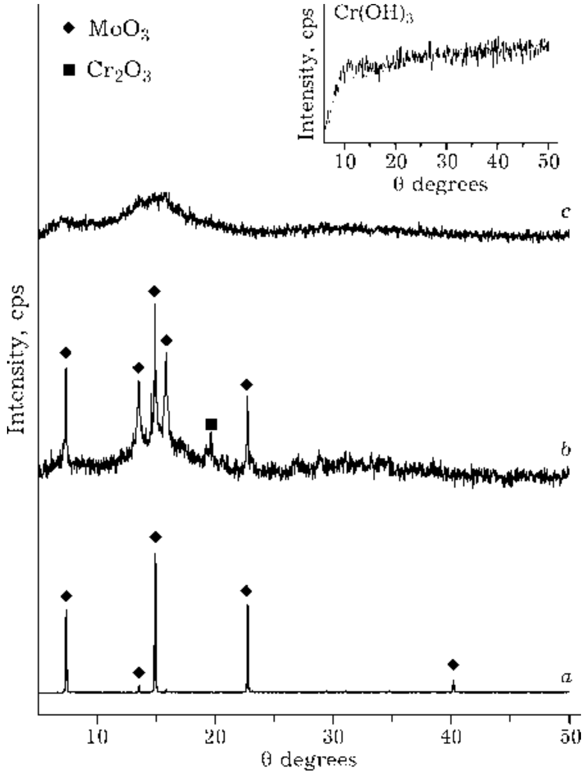

Fig. 1. X-ray patterns of reagent mixture before mechanical treatment (*a*), after 2.5 (*b*) and 5 h (*c*) mechanical treatment.

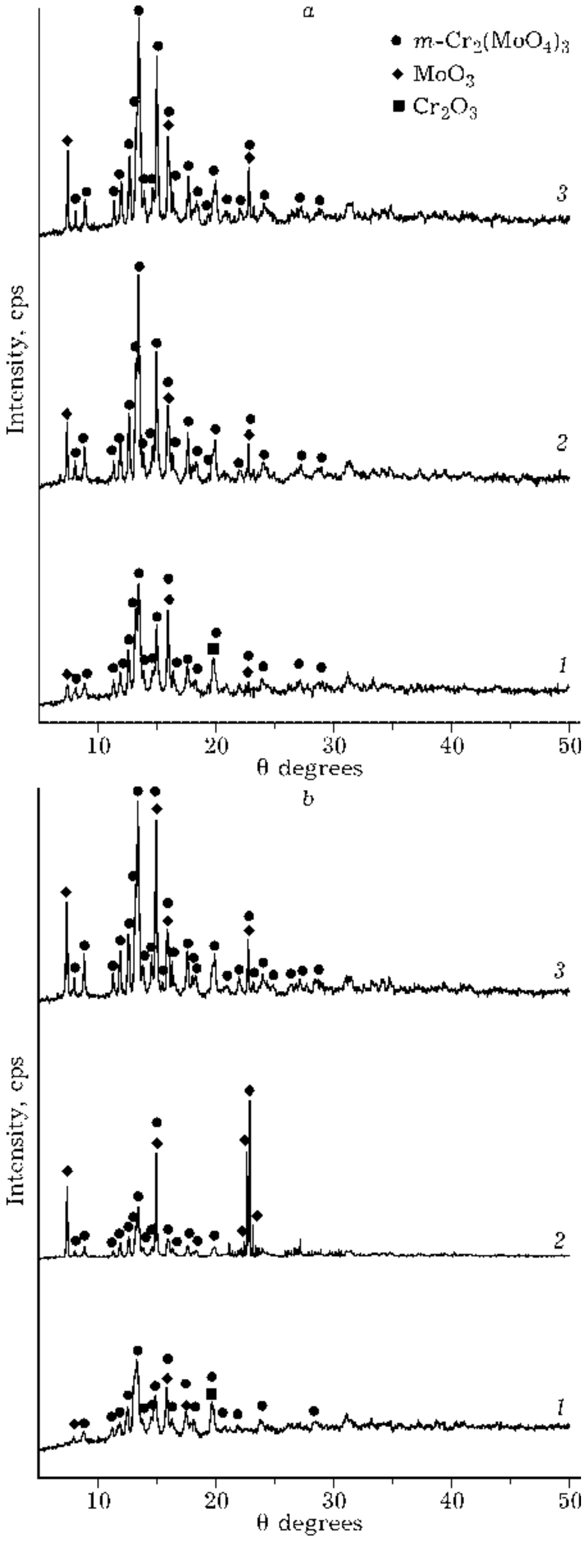

Fig. 2. XRD patterns of the reagent mixture after milling for 2.5 (*a*) and 5 h (*b*) thermal treatment for 3 h at 350 (*1*), 400 (*2*) and 450 °C (*3*).

principal peaks of MoO_3 are broadened and decrease in intensity and the main peak of Cr_2O_3 (38-1479 JCPDS) appears. This is an indication that the long-range order of MoO_3 is destroyed and the sample is more disperse. Further milling (5 h) leads to complete amorphisation of the sample. These changes are associated with formation of defects and their accumulation in the reagent crystal lattices. Figure 2, *a–c* shows X-ray patterns of the samples activated (milled for 2.5 h) and heated at different temperatures. The formation of *m*-$Cr_2(MoO_4)_3$ starts at 350 °C. Principal peaks of *m*-$Cr_2(MoO_4)_3$ along with peaks of the reagents (MoO_3 and Cr_2O_3) appear on the XRD patterns after heating at this temperature (see Fig. 2, *a*). Diffraction patterns of the activated samples heated at higher temperatures (400 and 450 °C) show presence of all diffraction lines characteristic of *m*-$Cr_2(MoO_4)_3$ (20-0310 JCPDS) and traces of MoO_3 (35-0609 JCPDS) (see Fig. 2, *b*, *c*).The presence of small amounts of MoO_3 is observed during XRD analysis by other authors [6, 12].

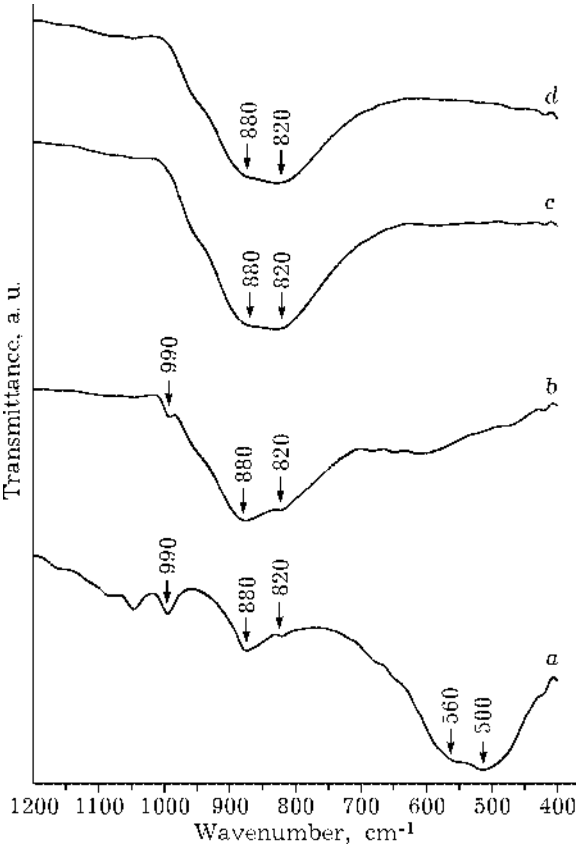

Fig. 3. IR spectra of the samples without mechanical activation (*a*), after 2.5 (*b*), 5 (*c*) and 7.5 h (*d*) mechanical activation.

Infrared analysis

The structural transformation undergone by mechanically and thermally-treated speciments was studied by infrared spectroscopy. Figure 3, *a–d* shows the infrared spectra of the initial mixtures before and after different times of mechanical activation. In the IR spectrum (see Fig. 3, *a*) of the non-activated sample there are bands characteristic of vibrations of MoO_6 polyhedra building MoO_3 [13, 14]. The band at 990 cm^{-1} corresponds to stretching modes of a Mo=O terminal bond present in each octahedron. The bands at 880 and 820 cm^{-1} are assigned to stretching vibrations of OMo_2 (Mo–O–Mo) entity [13]. The absorption bands below 600 cm^{-1} represent superposition of stretching vibrations of OMo_3 units and CrO_6 polyhedra [14–16]. The IR spectra (see Fig. 3, *b–d*) of the sample obtained after mechanochemical treatment for different times show a change in absorption bands. After mechanical activation (2.5–7.5 h) the absorption bands at 880 and 820 cm^{-1} are broadened and their intensity changes (see Fig. 3, *b–d*). High frequency (990 cm^{-1}) and low frequency bands (below 600 cm^{-1}) are absent. These spectroscopic results are an indication of destruction of the long range order of the reagents.

The IR spectra of samples mechanically activated and calcined at 350, 400 and 450 °C (Fig. 4, *a*, *b*) are typical of *m*-$Cr_2(MoO_4)_3$ [10, 17]. The high frequency bands at 990 and 970 cm^{-1} are due to activation of ν_1 vibrations of the distorted MoO_4 tetrahedra building the *m*-$Cr_2(MoO_4)_3$ crystal structure [3, 10, 17]. The bands at 870 and 820 cm^{-1} are attributed to ν_3 vibrations of the same groups. The bands below 600 cm^{-1} may be assigned to vibrations of MoO_6 units from MoO_3 present in these specimens [14]. This result is in agreement with XRD data which show the presence of MoO_3.

Figure 5 presents a SEM image of the product obtained at 400 °C from a mechanically amorphized sample. Globular aggregates consisting of spherical particles of $Cr_2(MoO_4)_3$ with submicrometer sizes are visible. Needle-like particles of MoO_3 can also be seen. This picture corresponds to the XRD data. We believe that a small correction of the ratio between the reagents will lead to a singe phase product.

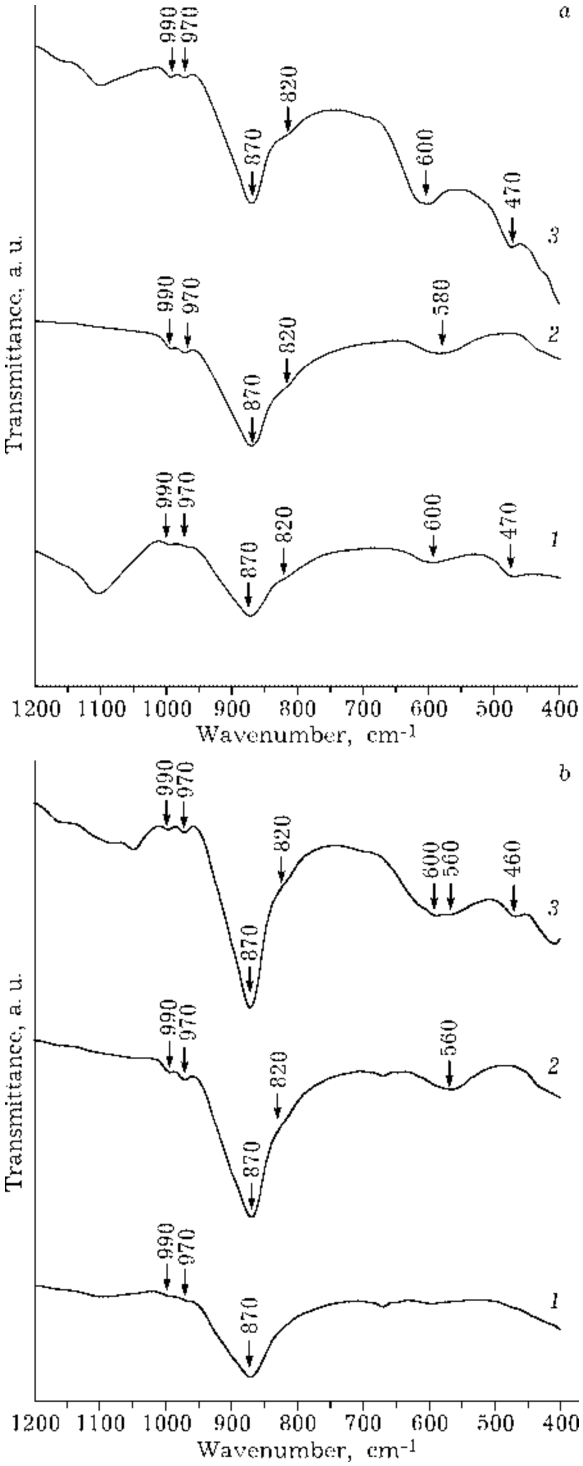

Fig. 4. IR spectra of the samples milled for 2.5 (*a*) and 5 h (*b*) and thermally treated at 350 (*1*), 400 (*2*) and 450 °C(*3*).

CONCLUSIONS

This study demonstrates the favourable effect of the mechanochemical treatment on the synthesis of $Cr_2(MoO_4)_3$. The mechanochemical treatment of the initial mixture leads to a drastic decrease in the synthesis temperature of $Cr_2(MoO_4)_3$ from 700 to 400 °C. Studies that are now in progress show that the purity of the reaction product can be further improved. It is shown that mechanical activation leads to completely amorpized samples. The SEM image of the product reveals particles with a mean size below 2 μm.

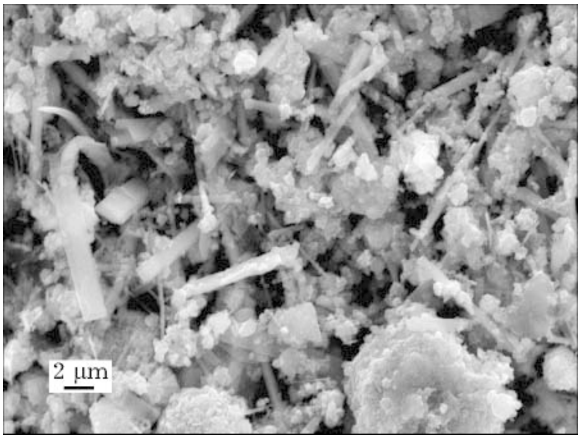

Fig. 5. SEM image of the sample obtained after milling for 5 h and thermally treatment at 400 °C.

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