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CONFERENCE

Interaction of Nickel Hydroxocarbonate, Ammonium Paramolybdate, and Ammonium Metatungstate under Mechanical Activation

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Abstract—The interaction of nickel hydroxocarbonate, ammonium paramolybdate, and ammonium metatungstate (Ni : Mo : W = 3 : 1 : 1) is reported. Under mechanical activation conditions, nickel hydroxocarbonate particles undergo comminution and ammonium paramolybdate and ammonium metatungstate particles soften and aggregate. It is demonstrated by DTA, X-ray diffraction, and IR spectroscopy that heat treatment of the mechanically activated mixture at 400–450°C yields the salts $NiMoO_4$ and $NiWO_4$.

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Mechanochemical activation (MCA) provides a basis for non-waste technologies for production of various materials, including catalysts. When used in catalyst synthesis, this method, in addition to being environmentally advantageous, usually improves the properties of the resulting catalyst. For example, MCA enhances the polymerization activity of titanium tetrachloride–based catalysts and the selectivity of molybdenum disulfide in thiophene decomposition [1]. These effects are due to the fact that MCA causes not only the grinding of the material, but also particle aggregation [2], because the particles heat up to their melting point at the instant of collision and the material passes into the viscoplastic state. The latter process is accompanied by extensive formation of defects and active species and radicals, making possible intensive chemical interactions between the starting reactants.

Another advantage of MCA is that the particle size in the resulting catalyst can be made no larger than 1–2 μm, one order of magnitude smaller than the particle size of bulk catalysts prepared by conventional "wet" techniques using water as the solvent. This decrease in the particle size makes the outer surface area of the catalyst several times larger and, accordingly, enhances the activity of the catalyst in slurry processes.

Here, we report the effect of MCA conditions on the interaction of Ni, Mo, and W compounds for obtaining active components of bulk catalysts for hydrogenation processes, such as hydrodesulfurization.

EXPERIMENTAL

The starting chemicals were nickel hydroxocarbonate $n\mathrm{Ni(OH)_2} \cdot m\mathrm{NiCO_3}$, ammonium paramolybdate $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, and ammonium metatungstate $(NH_4)_6H_2W_{12}O_{40}$.

The individual compounds and their mixture (Ni : Mo : W = 3 : 1 : 1) were mechanically activated in an SGO-2S planetary mill at an acceleration of 30 *g*. The milling bodies were steel balls 8 mm in diameter. The total weight of the balls in the drum was 170 g, the weight of the material to be activated was 2.5 g, the weight ratio between the material and the milling bodies was 1 : 70, and the MCA time was τ_{MCA} = 5–30 min. Preliminary experiments demonstrated that the optimum activation time is 15 min. The X-ray diffraction patterns of calcined mixtures that were preactivated for 15 min show no reflections from NiO, MoO_3, or WO_3. By contrast, the diffraction pattern from the same mixture that was calcined, but not preactivated, does show these peaks. Extending the MCA rime over 15 min results in the formation of X-ray-amorphous compounds.

Samples subjected to MCA were characterized by differential thermal analysis on an STA 449S thermal analyzer, X-ray diffraction on a D8 Advance diffractometer (Bruker), IR spectroscopy on a Nicolet 5700 spectrophotometer (Thermo Electron Corporation), and laser diffraction particle size analysis using an SALD-2101 instrument (Shimadzu). High-temperature X-ray diffraction studies were carried out using a D8 Advance diffractometer equipped with an Anton Paar HTK-16 chamber (heating rate of 5 K/min, delay time of 15 min before recording each diffraction pattern).

RESULTS AND DISCUSSION

The compounds examined in this study possess different acid–base properties. In addition, their interaction yields water, creating hydrothermal conditions in the places of contact. Hence, it was inferred that these compounds would be sufficiently reactive in mechanochemical reactions.

In order to elucidate the effect of MCA on the decomposition of nickel hydroxocarbonate, ammonium paramolybdate, and ammonium metatungstate, we first activated each compound alone (τ_{MCA} = 15 min). Using DTA, we compared the chemical compositions of the mechanically activated and initial compounds.

Figure 1 presents the DTA and DTG profiles of nickel hydroxocarbonate before MCA (Fig. 1a) and after MCA (Fig. 1b). The DTA profile of the initial nickel hydroxocarbonate indicates two endotherms. The fist endotherm, which occurs between 40 and 200°C, is due to the release of nonstructural water. The second endotherm, observed in the temperature range of 220–320°C, is caused by nickel hydroxocarbonate decomposition to NiO, CO_2, and H_2O. Nickel hydroxocarbonate decomposition is known to proceed in two steps [3]:

$$NiCO_3 \cdot nNi(OH)_2 \cdot mH_2O \xrightarrow[-mH_2O]{140^\circ C} NiCO_3 \cdot nNi(OH)_2 \xrightarrow[-CO_2]{320^\circ C} NiO, \quad (I)$$

$$NiCO_3 \cdot nNi(OH)_2 \xrightarrow{290^\circ C} (1+n)NiO + nH_2O + CO_2. \quad (II)$$

The DTA profile of mechanically activated nickel hydroxocarbonate (Fig. 1b) also indicates two endothermic events. However, while the first endotherm occurs in the same temperature range as for the initial sample (40–200°C), the second endotherm is shifted to higher temperatures of 240–340°C. These results can be explained as follows. The brucite structure of nickel hydroxide, a component of nickel hydroxocarbonate, can be either in β-form, which is more stable and more ordered and has an interlayer spacing of 4–5 Å, or in α-form, which is less stable and has an interlayer spacing of 7–8 Å [4]. It is likely that, during MCA, part of the nickel hydroxide turns from α-form to the more stable and more ordered β-form. This hypothesis is corroborated by adsorption measurements: the specific surface area of mechanically activated nickel hydroxocarbonate (105 m^2/g) is smaller than that of the unactivated compound (240 m^2/g).

According to TG data, the mechanically activated sample of nickel hydroxocarbonate loses 7% less weight than the initial sample, suggesting that reactions (I) and (II) occur during the MCA of nickel hydroxocarbonate.

The thermal analysis data for unactivated ammonium paramolybdate (Figs. 2a, 2b) indicate three endotherms between 200 and 340°C, which are due to the stepwise decomposition of the compound. The ammonium paramolybdate structure is conventionally represented as the complicated structural motif $[Mo_7O_{24}]^{6-}$ [5]. The reactions involved in ammonium paramolybdate decomposition are as follows:

$$(NH_4)_6Mo_7O_{24} \cdot 4H_2O \xrightarrow[-4H_2O]{110^\circ C} (NH_4)_6Mo_7O_{24} \quad (III)$$

$$\xrightarrow[-(5H_2O + 13NH_3)]{200^\circ C} 7(NH_4)_2Mo_7O_{13} \xrightarrow[-(7H_2O + 14NH_3)]{280\text{-}500^\circ C} 28MoO_3.$$

The DTA profile of unactivated ammonium paramolybdate (Fig. 2a) shows three endotherms arising from the stepwise decomposition of the compound according to the above reactions. These endothermic events are observed in the temperature ranges of 200–230, 230–280, and 280–340°C, respectively. After 15-min-long MCA, these intervals are shifted to lower temperatures of 100–150, 150–220, and 220–280°C, respectively. Thus, MCA shifts the endotherm temperature ranges by 60–100°C. Note that, for the highest temperature endotherm in the DTA curve for unactivated ammonium paramolybdate (280–340°C), there are two counterparts in the DTA curve for activated ammonium paramolybdate (220–280 and 280–340°C).

These data suggest that MCA causes the breakdown of primary ammonium paramolybdate particles. This shifts the temperature ranges of the depolymerization reactions (reactions (III)) to lower temperatures. The extra endotherm appearing in Fig. 2b, observed at 280–340°C, is assignable to the formation of MoO_4^{2-} anions. The absorption bands of these anions (832 and 925 cm^{-1}) were indeed observed in the IR spectrum of mechanically activated ammonium paramolybdate. According to TG data, the weight loss for the same sample is 5.5% lower than the weight loss for the unactivated sample.

The DTA profile of unactivated ammonium metatungstate indicates three endothermic events at 120–145, 145–170, and 260–370°C. As in the case of ammonium paramolybdate, all of the three endotherms are assignable to the polymerization of the complex polyanion and to the crystal water passing to

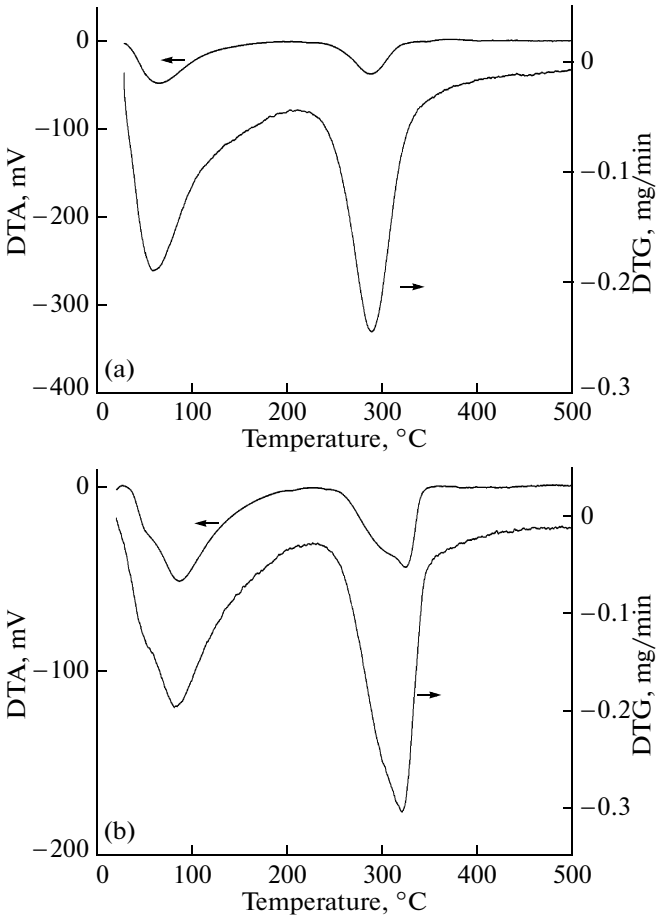

Fig. 1. DTG and DTA profiles of the (a) initial and (b) mechanically activated nickel hydroxocarbonate.

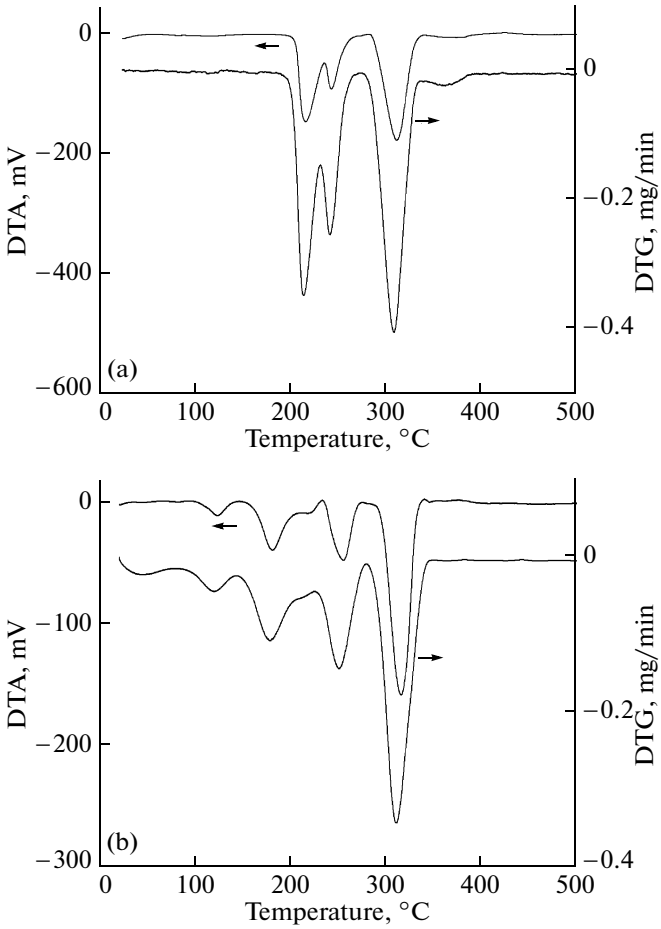

Fig. 2. DTG and DTA profiles of the (a) initial and (b) mechanically activated ammonium paramolybdate.

the adsorbed state. The DTA profile of mechanically activated ammonium metatungstate shows a single endotherm at 80–120°C. Therefore, the polymeric structure of the ammonium metatungstate molecules undergoes complete destruction during MCA. The decrease in weight loss due to MCA is 2.8% in this case.

Next, we studied the MCA-induced changes in the particle size of nickel hydroxocarbonate, ammonium paramolybdate, and ammonium metatungstate. It was found that, extending the activation time from 5 to 30 min for nickel hydroxocarbonate leads to a decrease in the particle size from 33 to 2.6 μm; that is, particle comminution takes place [2]. A different situation is observed for ammonium paramolybdate and ammonium metatungstate. For τ_{MCA} = 5 min, the minimum particle size is 1.7 μm for ammonium paramolybdate and 3.9 μm for ammonium metatungstate. Further increasing τ_{MCA} from 5 to 30 min causes aggregation and particle coarsening up to 4.1 and 4.9 μm, respectively. Therefore, the MCA of the molybdate and tungstate brings about a plastic flow [2, 6].

The next step of our work was a DTA study of the effect of MCA on the changes in the chemical composition of the nickel hydroxocarbonate + ammonium paramolybdate + ammonium metatungstate mixture. The main endotherm intervals in the DTA curve of the unactivated mixture coincide with the corresponding DTA peaks for the individual salts (Fig. 3a). X-ray diffraction data confirm that the salts do not interact during heat treatment: the diffraction pattern of the calcined mixture shows only reflections from the NiO, MoO_3, and WO_3 phases.

The DTA and DTG curves of the nickel hydroxocarbonate + ammonium paramolybdate + ammonium metatungstate mixture mechanically activated for 15 min are quite different (Fig. 3b). The DTA curve between 40 and 320°C indicates a single endothermic event, and the peak characterizing this endotherm has a complicated shape. It can be assumed that ammonium paramolybdate and ammonium metatungstate decompose in this temperature range, releasing both crystal water and H_2O that resulted from the partial decomposition of the salts under the MCA conditions. Between 320 and 430°C, the DTA curve shows an exo-

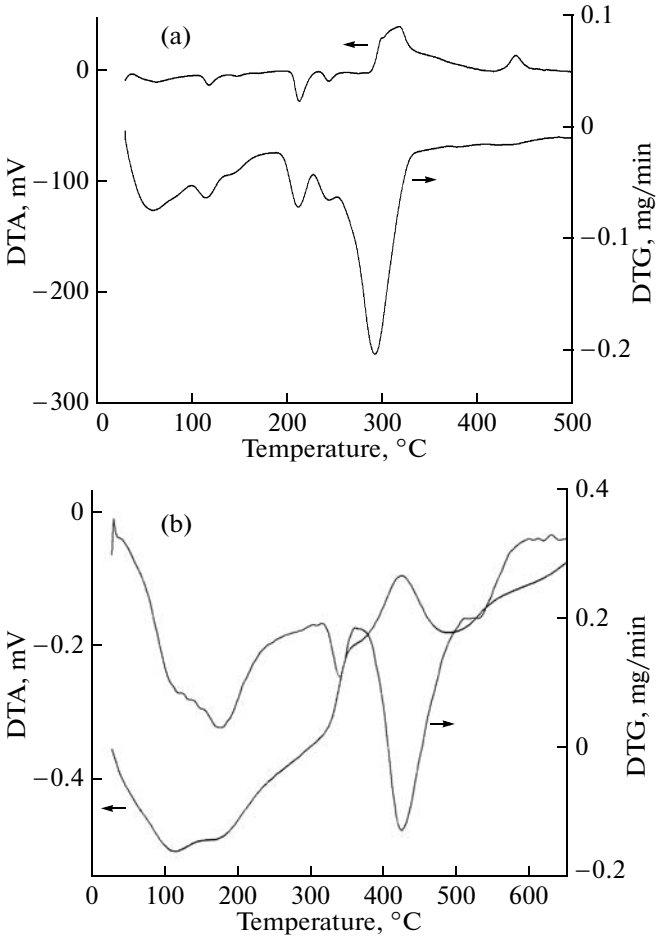

Fig. 3. DTG and DTA profiles of the nickel hydroxocarbonate + ammonium paramolybdate + ammonium metatungstate mixture (Ni : Mo : W = 3 : 1 : 1) (a) before and (b) after MCA.

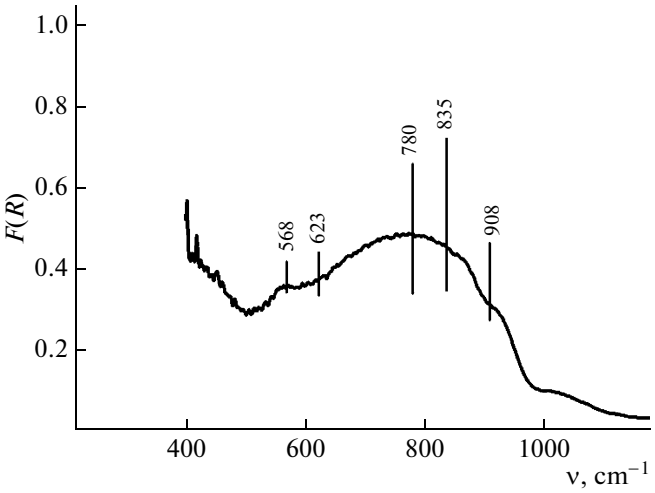

Fig. 4. IR spectrum of the nickel hydroxocarbonate + ammonium paramolybdate + ammonium metatungstate mixture (Ni : Mo : W = 3 : 1 : 1) after MCA and heat treatment at 400°C.

therm, which suggests the formation of new compounds of complex composition. This is also indicated by the sample changing its color from bright green (initial mixture) to mustard-yellow (after MCA).

These results are in agreement with X-ray diffraction and IR spectroscopic data. The IR spectrum of the Ni : Mo : W = 3 : 1 : 1 mixture subjected to MCA and heat-treated at 400°C exhibits a broad absorption band at 835 cm^{-1} and shoulders at 623 and 908 cm^{-1} (Fig. 4). The band at 908 cm^{-1} is due to the double bonds Mo=O and W=O and to the vibrations of the nonlinear bridge W–O–W. The broad band at 835 cm^{-1} and the shoulder at 623 cm^{-1} are assignable to the vibrations of Mo–O–Mo and W–O–W bridges because of the possible formation of nickel molybdate and nickel tungstate, which likely have low-symmetry, defective crystal lattices. This gives rise to extra IR absorption bands and complicates the spectrum as a whole. In addition, the 835 cm^{-1} band indicates the presence of free molybdate and tungstate ions.

Figure 5 presents high-temperature X-ray diffraction data for the mechanically activated Ni : Mo : W = 3 : 1 : 1 mixture heated between 30 and 550°C. Above 450°C, the formation of the nickel salts $NiMoO_4$ (ICDD card no. 31-902) and $NiWO_4$ (ICDD card no. 72-480) takes place. No reflections from oxide phases are observed. The two peaks at $2\theta = 39.4°$ and 46.7° are assignable to Pt (ICDD card no. 04-802) from the heater. We failed to identify the well-crystallized phase responsible for the reflection at $2\theta = 35.1°$. It can only be hypothesized that this reflection is due to a ternary salt of all of the three metals—Ni, Mo, and W.

Note that nickel molybdates and tungstates are the best precursors for obtaining highly active sulfide catalysts for hydrogenation processes [7]. Note also that the reflection at $2\theta = 35.1°$ is observed for the nonsulfided precursor of the highly active bulk catalyst Nebula [8]. Therefore, the introduction of an MCA step into the synthesis of catalysts (e.g., for hydrorefining) can enhance their activity by increasing the proportion and surface area of the necessary phases.

The above data suggest the following mechanism of the interaction of nickel hydroxocarbonate, ammonium paramolybdate, and ammonium metatungstate during MCA. Nickel hydroxocarbonate serves as a stable, low-reactive matrix. The surface of the particles of this matrix has hydroxyl groups and adsorbed water. According to DTA data, the latter stays in the material up to 320°C. The water remaining in materials up to 300°C and above creates hydrothermal conditions during MCA and dissolves the reactants [9, 10]. Since plastic flow is observed for the ammonium paramolybdate and ammonium metatungstate particles even after 5-min-long MCA, it is likely that these particles soften and coat nickel hydroxocarbonate particles,

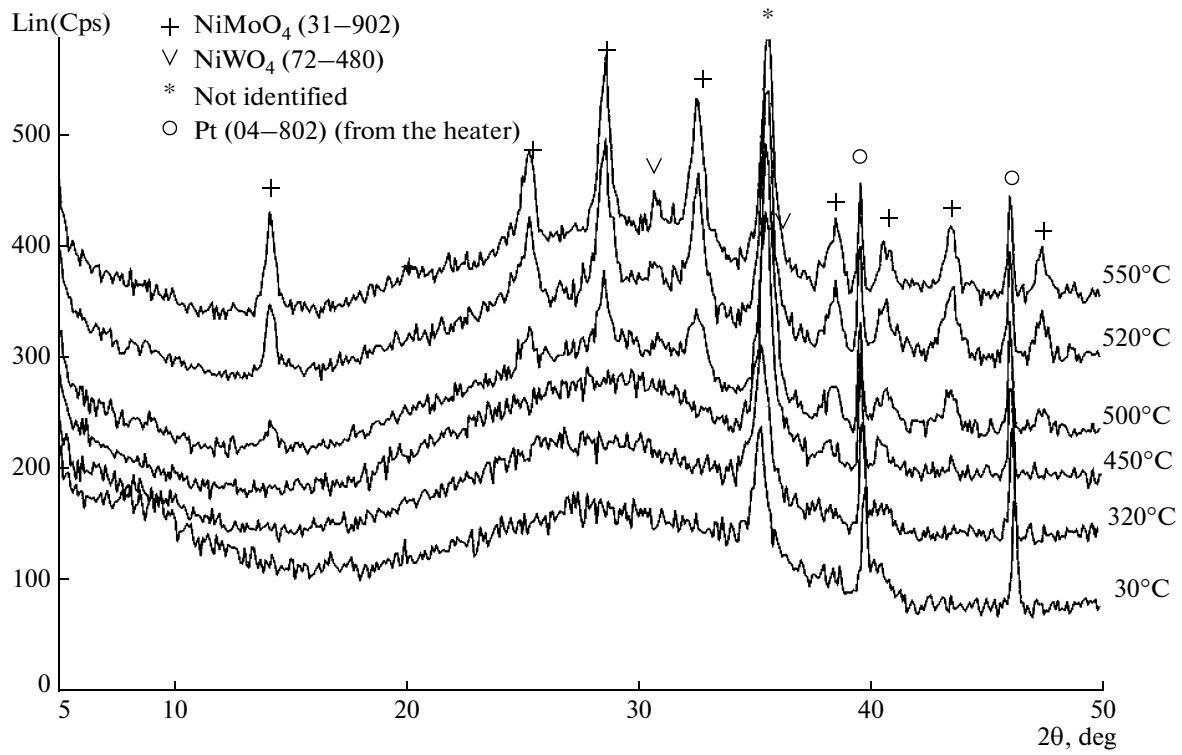

Fig. 5. Phase composition of the nickel hydroxocarbonate + ammonium paramolybdate + ammonium metatungstate mixture (Ni : Mo : W = 3 : 1 : 1) after MCA according to high-temperature X-ray diffraction data.

interacting with surface water and partially dissolving in it. The mechanochemical reactions yield new compounds of complicated composition, such as $NiMoO_4$, $NiWO_4$, and ternary salts. These ternary salts can be identified by further, more detailed examination of the products.

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