Thermal decomposition of Keggin-type ammonium bismuth phosphomolybdates

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Heteropolymetalates of the Keggin-type attract attention due to their potential application in catalysis and material science as well as analytical and clinical chemistry. This class of anions includes the parent Keggin anions $\{XM_{12}O_{40}\}$, their lacunary derivatives $\{XM_{11}O_{39}\}$, and metal complexes [1]. We were interested in preparation of pure and mixed ammonium Bi/Fe phosphomolybdates as precursors for heterogeneous Mo-based complex oxide catalysts for selective oxidation reactions [2,3]. For this purpose, several compositions and reaction conditions were applied to synthesize different precursor phases, and consequently, different mixed oxide phases, formed after thermal decomposition of the respective ammonium salts. Here we report on the thermal decomposition of two bismuth phosphomolybdates with different structural features. On the one hand there is a novel bismuth phosphomolybdate containing tetrameric lacunary $[(BiPMo_{11}O_{39})_4]^{16-}$ anions ($BiPMo_{11}$), and on the other hand a bismuth phosphomolybdate consisting of Keggin anions $[PMo_{12}O_{40}]^{3-}$ and Bi^{III} as counter ions ($BiPMo_{12}$). Besides structural characterization of both compounds, it was the aim to elucidate kind and nature of intermediates and final products formed during thermal decomposition.

The thermal decomposition was studied by simultaneous TG-DSC-MS analysis in air and He. After the observed different TG steps the analysis was broken, respectively, to determine the phase composition of the intermediate decomposition products by XRD. Additionally, the decomposition products were characterized by ATR-IR spectroscopy to inspect the characteristic P–O, Mo–O and ammonium bands.

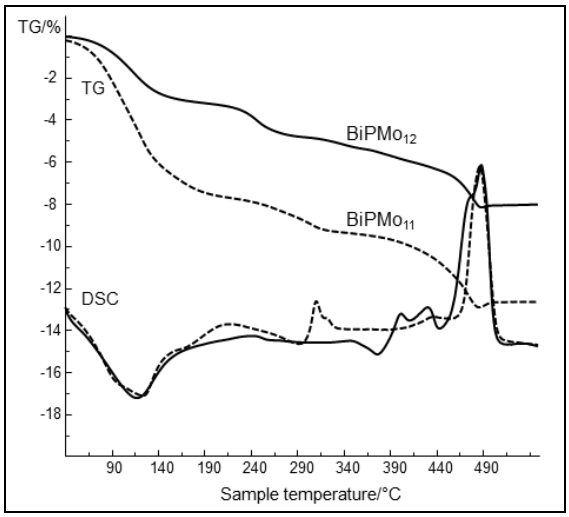

Fig.1. TG and DSC curves of $BiPMo_{11}$ and $BiPMo_{12}$.

In principle, both compounds exhibit three steps of weight loss (Fig. 1) the extents of which depend on their water and ammonium content. While the DSC curve of $BiPMo_{11}$ is characterized by an exothermic effect at comparable low temperature (311°C) such effect is observed at essential higher temperature for $BiPMo_{12}$ (400/430°C). This suggests a higher thermal stability of the latter.

During decomposition of $BiPMo_{12}$ the Keggin-ions remain still intact as proved by XRD from the products obtained after the respective TG steps below 450°C. Surprisingly, after heating $BiPMo_{11}$ to 350°C only one ν(P–O) band at 1061 cm^{-1} was detected in the ATR-IR spectrum of the sample instead of a splitted band typically found for lacunary Keggin ions. The XRD pattern of this sample points to cubic symmetry. Both findings indicate the destruction of the tetrameric lacunary Keggin ions and formation of a crystalline phase containing intact Keggin ions. The latter decompose at comparable temperatures as observed for the $BiPMo_{12}$, accompanied by a strong exothermic effect. The final decomposition products consist of MoO_3 and $BiPO_4$. In the case of $BiPMo_{12}$ bismuth molybdate is additionally formed because of the greater Bi/Mo ratio.

Regarding to catalytic applications the decomposition products obtained after heating to 350°C attract attention because the exhibit Keggin-type structures. Investigations of respective iron-containing samples are in progress.

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