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Letter to the Editor

In a recent paper on the "Characterization of unsupported CoMo sulfide catalysts and their precursors by temperature-programmed reactions", Wu et al. [1] refer to the study of Breysse et al. [2] and state: "Contrary to the explanation of Breysse et al., the highly exothermic peak at ~ 450 K, during the decomposition of CoMo-HSP precursors is attributed to the decomposition of NH_4NO_3 and not to a precursor of the Co–Mo–S phase".

We continue to believe that this strong exothermic peak is not due to the decomposition of NH_4NO_3, and would like to add some remarks and complementary experiments which have not been previously reported.

First of all, Wu et al. [1] refer to the paper of Hincu et al. [3] who reported thermal transformations for binary mixtures of MoS_2 and NH_4NO_3 followed by differential thermal analysis (unfortunately under an unknown atmosphere). These workers observed an explosive reaction at ~ 443 K, which is close to the melting point of NH_4NO_3, but this reaction must be attributed to the oxidation of sulfide by nitrate and not to the decomposition of NH_4NO_3 alone. This fact is corroborated by experimental observations: an MoS_2–NH_4NO_3 (1 : 2.5) mixture presents an endothermic effect at 443 K (melting point of NH_4NO_3) and an exothermic effect at 613 K. Moreover, according to literature data, the explosive character of NH_4NO_3 is only observed at temperatures higher than 573 K [4].

During DTA studies of the decomposition of different HSP catalysts (CoMo, CoW, NiMo, NiW), it has been observed that an exothermic peak is present in the same temperature range whatever the system considered [5]. However, it must be pointed out that the position of these thermal effects is dependent on the nature of the group VIII metal, i.e., the following order appears: CoMo (423 K) < CoW (455 K) < NiMo (479 K) < NiW (513 K).

On the other hand, in the case of the NiW system, the influence of the transition metal content on the intensity of the exothermic peak has been studied [6]. From these experiments, we found that the DTA signal always appears at the same temperature, but its intensity increases with the Ni amount up to the ratio $r = \text{Ni}/(\text{Ni} + \text{W}) = 0.6$. At higher contents, a sharp decrease is observed. The catalytic activity in hydrodesulfurization of dibenzothiophene follows the same trend, that is to say, the synergetic effect reaches a maximum at $r = 0.6$.

In order to check if this exothermic peak could not be due to NH_4NO_3, the decomposition of this salt was studied by DTA under nitrogen flow. The recording presents only weak endothermic effects at 313, 393 and 442 K, followed by a broad exothermic one at 558 K. Therefore, it appears that the presence of free NH_4NO_3 must be revealed by endothermic effects at low temperature, in agreement with literature data [7]. This assumption is con-

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firmed by the decomposition of a mixture of NH_4NO_3 and NiW (HSP) $r = 0.3$ precursor (ratio 1 : 1); both endothermic peaks of NH_4NO_3 decomposition and exothermic peaks of precursor decomposition (513 K) are recorded.

The HSP procedure consists of the addition of a solution of ammonium sulfide to a very dilute solution of group VIII nitrate and ammonium molybdate or tungstate. In the case of the CoMo system, this procedure leads to a solution containing: MoS_4^{2-}, NO_3^- and NH_4^+ ions, a precipitate of cobalt sulfide and probably a mixed species which may be represented by $[Co_xMo_yS_z]^{n-}$. The precursor obtained by elimination of the solvent certainly contains ammonium nitrate, but in close contact with all the previous sulfide species. The thermal decomposition of this precursor leads to the high exothermic peak observed by DTA.

In order to reproduce the intimate contact between ammonium nitrate and a sulfided compound, molybdenum trisulfide was prepared by acidification of a solution of ammonium thiomolybdate by nitric acid until pH 1. Under these conditions, along with the precipitate of MoS_3, ammonium nitrate is formed. After evaporation to dryness, the DTA diagram shows only the exothermic transformation of MoS_3 into MoS_2.

For the preparation of the HSP catalysts, the precursor is thermally decomposed in a flow of 15% H_2–H_2S up to 673 K and kept at this temperature for 4 h. During this treatment, recording the temperature shows an exothermic effect which is observed at exactly the same temperature as that noted during DTA experiments. This phenomenon is accompanied by a sulfur condensation on the cold walls of the reactor. This reaction could not be attributed to the NH_4NO_3 decomposition reaction in which only "non condensable" products are formed [8]. Morever, it must be pointed out that this observation was made for all CoMo, CoW, NiMo and NiW-HSP precursors.

In conclusion, these observations permit the assumption that the exothermic peak observed at ~ 470 K during the decomposition of the HSP precursors is not due to free NH_4NO_3.

In the case of the CoMo-HSP catalysts, the presence of a "mixed phase" has been evidenced by emission Mössbauer spectroscopy [9] and the DTA results [10,11] suggest that the exothermic peak may be related to a "mixed phase" or at least to the precursor of such a phase. The similitude of the DTA patterns and the catalytic behaviour of the different systems studied lead us to extend the concept of a "mixed active phase" to the CoW, NiMo and NiW systems.

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