

Synthesis of Layered Transition Metal Molybdates: Investigating the Influence of Synthetic Route on the Resulting Products

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INTRODUCTION.

Mixed metal oxides containing molybdenum and a second transition metal species (e.g. Co/ Ni/ Cu/ Fe) have long held significant industrial interest for their catalytic properties, particularly in the area of crude oil refinery (see recent reviews by Song and Ma and Breyse et al., 2003). In order to achieve a homogeneous distribution of the active metal species within the catalyst, precursor compounds such as transition metal molybdates (TMMs) or molybdate pillared layered double hydroxides (LDHs) may be used (see Gardner, Levin). One series of TMMs which have been used as catalyst precursors was first reported by Pezerat et al. during a study of the products obtained from solution precipitation of metal salt solutions under basic conditions (Pezerat, 1965 and 1967). Possessing the general formula $AT_2OH(MoO_4)_2(H_2O)$ where $A = K^+, Na^+, NH_4^+$ and $T = Co^{2+}, Cu^{2+}, Zn^{2+}$ or Ni^{2+} , two structural forms were identified, designated as the Φ_y and Φ_x phases respectively.

While studying the incorporation of molybdate species into LDHs by calcination and rehydration, Levin et al. reported the soft chemical synthesis of a layered ammonium zinc TMM possessing the Φ_y structure. The so called chimie douce (CD) method provided an alternative synthetic route for TMM preparation. Here we report on the influence of preparation route on the transition metal molybdates formed. We report the synthesis of layered ammonium zinc and ammonium copper molybdates by both the conventional precipitation (P) route and via rehydration of calcined LDH precursors via the CD synthesis method. The TMM products have been characterised by PXRD, FTIR, SEM, EDX and TGA.

EXPERIMENTAL DETAILS.

TMMs were prepared by two methods: chimie douce (CD) and precipitation (P). The CD method was undertaken as reported in the work of Levin et al. Precursor LDHs were prepared by the standard route of coprecipitation (ref. Rives), in which a 50 ml solution containing a mixture of $T(NO_3)_2 \cdot xH_2O$ (0.02 mol), (where $T = Zn^{2+}$ or Cu^{2+}), $Al(NO_3)_3 \cdot 9H_2O$ (0.01 mol) and an aqueous solution containing NaOH (2 M) and Na_2CO_3 (2M) were prepared. These solutions were combined by dropwise addition to distilled water heated to 55 °C, at relative rates such that a constant pH of 9.0 +/- 0.1 was maintained. Following precipitation the resulting solution was then aged overnight at a temperature of 70 °C after which the precipitate was collected by filtration, washed with distilled water and oven dried at 100 °C. The precursor LDHs were then calcined to form mixed metal oxides (MMO) in a Carbolite furnace at 500 °C for 3.5 hours.

For the CD step 0.25 g of the MMO was reacted with a solution of ammonium heptamolybdate (0.025 M) prepared with distilled water. The mixtures were stirred for 4 hours and the resulting products were collected by filtration, washed in distilled water and dried at 100 °C. The products obtained were named Zn_TMM_CD and Cu_TMM_CD respectively.

TMMs were also prepared by solution precipitation from the metal salts. Aqueous solutions containing the desired transition metal nitrate ($T = Zn$ or Cu) and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ were prepared using distilled water with a T: Mo ratio of 1. Precipitation was induced by the addition of a basic solution of NH_4OH (35 %). The resulting solutions were then aged at 60 °C for 4 hours. After ageing the precipitates were

collected by filtration, washed with distilled water and dried at 100 °C. The resulting products are designated Zn_TMM_P and Cu_TMM_P respectively.

RESULTS AND DISCUSSION.

Figure 1 shows the PXRD patterns of the materials obtained during the principal stages of the CD method for the case of Zn. Single phase TMMs were successfully obtained by both the precipitation and CD methods. PXRD patterns of the products were found to be isostructural with that of the simulated pattern of the Φ_y phase reported by Pezerat. The MMO formed on calcination of the LDH precursor has reflections in positions corresponding to those expected for ZnO. The product obtained after CD reaction of the MMO contains new reflections which appear in positions corresponding to the Φ_y phase. FTIR spectra of the TMM products confirms the incorporation of NH_4^+ with the appearance of the characteristic ν_4 (H-N-H) deformation at 1410 cm^{-1} and the disappearance of the CO_3^{2-} stretch present in the precursor LDH.

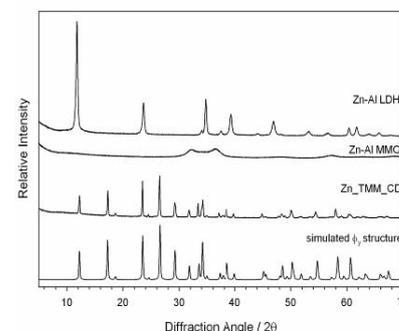


Fig 1. PXRD patterns of the precursor LDH, intermediate MMO, and TMM product obtained during CD synthesis with Zn compared to the simulated pattern of the Φ_y structure.

An SEM study of the products of the CD method and the products of precipitation synthesis revealed clear

palabras clave: Molybdatos, Chimie Douce, Precipitación, HDL.

key words: Molybdates, Chimie Douce, Precipitation, LDH.

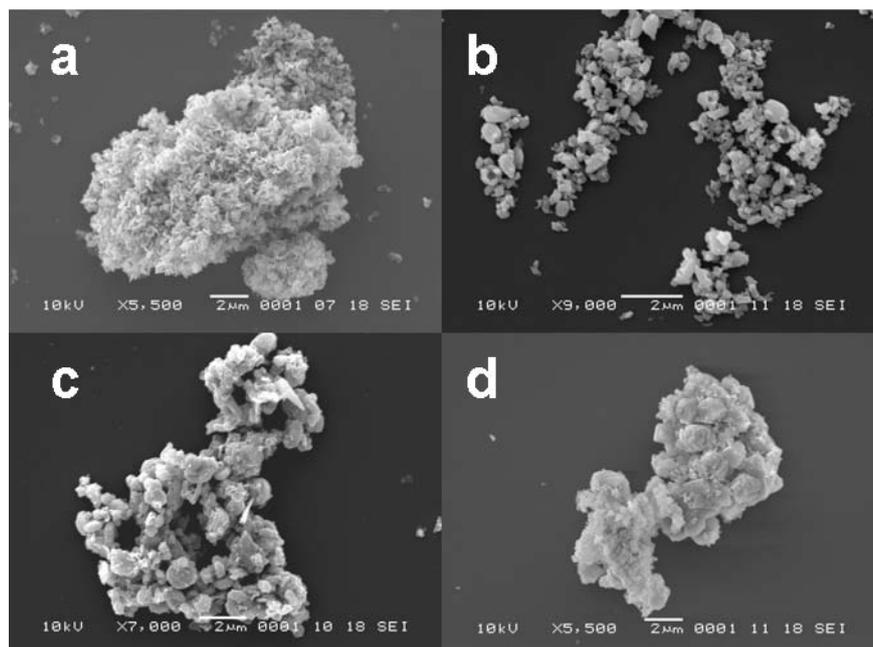


fig 2. SEM comparison of TMM products (a) Cu_TMM_P, (b) Zn_TMM_P, (c) Cu_TMM_CD and (d) Zn_TMM_CD.

differences between the resulting crystallites (Figure 2). The products Cu_TMM_P and Zn_TMM_P prepared by precipitation have distinct morphologies. The Zn containing product has block like crystals whereas for Cu the crystallites appear plate-like and aggregated, and similar to the common morphology observed for LDHs prepared by coprecipitation. The average particle size of products prepared by precipitation is smaller than that of products synthesised by the CD route.

Compositional analysis was also performed on all collected intermediate and product phases. The TGA and DTG curves for Zn_TMM_CD and Cu_TMM_CD were also compared to those of Zn_TMM_P and Cu_TMM_P. One principal endothermic event was observed in all cases but the exact profile differed between products. TMMs containing Cu are found to have a higher thermal stability than those containing Zn. In addition the products prepared via the CD route start to lose weight at lower temperatures but do not reach a constant weight until higher

temperatures than those prepared by precipitation. The total mass losses (TMLs) measured are all higher than the estimated weight loss based on the decomposition of compounds possessing the aforementioned general formula for the Φ_y phase. Analysis of the PXRD patterns of the residues remaining after thermal treatment to 800 °C revealed that the phases obtained (summarised in Table 1) also differ.

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Sample	T _c / °C	TML / %	Crystalline phase(s)	ICSD
Zn_TMM_P	265	11.7	Mo ₂ O ₉ Zn ₃	401828
Zn_TMM_CD	290	12.0	MoO ₄ Zn	411378
Cu_TMM_P	300	11.0	CuMoO ₄ + Other	411384
Cu_TMM_CD	315	11.5	Cu ₃ Mo ₂ O ₉	154263

Table 1. Calculated TMLs, T_cs from the measured TG profiles and the crystalline phases identified by PXRD in the remaining residues for TMM products.