



Study of intermediates involved in the hydrothermal synthesis of the M1 phase of MoVTenbO_x selective oxidation catalysts

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Introduction

Mo-V-Te-Nb mixed metal oxides have received increasing attention in the last years due to their activity and selectivity in partial oxidation of light alkanes. Among the different crystalline phases, it is generally accepted that M1 is the principal active phase [1]. The study of preparation of a complex mixed oxide like M1 is very challenging, due to the high number of steps included in the synthesis procedures applied, and the lack of knowledge about the inorganic reactions taking place. In this work, we have studied the hydrothermal synthesis of mixed Mo-V-Te-Nb oxides, which is one of the most promising synthesis methods. Intermediates of the reaction have been identified with the help of in-situ Raman spectroscopy and complementary ex-situ analysis of samples extracted from the autoclave. The understanding gained in the chemistry occurring in the hydrothermal stage is very valuable for directing the synthesis of Mo-V-Te-Nb oxides.

Experimental

In-situ Raman measurements were done with a Kaiser Optics Spectrometer equipped with a fiber-optic probe head for in-situ analysis. In order to elucidate the time dependence of the synthesis, the hydrothermal reaction was carried out at 448 K during times ranging from 1 to 48 hours. An aqueous suspension was prepared containing the metals Mo/V/Te/Nb in a molar ratio of 1/0.25/0.23/0.12. The washed and dried precursors were treated in Ar flow at 923 K for 2 h. Precursors and final crystalline oxides were characterized by XRD and XRF.

Results

XRD of activated samples generated in the autoclave for 1 to 48 hours has shown that a Mo₅O₁₄-like oxide is formed in the early stages of the hydrothermal reaction, with minor amounts of M2 and M1 phases as admixtures. With increasing reaction times, the fractions of Mo₅O₁₄ and M2 decrease while M1 becomes the main product after ca. 6 h. Chemical analysis of the amorphous precursors (Figure 1) has proven that Nb precipitates in the initial stages of the synthesis, while V incorporation in the

solid is a slow process, that takes place at the expense of a re-dissolution of Mo and Te species.

In-situ Raman spectra (Figure 2) show a broad complex band in the region 700-1000 cm^{-1} that points to the formation of diverse M-O-M bonds. At short reaction times, the most intense contribution is centered at 835 cm^{-1} . This band is typically assigned to M-O-M vibrations in nanocrystalline M_5O_{14} ($\text{M}=\text{Mo},\text{V},\text{Nb}$) [2]. The appearance of shoulders at 800, 894, 880 and 325 cm^{-1} with reaction time is assigned to the formation of M1 nanocrystalline precursor [3], in good agreement with our XRD results.

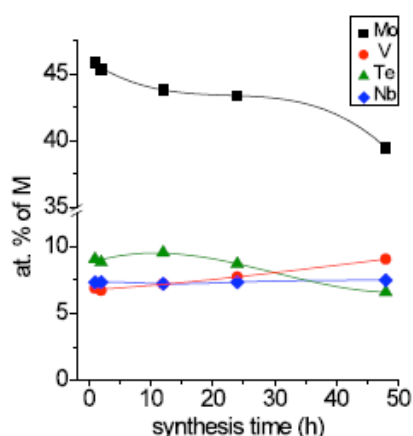


Figure 1. At. % of each metal in amorphous precursors (with respect to initial mixture) after 1-48 h of HT reaction at 448 K.

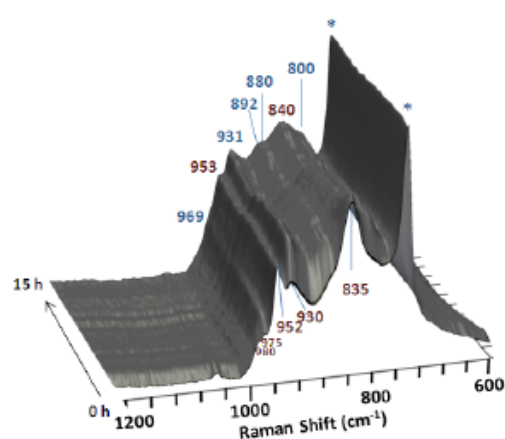


Figure 2. In-situ Raman spectra of first 15 h of Mo-V-Te-Nb hydrothermal reaction at 448 K. (*) Raman bands of sapphire in probe.

Conclusions

In-situ Raman spectroscopy and ex-situ characterization provide valuable information for unraveling the chemical reactions involved in the generation of M1 phase precursor under hydrothermal conditions. We conclude that the formation of nanocrystalline M1 occurred through the formation of a Nb-enriched M_5O_{14} intermediate.

References

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