Development of molybdenum nitride catalysts: New Insights into formation mechanisms of β and γ-Mo_2N

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Metal nitrides represent a promising alternative to metal catalysts for different reactions such as hydrogenation and ammonia synthesis [1-2]. These materials with metallic character are chemically resistant, cheaper and more environmentally acceptable. Studies on nitride systems were mainly focused on the synthesis of unsupported molybdenum nitride (Mo_2N) while little work has been done on examining the surface structure and properties of supported nitride materials. Bulk materials are usually prepared by temperature-programmed reduction-nitridation of Mo-containing precursor under NH_3 or N_2/H_2 flow and face centered cubic γ-Mo_2N is the most commonly synthesized phase. Formation of a tetragonal β-Mo_2N, which exhibits different catalytic properties, is possible only under N_2/H_2 flow with adjustment of the reaction conditions. Different formation mechanisms were cited in literature, but were not elucidated. Nitride supported catalysts are prepared by impregnation followed by reduction and nitridation steps. It has been shown that some of the critical parameters (e.g. nitride dispersion) can be affected by the nature of the support; however, there is no study reporting the impact of the support on the formation of Mo_2N [1,3]. In this work we systematically investigated the influence of synthesis conditions and support type on the catalysts' structural characteristics. MoO_3 was chosen as the precursor for molybdenum nitride phase, while TiO_2, CeO_2 and activated carbon were used as supports.

First, we investigated the influence of the heating rate (T_{rate}), feed composition, final nitridation temperature, GHSV, and cooling gas on the formation of β or γ-Mo_2N. Finally, we have established a simple synthesis procedure leading to β or γ-phase formation. Results obtained on the bulk Mo_2N were compared with results obtained for the supported Mo_2N catalysts. Thermal and chemical analysis, XRD, XPS, UPS, and Raman spectroscopy were undertaken in order to understand the nitridation reaction mechanism. Considering bulk catalysts, *in situ* XRD, Raman and XPS/UPS studies under 15% v/v N_2/H_2 flow revealed that for T_{rate} equal to 5 °C/min pure β-phase was synthesized at 700 °C, following the mechanism: $MoO_3 \rightarrow H_xMoO_3 \rightarrow MoO_2 \rightarrow Mo \rightarrow$ β-Mo_2N. Compared to previously published results for β-phase formation mechanism we have identified presence of one new intermediate-H_xMoO_3. γ-Mo_2N was obtained for T_{rate}= 0.5 °C/min and, contrary to previously published results, formation route is the same as for β-Mo_2N. It seems that T_{rate} impacts the crystallite size and determines whether β or γ-Mo_2N is formed. TGA experiments performed on the precursors for the supported catalysts under flow of reactive gases revealed general rule that the presence of support decreases the reduction temperature of MoO_3 and promote nitride phase formation at lower temperatures than for bulk catalysts. For example, for the TiO_2-supported catalyst complete molybdenum nitride formation took place at already 500 °C and Mo_2N crystallite size on support is lower than for bulk catalyst. Heating rate influence seems to be the same like for bulk catalysts.

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