Synthesis of nickel molybdate from zwitterionic hybrid precursors: benefiting of the memory effect in the frame of the catalytic propane activation.

B. Farin[*, 1], M. Devillers, E. M. Gaigneaux[*].

[1]*Institute of Condensed Matter and Nanosciences - IMCN, Division « MOlecules, Solids and ReactiviTy–MOST », Université catholique de Louvain, Croix du Sud 2/17, B-1348 Louvain-la-Neuve, Belgium*
e-mail address of corresponding author (: benjamin.farin@uclouvain.be; eric.gaigneaux@uclouvain.be)

Introduction

Mixed oxides are usually considered as efficient catalysts to activate light hydrocarbons like propane [1]. In this context, nickel molybdate ($NiMoO_4$) are thought to be one of the most interesting oxides in the oxidative dehydrogenation of propane (ODHP) [2]. The α-phase seems to be the most active but the β-phase tends to be more selective in propene and gives better propene yields [3]. However, the great stability of alkanes makes their activation difficult. This leads to a never-ending necessity of catalysts improvement in order to plan any industrial valorization of such low-cost and abundant reagent. A widespread way to achieve it is the development and optimization of catalytic formulations. An alternative way consists in improving the catalysts physico-chemical properties (structure, texture…) that are responsible of good performances. The synthesis step is therefore crucial to obtain the desired effect on the final catalysts. One possibility could be the formation of mixed oxides through thermal degradation of a hybrid precursor. The aim of this project consists in taking advantage of a zwitterionic organic polymer matrix (poly(N,Ndiallyl-N-hexylamine-*alt*-maleic acid) displaying a supramolecular organization thanks to its alkyl side chains [4]. Inorganic ions ($[Ni(H_2O)_6]^{2+}$, MoO_4^{2-}) are inserted and dispersed along the matrix through interactions with the charged moieties of the polymer. The matrix is then removed upon heat treatment to generate final mixed oxides active in the ODHP. The impact of the presence and the degradation of the polymer matrix on the catalysts behavior is a key point of this study. Moreover, concerning the oxides textural properties, the occurrence of "memory effects" related to the genesis of the pre-organized matrix is also investigated.

Experimental

Hybrid precursors are obtained by adding drop by drop solutions of inorganic ions to a polymer solution. The amount of added ions is expressed through molar ratios: Inorganic ions/Polymer repeated units (I/R ratio). pH 6 is maintained constant during the addition. The final solution is stirred during two hours and lyophilized. The recovered hybrid precursors are burned upon heat treatment with a decomposition treatment at 300°C for 16 h under air. The corresponding mixed oxides are then generated with a subsequent calcination at 550°C for 4 h under air. The organization and structuration of the hybrid precursors have been studied by XRD, FTIR and SEM. As the transformation of hybrid materials into mixed oxides is a key point of this study, it has been studied by thermodiffractometry (XRD-T), TGA, DTA. The catalysts are tested in the ODHP reaction which is performed in a U-shape quartz reactor at 450 – 475 and 500°C with a total flow of 40 ml/min ($C_3H_8/O_2/N_2$ = 10/12.5/77.5). The analysis of products is done using an on-line GC equipped in TCD and FID detectors.

Results/Discussion

From XRD, FTIR and SEM analysis, the hybrid materials seem to be homogeneous when I/R ratios do not exceed 1. In such case, inorganic ions are well-dispersed through the polymer matrix thanks to interactions with the charged moieties of the polymer chains.

By XRD-T, DTA, and TGA studying the hybrid precursor transformation into mixed oxides, one concludes that the exothermic burning of the polymer helps the formation of crystalline nickel molybdate oxides at lower temperatures: 100°C earlier than for $NiMoO_4$ formation through other techniques like co-precipitation. Furthermore, for I/R ratios ≤ 1, XRD-T shows that a β-$NiMoO_4$ is present at room temperature whereas generally this crystallographic phase is unstable at such temperature in opposition to the α-$NiMoO_4$ phase (**Figure 1**). Interactions and dispersion of the inorganic ions through the polymer matrix coupled with the presence of carbon during the burning step might explain the stabilization of such metastable $NiMoO_4$ phase.

Besides, when a large amount of inorganic ions is added (I/R ratio = 4), only a few part of ions are able to interact with the matrix. In such case, the α-$NiMoO_4$ is the only phase that is formed. The two later points – early crystallisation temperature of $NiMoO_4$ and phase stabilisation argue in favour of the existence of a memory effect of the hybrid precursor on the final mixed oxides.
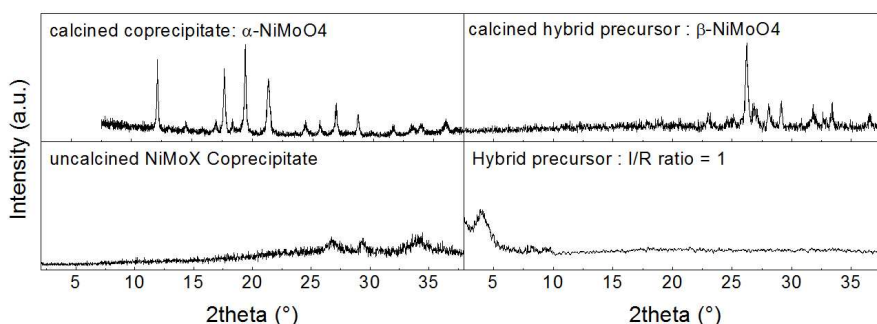

Figure 1: Thermodiffractograms realized at room temperature before and after calcination of : the nickel molybdate co-precipitate (left), the hybrid precursor I:R ratio = 1 (right)

Currently the research is going on to verify if these effects could help to obtain more efficient catalysts in the ODHP. Nickel molybdates synthesized through the hybrid precursors method have already demonstrated to be able to activate propane in the ODHP. Other catalytic tests are in progress in order to : i) improve the performance of nickel molybdates synthesized through the hybrid precursor method, ii) compare the performance of these catalysts with catalysts synthesized through more classical methods (co-precipitation, complexation method), taking into account the oxides textural properties.

References

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