Towards using the Reorganization of Heteropoly Compounds: Taking Advantage of Intermediate States in the Frame of the Propylene Oxidation

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Introduction and Objectives

Heteropoly compounds (HPCs) are unstable materials during oxidation reactions. However, by applying adequate treatments, they can act as precursors of active species [1-4]. This work aims at understanding the genesis, evolution and functioning of the catalytic active phases obtained from HPCs. We therefore studied the evolution of their structural rearrangement when being used in the propylene oxidation. Our recent research has shown that Dawson HPC rearranged into a 3D network of Mo oxide, which could easily alternate the formation of corner- and edge-sharing MoO_6^{-6} octahedra [3]. The present contribution now concerns the influence of the redox strength of the gas feed on the HPCs catalytic performance. The purpose is to gain insight into the formation of catalytic active phases obtained from HPCs as a function of the environment. The strategy is thus to perform *operando* Raman investigation of Dawson and Keggin HPCs under the atmosphere of propylene oxidation with O_2:C_3H_6 molar ratios varied within the range [0.5-2].

Experimental

The Dawson $(NH_4)_6P_2Mo_{18}O_{62}$ and Keggin [$(NH_4)_3PMo_{12}O_{40}$ and $H_3PMo_{12}O_{40}$] HPCs were synthesized and characterized as explained in [1]. The *operando* Raman investigation was done in a setup combining a fixed bed reactor, a Raman spectrometer and GC on line analysis. Reactions were run between 250 and 450°C with a stepwise temperature of 50°C. A staying time of 2 h was respected at each step, except for the last step at 450°C at which the samples were kept for 8 h. The concentration of C_3H_6 was 10 vol.% with He and O_2 flows adjusted to have 30 mL min^{-1} in total. The recovered samples were characterized by *ex situ* XRD and FTIR analyses.

Results and Discussion

Below 350°C, the Dawson HPC was no active whatever the redox condition. With the molar ratio of 2, at 450°C, the conversion increased (with acrolein as main product), reaching 13%. A small decrease in the C-balance (down to 95%) was noted. On the contrary, when Dawson HPC was tested with the ratios of 1 and 0.5 at 450°C, the conversion increased, but only apparently as it was related to a C-balance of only 80%, not linked to any increase in any selectivity. Keggin HPCs were active at a lower temperature than

Dawson; *e.g,* at 350°C, a conversion of 25% (mainly in COx) was observed with $(NH_4)_3PMo_{12}O_{40}$ tested with a ratio of 2. A lower conversion was noted under ratios of 1 and 0.5 (12 and 8 %, respectively). In these 3 cases, there was no deficit in the C-balance.

Based on these catalytic results we hypothesised that propylene was trapped in the working Dawson catalyst whatever the conditions (but mainly with the ratios of 1 and 0.5). This phenomenon was thus facilitated by a more reductive atmosphere: the catalysts released more O atoms and were thus more able to change their configuration. The Dawson HPCs adapted their structure forming a lattice with channels occupied by propylene. However, differences exist between the structures of the recovered samples. Unlike Dawson samples tested under ratios of 1 and 0.5 which displayed Keggin features, the one tested under a ratio of 2 acquired a MoO_3-looking structure. These differences could be explained as follows: (i) Highly reductive feeds promoted the Dawson rearrangement; more channels were formed making the retention of propylene more effective. The structure formed was then stabilised with no more rearrangement possible. The rearrangement consequently stopped at the Keggin state. (ii) In a less reductive feed (ratio of 2), the Dawson sample rearranged slower and modifications occurred. A Keggin structure was formed (attested by *operando* Raman) and then decomposed to yield a 3D network of Mo oxide (attested by *ex situ* characterisations) extremely selective to acrolein. The formation of such peculiar phase did not occur when starting with the Kegin HPCs. Typical Keggin features remained more visible on the tested samples with the molar ratios of 1 or 0.5. It seems that a highly reductive feed stopped the Keggin rearrangement into MoO_3 at an earlier stage than under a molar ratio of 2, as observed for the Dawson HPC. The working Keggin catalyst thus never acquired the very active MoO_3 structure which display good selectivity towards acrolein product.

Conclusions

Working in a moderately reductive feed, it is possible to control the rearrangement of Dawson HPC to a Mo oxide like structure very selective to acrolein. This structure was never acquired with more reductive feeds, or starting from Keggin HPCs. The combined adjustment of the redox strength of the feed and the nature of the starting catalyst dictated the formation of the species generated via the HPCs rearrangement and thus allowed to optimize the HPC catalytic performance.

References

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