The role of Nb in rutile-type antimonates, catalysts for propane ammoxidation to acrylonitrile

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The ammoxidation of propane to acrylonitrile represents an alternative to the current commercial production from propylene. Different catalysts have been claimed to be active and selective for this reaction; amongst best systems are those based on rutile-type metal antimonates. Recently, we have published about the performance of Cr/V mixed antimonates as catalysts for this reaction [1]. We found that mixed solid solutions containing the three metal ions are formed, where a synergic effect between V and Cr leads to active compounds, more active than the corresponding single-component antimonates. Excess antimony was necessary to develop systems characterized by good selectivity to acrylonitrile. Aim of the present work was to study the effect of Nb addition in Cr/V/Sb mixed oxides; indeed, Nb is known to form mixed oxides which are active in propane oxidehydrogenation, and is sometimes included in the composition of catalysts for propane ammoxidation.

Catalysts have been prepared by the co-precipitation technique from alcoholic solutions, and the solids obtained have been calcined in air at 700°C. Several catalysts were prepared, having different ratios between components: Cr/V/Sb/Nb 1/1/5/x (with equiatomic ratio between V and Cr, excess Sb and variable amount of Nb), 1/0.2/5/x (with lower V content) and 1/0.2/1/x (with both low V and Sb contents as referred to Cr). Common to all catalysts was the increase of selectivity to acrylonitrile with temperature, which occurred at the expense of carbon oxides, cyanhydric acid and acetonitrile. The selectivity to propylene instead was very low for all catalysts; this is a peculiarity of Cr/Sb/O-based systems [1], and was attributed to Sb-surface enrichment in rutile crystallites.

The addition of Nb caused a small but non negligible increase in catalytic activity; the main positive effect, however, was on the selectivity to acrylonitrile. Maximum selectivity achieved was around 45%, for the catalyst having the highest Nb content. At the same time, the extent of ammonia combustion to molecular nitrogen decreased on increasing the Nb content in samples. The effect of Nb was a function of the V + Cr amount as compared to Sb; in fact the positive effect of Nb on selectivity became evident only provided (i) an excess of Sb was present with respect to the sum of V and Cr, and (ii) the amount of Nb was comparable to the amount of excess Sb.

Catalysts were characterized by means of X-ray diffraction, Raman spectroscopy, FT-IR spectroscopy. The rutile mixed oxide, containing V (mainly as V^{3+}), Cr (mainly as Cr^{3+}) and Sb^{5+} was the main component of the system; microcrystalline antimony oxide was also present. Evidences were found which supported the development of new sites, arising from the interaction between antimony and niobium, which were specifically selective in the transformation of the unsaturated intermediate obtained by propane activation.

Results obtained have been compared with catalytic performance of reference antimonates and niobates.

[1] N. Ballarini, F. Cavani, C. Giunchi, S. Masetti, F. Trifirò, D. Ghisletti, U. Cornaro, R. Catani, Topics Catal., 15 (2001) 111. Stud. Surf. Sci. Catal., 136 (2001) 135.