Niobium-doped metal antimonates, catalysts for propane ammoxidation to acrylonitrile

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Introduction

The synthesis of acrylonitrile is carried out by means of propene ammoxidation. However, recently Asahi Chem announced the start-up of an industrial unit for propane ammoxidation, that offers advantages with respect to the process from the alkene because of the lower cost of the alkane. Catalysts described in the literature for this reaction are based either on rutile-type metal antimonates (V/Sb/O, V/Sn/Sb/O, Fe/Sb/O, Cr/V/Sb/O) [1], or on mixed molybdates (Mo/V/Te(Sb)/Nb/O). These catalysts are polyfunctional systems, containing both elements playing the key-role of alkane activation and transformation into propene (e.g., Fe^{3+}, Cr^{3+}, Ga^{3+}, $V^{4+}/^{5+}$), and elements that are efficient in the allylic ammoxidation of the intermediately formed propene, i.e., Sb^{5+}. In the present work we report about the preparation and characterization of Ga/V/Sb and Cr/V/Sb rutile-type mixed oxides, and compare their reactivity with that of corresponding Nb-doped rutile systems.

Experimental

Catalysts were prepared with the co-precipitation technique, developed for the preparation of rutile SnO_2-based systems claimed by Rhodia. The preparation involved dissolving salts or chlorides of each element in absolute ethanol, followed by dropping the solution into an aqueous solution maintained at pH of about 7. A precipitate was obtained, which was separated from the liquid by centrifugation and filtration. The solid was then dried at 120°C, and calcined in air at 700°C for 3 hours. The following reaction conditions were used for catalytic experiments: feed composition 25 mol.% propane, 10% ammonia, 20% oxygen, remainder helium; residence time 2.0 s. Products were analysed by means of on-line gas chromatography.

Results/Discussion

Catalysts based on rutile-type Cr/V/Sb mixed oxides were active and moderately selective in propane ammoxidation to acrylonitrile. However, the addition of Nb led to a considerable improvement in catalytic performance. A higher selectivity to acrylonitrile (up to 15 points % more) and a small increase of propane conversion were obtained, with a corresponding remarkably lower combustion of ammonia to N_2. Specifically, in order to have a positive effect of Nb on catalytic performance of Cr/V/Sb/Nb mixed oxides, the required composition was as follows:

a) A (Cr+V)/Sb ratio largely lower than 1; this is related to the need for excess Sb in order to develop Sb-enriched rutile mixed antimonate/niobate of Cr and V.
b) A Nb/Sb ratio largely lower than 1, but greater than 0.05-0.1 (e.g., equal to 0.2-0.3); in fact, low amounts of Nb had a negligible effect on catalytic performance.

The positive effect of Nb was attributed to the formation of defective multi-component rutile mixed oxides, containing the four elements in the same structure. These systems were also characterized by Sb^{5+} enrichment with respect to the stoichiometric composition, which provided surface sites for allylic ammoxidation of the unsaturated intermediate. Data obtained indicate that the concomitant presence of Nb and Sb in the rutile structure improved the efficiency of sites active in the insertion of ammonia, with a decrease of the rate of ammonia transformation into molecular nitrogen.
In the case of rutile Ga/V/Sb mixed oxides of general composition Ga/V/Sb 1/y/3 (atomic ratios), the XRD patterns of all catalysts showed the presence of the rutile mixed oxide only. The prevailing products at low temperature were CO_2 and cyanhydric acid; the selectivity to propene was low – as it was also in the case of Cr/V/Sb/O rutile catalysts - and this was attributed to the incorporation of excess Sb in the rutile structure, and to the development of an Sb-enriched structure. The increase of temperature led to an increase of selectivity to acrylonitrile (Figure 1). Samples containing V (y=0.2 and 0.4) were remarkably more active than Ga/Sb/O (y=0); the catalyst offering the higher TOF (propane conversion rate per unit time per unit V atom) was that one having y=0.4, that also gave the highest yield to acrylonitrile. On the other hand, the best selectivity to acrylonitrile was shown by the Ga/Sb/O sample, having no V at all. However, the addition of Nb (sample Ga/V/Nb/Sb 1/0.2/1/3) led to a remarkable improvement of both activity and selectivity as compared to the corresponding catalyst that did not contain Nb.

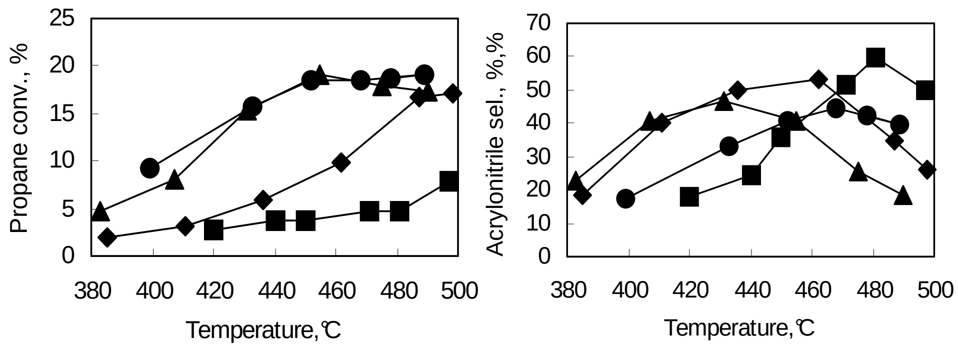

Figure 1. Conversion of propane (left) and selectivity to acrylonitrile (right) in function of the temperature. Catalysts: Ga/V/Sb 1/0/3 (■), 1/0.2/3 (◆), 1/0.4/3 (▲), 1/1/3 (●).

References

1. F. Cavani, G. Centi, and P. Marion, in "*Metal Oxide Catalysts*", (S.D. Jackson, and J.S.J. Hargreaves, eds), Wiley-VCH, Weinheim, p. 771, 2009.