

An investigation on the role of components in V/Ti/O-based catalysts for the gas-phase oxidation of o-xylene to phthalic anhydride

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Several industrial catalysts for applications in the field of selective oxidation are made of an active phase, typically a transition metal oxide, supported over inert carriers such as alumina, silica or titania. One relevant example is the catalyst for the gas-phase oxidation of o-xylene to phthalic anhydride, which is made of vanadium oxide supported over titania (anatase).

Indeed, the industrial system is much more complex, since it does include several dopants, the nature and the relative amount of which may vary depending on catalyst supplier and on the technology employed for the process, either a single-bed or a multi-layer catalytic bed. The dopants included in catalyst formulation do not simply promote the performance, but rather have a quite remarkable effect on both activity and selectivity to phthalic anhydride, and on the active phase stability under reaction conditions.

Despite the large number of papers published starting from early 80's dealing with the characterization of V/Ti/O catalysts [1], several aspects concerning the industrial catalyst and its performance are still unravelled. Specifically, of relevance from both the applied and the scientific points of view are (i) the role of dopants in affecting the nature of the vanadium species which constitute the active phase (the so-called "monolayer"), and (ii) the modifications on the active phase which occur under reaction conditions. In the present work, we report about the investigation of industrial-like, doped V/Ti/O catalysts, and develop a method to quantify the amount of each V species which constitute the active phase, in the presence of the dopants Cs and Sb oxides. Also, the effect of modifications occurring during reaction on catalyst features are examined.

The promoters investigated, Cs and Sb, had different effects on catalytic performance. Cs improved the activity, but the most important effect was on the selectivity to phthalic anhydride. Antimony instead improved only the activity, when amounts of Sb lower than 0.7 wt.% Sb₂O₃ were added in catalyst composition. The activity-enhancement effect was found to derive from two factors: (i) the increase of the isolated V species, chemically bound to the support, and (ii) the stabilization of this species towards segregation into bulk vanadium oxide under reaction conditions.

The isolated V species could be discriminated from polyvanadates and bulk vanadium oxide by means of TPO, since the former did not spontaneously release molecular oxygen under oxidizing environment during the thermal analysis, while the latter self-reduced to yield V₆O₁₃. This made possible to discriminate between the different V species which develop on titania support. By combination of the information from several characterization techniques, it was possible to infer that Sb oxide develops a sort of "secondary support" for the dispersed V species; the latter is characterized by the higher intrinsic catalytic activity. In the latter case, the decomposition of the monolayer and the re-crystallization of bulk vanadium oxide under reaction conditions could be well evidenced by comparing the effect of temperature on the self-reduction of V₂O₅.

1) G. Centi, *Appl. Catal.*, **1996**, *147*, 267.