3rd IDECAT Conference on Catalysis, Porquerolles (France), 19.05.-24.05.2009

Selective oxidation of propane on $MoVTeNbO_x$ catalysts. The effect of steam on the catalytic performance

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During the last decades, a lot of effort has been undertaken in order to replace the current two-step acrylic acid production starting from propylene with a direct (one-step) propane oxidation process. The main reason is that the latter process would be more energy- and ultimately cost-efficient, because propane is a cheaper starting material than propylene. Moreover, the reduction of process stages may lead to simpler reactor design and operation, less separation steps, less energy waste and less pollutant emissions [1,2]. However, propane is less reactive than propylene, therefore, higher temperatures or more active catalysts are needed to activate it. MoVTeNb mixed oxides, originally patented by Mitsubishi [3], are characterized by high activity and selectivity in oxidation of propane to acrylic acid. Steam is an important feed additive to increase the acrylic acid yield. The co-fed water vapor may affect the mechanism as well as the nature of active sites [2]. Change of the reaction pathway in presence of water may be related to the enhancement of acetic acid and CO_x by hydration of intermediately formed propylene to 2-propanol that can be easily oxidized further to the CH_3COOH / CO_x precursor acetone. Moreover, water may act as nucleophilic or oxidizing agent in the oxidation of the intermediate acrolein to acrylic acid. The nature of the catalyst can be modified by changing the ratio of Lewis and Brønsted acid sites, the oxidation state of the metals and the surface composition of the catalyst depending on the steam concentration.

In this study, the effect of steam on the catalytic properties of MoVTeNb oxide is presented. The catalyst was prepared by mixing the aqueous metal salt solutions of the catalyst components and spray-drying the resulting suspension. The dried product was calcined in air at 548 K and subsequently annealed in Ar at 873 K. The resulting crystalline material was composed of the two phases M1 (ICSD 55097) and M2 (ICSD 55098). Since propane activation has been attributed to the phase M1 exclusively, M2 was removed by washing with H_2O_2 solution. Finally, heat treatment at 873 K in Ar was repeated resulting in a phase-pure M1 with the stoichiometry $Mo_{1.00}V_{0.26}Te_{0.09}Nb_{0.17}O_{4.0}$

as determined by ICP-OES and a specific surface area of 8.8 m^2/g. Propane oxidation was performed at 673 K applying approximately 3 vol.-% propane in the feed and a 1:2 molar ratio of propane to oxygen. The steam concentration was varied between 0 and 40 vol.% in 10 vol.% steps. N_2 was used as balance. In Figure 1, the composition of the product gas is shown as a function of contact time. In a dry feed, the only products observed by gas chromatography are propene, acrylic acid, and CO_x. Interestingly, no acetone or acetic acid is detected even though H_2O is present as a by-product. Propane consumption is accelerated substantially after adding 10 vol.-% or more steam to the feed. In presence of steam, the formation of acrylic acid is enhanced, acetic acid detected and CO_x formation suppressed. The propene concentration is changed only little in the contact time range studied and it is not affected by the concentration of steam in the feed. These observations suggest that avoiding over-oxidation of acrylic acid is an important function of co-added steam. The results are discussed in relation to previously reported reversible changes of the surface composition of M1 in presence and absence of steam.

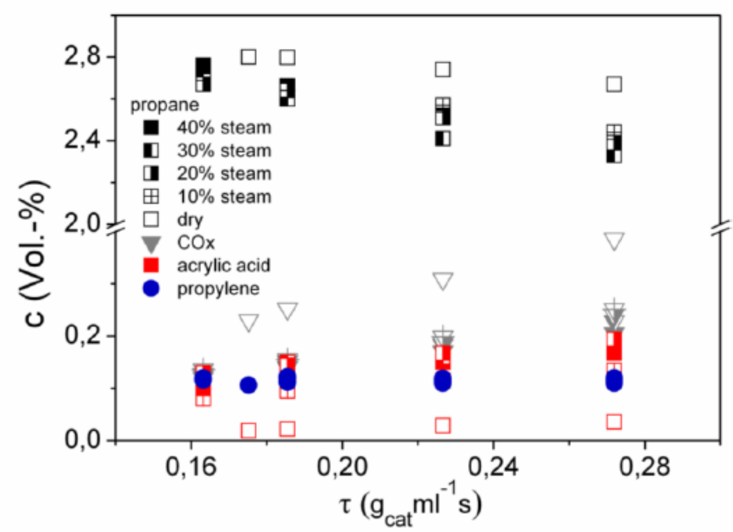

Figure 1. Composition of the product gas in propane oxidation to acrylic acid at 673K over M1 as a function of contact time and steam content in the feed.

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