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Synergetic effect between phases in MoVTe(Sb)NbO catalysts used for the oxidation of propane into acrylic acid

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Abstract

Results are reported concerning the synergetic effect observed in the oxidation of propane to acrylic acid over the orthorhombic *M1* and hexagonal *M2* phases present in the most active and selective MoVTe(Sb)NbO catalysts. The pure phases and phase mixtures containing either tellurium or antimony have been prepared and individually tested as catalysts. The results obtained confirm that the phase responsible for the catalytic properties of the efficient catalysts is phase *M1*, and that *M2* is poorly active. Mechanical mixtures of the pure phases have also been prepared and tested. All of the catalysts have been characterized before and after the catalytic reaction by X-ray diffraction, X-ray photoelectron spectroscopy, and high-resolution electron microscopy with EDS analyses. Although the synergetic effect previously described (bifunctional catalysis with the oxidative dehydrogenation of propane molecules on the orthorhombic *M1* phase and the subsequent oxidation of propene on the hexagonal *M2* phase) was observed, another cause related to migration of tellurium from the *M2* phase to the surface of the *M1* phase was indicated. This migration should balance a loss of tellurium in the active phase occurring under the conditions of a catalytic test, but may also create new dehydrogenation sites for propene and/or anneal total oxidation sites. The hexagonal *M2* phase would thus play a role of tellurium reservoir for the active *M1* phase. This effect was not reversible and concerned only the tellurium. Antimony, which is less volatile, should not be lost by the active phase. Furthermore, it was shown not to diffuse at the surface of the phases.

Keywords: Propane mild oxidation and ammoxidation; Synergetic effects; Phase cooperation; MoVTeNb and MoVSbNb oxide catalysts

1. Introduction

In recent years, many investigations have been conducted on multiphasic catalysts used for partial oxidation reaction. One reason for this is the great differences generally observed in catalytic properties between this type of catalysts, which correspond to industrial catalysts, and single-phase catalysts. This improvement of performance for a mixture of phases with respect to each phase component, designated the synergetic effect, has been attributed to different effects [1–4]. These effects have been described as resulting from phenomena as different as bifunctional catalysis, solid-state reaction affecting the bulk phases, surface chemical interaction (migration, contamination), formation of coherent interface, and supporting effect with the spreading of one phase on the other. When experimental evidence for such effects is lacking, a remote effect control mechanism based on an oxygen spillover from one phase to the other has been proposed [5,6]. One of the most spectacular synergetic effects reported is that observed when mixtures of bismuth and cobalt molybdates are used as catalysts in the oxidation and ammoxidation of propene. In this last case, several phenomena have to be considered to explain the synergetic effect: (i) the spread of one phase on the other, (ii) formation of a coherent interphase, and (iii) bifunctional catalysis with the concomitant activation of propene and oxygen on the different phases [7–9].

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Recently very efficient catalysts based on MoVTeNbO mixed oxides have been developed by Mitsubishi for the ammoxidation of propane [10,11]. These catalysts were later claimed to be efficient for several different reactions of alkane oxidation, including oxidation of propane to acrylic acid and oxidative dehydrogenation of ethane [12–14]. The patented catalysts systematically contain several phases; among these, two have been claimed to be necessary for obtaining high performances. These two phases, called *M1* and *M2*, have orthorhombic and hexagonal structures, respectively. The active phase of these catalysts has been proposed to be the phase *M1* [11], and later this was clearly demonstrated when both phases were tested pure [15]. However, the presence of the phase *M2* was shown to improve the selectivity of the catalysts for acrylic acid, even when the biphasic catalysts were prepared from simple mechanical mixtures [16]. This improvement of performances for a mixture of phases with respect to each phase component has been proposed to be related to a bifunctional catalysis, with one phase catalyzing the oxidative dehydrogenation of propane (*M1* orthorhombic) and the other one catalyzing the oxidation or ammoxidation of the formed propene (*M2* hexagonal) [11]. In a recent publication we confirmed this effect on the kinetic data obtained with a prepared mechanical mixture catalyst and extended it to other phase mixtures [15]. More recently, a study by Holmberg et al. [16] of mechanical mixtures of *M1* and *M2* phases containing Te also confirms the existence of the synergetic effect and its bifunctional origin. However, it is difficult to believe that this effect alone can explain the synergetic effect, since it was shown that the active *M1* phase has all the sites needed to transform propane into acrylic acid or acrylonitrile, and it is also very efficient at oxidizing propene to acrylic acid [17,18]; we have therefore undertaken further study of this two-phase system to find other possible origins of the synergetic effect. Moreover, the latter effect did not seem to take place when antimony was substituted for tellurium. We have thus investigated the influence of the ratio of the two phases containing either Te or Sb on the catalytic properties of the mixture, and we have tried to characterize the catalysts by XPS and high-resolution electron microscopy (HREM) with EDS analyses before and after the catalytic reaction to detect a possible transformation of the solids. The results obtained are presented and discussed in this paper.

2. Experimental

2.1. Catalyst preparation

Three types of catalysts were prepared that contained either tellurium or antimony. The first one corresponded to *M1* (orthorhombic) and *M2* (hexagonal) phase mixtures. These compounds were prepared, according to a patented procedure [19,20], from an aqueous slurry comprising Mo, V, Te(Sb), and Nb in the ratio Mo/V/Te(Sb)/Nb = 1:0.33:0.22(0.15):0.11. The slurries were evaporated to dryness at 423 K and successively calcined at 573 K under air and at 873 K under nitrogen for 2 h. In the case of the antimony-containing catalysts, colloidal silica (Ludox) was added to the slurries before the drying step ($\mathrm{Mo/Si} = 0.76$).

The second type of catalysts corresponded to the pure *M1* and *M2* phases. *M1* phases were obtained by treating a *M1* and *M2* phase mixture prepared as described above for 5 h with stirring in a 15% hydrogen peroxide aqueous solution at 298 K. Under such conditions, the *M2* phase was totally dissolved. The *M1* phases were then washed, dried at 383 K, and calcined under nitrogen at 873 K for 2 h. *M2* phases were prepared by solid-state reaction. V_2O_5, TeO_2 or Sb_2O_3, MoO_3, and Mo were mixed in relative proportions corresponding to the theoretical stoichiometry $(Te(Sb)O)_2M_6O_{18}$ ($M = Mo$ and V, where $V/Mo = 0.8$) [21]. The oxide mixtures were sealed in a silica tube under vacuum and heated at 873 K for 72 h. With this preparation procedure it was not possible to synthesize pure Nb-containing *M2* phases. To determine whether the presence of niobium in the *M2* phase was important in the occurrence of a synergetic effect between the *M1* and *M2* phases, we have prepared and studied a *M2* phase containing tellurium and niobium. For that purpose the same protocol was used as for the *M1* + *M2* phase mixtures, but with the starting ratio Mo/V/Te/Nb = 1:0.30:0.41:0.10.

The third type of catalysts corresponded to mechanical mixtures of the prepared pure phases. We obtained these mixtures by mixing the respective powders and hand grinding them for 5 to 10 min. The different phases are referred to here by their type and Nb and Te or Sb contents (*M1*(Sb), *M2*(Nb/Te), *M2*(Sb), etc.). The phase mixtures are denoted as *M1* + *M2*(Nb/Te) and *M1* + *M2*(Nb/Sb) when they were synthesized and *M1*(Te) + *M2*(Nb/Te) when they were prepared by mechanical mixing.

2.2. Catalyst characterization

Crystal structures of the pure phases and phase mixtures samples were controlled by X-ray diffraction with a Brüker D5005 diffractometer and Cu-K_α radiation. Metal contents of the solids were determined by atomic absorption (ICP), and specific surface areas were measured by the BET method with nitrogen adsorption. XPS measurements were performed with a VG ESCALAB 200 R. Charging of samples was corrected by setting the binding energy of adventitious carbon (C 1s) at 284.5 eV. Deconvolution of the Mo $3d^{3/2}$ peak was accomplished with a Voigt function.

High-resolution electron microscopy was performed with a JEM 2010 ($Cs = 0.5$ mm). Accelerating voltage was 200 kV with a LaB_6 emission current, a point resolution of 0.195 nm, and a useful limit of information of 0.14 nm. The instrument was equipped with an EDS LINK-ISIS (spatial resolution: 1 nm). It allows the use of a probe size of 25 nm to analyze isolated grains of each of the phases and avoid simultaneous analysis of grains of the two phases.