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Molybdenum–vanadium–antimony mixed oxide catalyst for isobutane partial oxidation synthesized using magneto hydrodynamic forces

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ABSTRACT

A peculiar effect was observed that the oxidation behavior of antimony oxide prepared in presence of a weak permanent magnetic field is changed. Reactivity of α-Sb$_2$O$_3$ (senarmontite) toward oxidation is significantly enhanced after recirculating its suspension in a magneto hydrodynamic (MHD) system. This inspired the MHD synthesis of a molybdenum–vanadium–antimony mixed oxide with superior catalytic activity for selective partial oxidation of isobutane. Traditionally these mixed oxides are synthesized via sol–gel processes involving complexing agents and/or costly alkoxides. Here a new convenient way is presented to synthesize Mo–V–Sb mixed oxide catalysts departing from senarmontite (α-Sb$_2$O$_3$), ammonium heptamolybdate and ammonium vanadate. The MHD treated mixed oxide prepared from suspensions of Sb$_2$O$_3$ with Mo and V salts was evaluated in isobutane partial oxidation and compared with conventionally prepared catalysts. Improved performance was observed for MHD catalysts, with a peak methacrolein selectivity of 40% and decreased CO$_x$ selectivity as compared to a reference 'slurry-type' catalyst. Although the MHD synthesis mechanism cannot yet be explained on a molecular level, it represents significant scientific and economical potential. This report is intended as an invitation to assist in formulating a molecular mechanism capable of explaining these observations.

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1. Introduction

Selective oxidation of short alkanes using molecular oxygen is an attractive route to chemical intermediates such as alcohols, aldehydes, acids, anhydrides and their derivatives [1]. Partial oxidation catalysts typically are based on mixed metal oxides. Especially antimony containing oxides are popular catalysts for the selective oxidation of hydrocarbons [2–7]. SbVO$_4$ is selective to acrylonitrile in propane ammoxidation [8], while its performance can be improved by addition of Mo and Nb promoters. Mo–V–Sb^{IV} mixed oxides have been shown to be active in oxidative dehydrogenation of ethane to ethylene and in selective (amm)oxidation of propane to (acrylonitrile or) acrylic acid [9,10]. Successful promotion by elements such as K and La [11,12] has also been reported. In the conversion of isobutane over such catalysts, oxidative dehydrogenation to isobutene mainly proceeds on the VSbO$_4$ phase and

is initiated by H-abstraction in an acid–base concerted mechanism involving a Lewis acid site on a V atom and a basic lattice oxygen atom [13]. The formation of oxygenated molecules then proceeds on highly dispersed molybdenum sub-oxides present on the catalyst [5]. The synergetic effect between α-Sb$_2$O$_4$ (cervantite) and low amounts of molybdenum oxides can be explained by the stabilization and exposure of selective (1 0 0) faces of the microcrystalline molybdenum oxide, while in absence of cervantite the non-selective (0 1 0) crystal faces of MoO$_x$ are more abundant [14]. However, at high concentrations of molybdenum, increasingly sized MoO$_3$ crystals again preferentially expose non-selective (0 1 0) crystal faces, responsible for undesired C-C bond cleavage and total oxidation reactions [14,15].

The preparation method of these mixed oxide catalysts was found to be critical [16]. For synthesizing Mo–V–Sb mixed oxides Shishido et al. used a slurry type method involving organic complexing agents [5,13]. Through systematic variation of the V and Mo concentration in the catalyst, the composition of Mo$_1$V$_1$Sb$_{10}$O$_x$ was found to be optimal for partial oxidation of isobutane. In the oxidation of isobutane with molecular oxygen at 440 °C a methacrolein selectivity of 27.6% was reached at an isobutane conversion level of

8.1% [5]. Paul et al. used a high throughput method and combinatorial chemistry for identifying mixed oxides suitable for isobutene partial oxidation catalysis [17–20]. A costly, acid-catalyzed sol–gel procedure was used to prepare mixed oxides, but allowed identification of a catalytically optimal composition of $Mo_8V_2Sb_{90}O_x$ [20]. The mixed oxide prepared via this sol–gel procedure resulted in full suppression of total oxidation, with a methacrolein selectivity (28% selectivity, 1.7% yield) [18–20] close to that of the slurry type catalysts prepared by Shishido et al. [5].

This manuscript demonstrates a convenient methodology for the synthesis of Mo–V–Sb mixed oxide catalysts starting from less costly, commercial α-Sb_2O_3 oxide (senarmontite), in combination with common ammonium heptamolybdate and ammonium vanadate. Senarmontite usually is avoided as direct starting material for heat-activated mixed-oxide catalysts as it is prone to sublimation during activation [21]. Similar to other oxides of non-transitional group V elements (e.g. α-Bi_2O_3), senarmontite contains ordered local magnetic fields originating from an anisotropy in the triplet states of unshared electron pairs present in these oxides [22,23]. MHD treatment was speculated to affect the material by affecting the ordering of internal magnetic moments and hence may also affect its reactivity. In very different contexts, MHD treatment has been shown to assist nanoparticle aggregate breakup for calcium carbonate and silica suspensions [24,25], and to favor the formation of uniformly sized emulsion droplets [26]. A direct change of the chemical reactivity of a material prepared under MHD conditions has however not yet been reported.

The present study demonstrates a decreased sublimation of senarmontite as result of MHD treatment, without alterations to particle morphology or bulk crystalline structure. Sublimation typically occurs at the onset of senarmontite oxidation. Since mixed oxide catalysts are typically activated by oxidation and sublimation should be avoided, this peculiar observation inspired a new and superior MHD synthesis procedure for Mo–V–Sb mixed oxides from a suspension of senarmontite in water with dissolved Mo and V salts. The new catalyst was evaluated in partial isobutane oxidation and exhibited excellent catalytic performance for partial oxidation of isobutane into isobutene and methacrolein, thereby indicating MHD synthesis as a viable alternative to more costly slurry-type or sol–gel methods for the preparation of mixed oxide catalysts.

2. Materials and methods

2.1. Magneto hydrodynamic treatment

Hydrodynamic (HD) and MHD treatment was performed using a setup similar as described by Emmerich et al. [27]. Suspensions (200–210 mL) were recirculated in a closed circuit (9.5 mm inner diameter Tygon Lab tubing, total volume 210 mL) using a peristaltic pump. MHD forces were generated using a 2 mm slit shaped flow restriction made of stycast. The orthogonal static magnetic field was generated by mounting two permanent NdFeB block magnets on the outside of this dispersing device in attractive mode, with 6 mm distance between the magnet faces. The magnetic field strength in the middle of the channel was 0.33 T as determined by Hall probe measurements. Circulation was carried out at 5 L/min corresponding to a Reynolds (Re) number of 6.0×10^4. After 30 min of circulation, the suspension was poured into a beaker separating sediment and supernatant after 15 min static equilibration. The sediment was separated from its supernatant, recovered and dried at 65 °C for 20 h prior to further use.

2.2. $Mo_8V_2Sb_{90}O_x$ synthesis

A reference catalyst was synthesized following the slurry type procedure of Shishido et al. [5]. Sb_2O_3 was dispersed in an oxalic acid aqueous solution, to which a hot aqueous solution of $(NH_4)_3Mo_7O_{24} \cdot 4H_2O$ (99.98%, Sigma–Aldrich) and NH_4VO_3 (99%, Sigma–Aldrich) was added to obtain the molar composition of $Mo_8V_2Sb_{90}O_x$ (Table 1). The mixture with a total volume of 210 mL was heated under reflux conditions at 90 °C for 24 h. The precipitate was recovered and dried by evaporation of the solvent, first at 60 °C and 100 mbar pressure and then at 100 °C for another 20 h. Finally the product was ground into a fine powder and calcined at 350 °C for 4 h (heating rate 1 °C/min) and at 600 °C for 6 h (heating rate 1 °C/min).

MHD synthesis of the $Mo_8V_2Sb_{90}O_x$ catalysts was achieved by dispersing Sb_2O_3 in 200 mL aqueous solution. To this suspension, 10 mL salt solution was added containing suitable amounts of dissolved $(NH_4)_3Mo_7O_{24} \cdot 4H_2O$ and NH_4VO_3 reflecting the desired final molar ratio in the catalyst (Table 1). HD treated reference samples were prepared by recirculating similar suspensions without mounting the magnets over the slit shaped flow restriction. After MHD treatment, the precipitates were recovered, dried and calcined according to the reference method [5] described for the slurry type catalyst.

2.3. Isobutane partial oxidation experiments

Catalytic testing was performed in a quartz 4-way gas-phase tubular flow reactor at atmospheric pressure at 5 reaction temperatures between 350 and 450 °C with a temperature step of 25 °C. The catalyst powder (0.5 g), previously calcined at 600 °C (see Section 2.2), was pelletized to a fraction between 125 and 250 μm and packed between two layers of quartz wool. Prior to reaction, the catalysts were dehydrated in situ at 400 °C in a flow of 20% oxygen in helium for 2 h. During reaction, an isobutane:oxygen:helium gas mixture with a relative volumetric composition of 3:1:2 and a total feed flow equal to 40 mL/min was continuously fed to the 4 quartz reactors. For each of the 4 catalysts and at each of the 5 reaction temperatures, the reaction product stream was sampled twice. Gas selection, gas flow, reactor temperature, valve selection and gas chromatography operations were controlled by Camille process control software (Argonaut Technologies, Foster City, CA, USA). Feed and products were analyzed with an on-line HP 5890 series II gas chromatograph equipped with (i) a CP-Sil 5 CB dimethylpolysiloxane column of 60 m length, 0.32 mm internal diameter and 3 μm film thickness (Varian, Palo Alto, CA, USA), connected to a methanizer and a flame ionization detector (FID) and (ii) a home-made 3 m, 1/8 in. internal diameter column filled with 80–100 mesh molecular sieve 5 A connected to a thermal conductivity detector (TCD).

2.4. Sample characterization

X-ray powder diffraction patterns were recorded on a STOE Stadi P diffractometer using Cu $K_{\alpha 1}$ radiation. Particle size distribution was determined with laser diffraction on an LS100 Coulter instrument (Beckman). Thermogravimetric analysis was performed at 100 mL/min either in synthetic air or a O_2:N_2 mixture in a volume ratio of 90:10, with a Q500 (TA Instruments) and a Q600, the latter enabling simultaneous TGA and DSC in air with strict control of the experimental conditions. All TA instruments were re-calibrated before analyzing a sample series with new materials. For nitrogen physisorption, a Micromeritics Tristar 3000 was used and samples were outgassed using a Micromeritics Smartprep 065 at 200 °C for 10 h prior to recording isotherms. Whereas SEM micrographs were taken on a Philips XL30 FEG, a Philips CM200 microscope was used for TEM analysis.

XPS was performed with an X-probe (SSX-100/206) spectrometer from Surface Science Instruments working with a monochromatic Al K_α radiation (10 kV, 22 mA). Charge compensation was