# Molybdenum-Vanadium-Antimony Mixed Oxide Catalyst for Isobutane Partial Oxidation Synthesized using Magneto Hydrodynamic Forces

Bernard Stuyven<sup>§</sup>, Jens Emmerich<sup>§</sup>, Pierre Eloy<sup>†</sup>, Jan Van Humbeeck<sup>#</sup>, Christine E.A.

Kirschhock<sup>§</sup>, Pierre A. Jacobs<sup>§</sup>, Johan A. Martens<sup>§,\*</sup>, Eric Breynaert<sup>§</sup>

<sup>†</sup> Institute of Condensed Matter and Nanosciences (IMCN), BSMA - Croix du Sud 1 bte

L7.04.01, B-1348 Louvain-la-Neuve, Belgium

<sup>#</sup> Surface and Interface Engineered Materials, Department of Metallurgy and Materials

Engineering (MTM), KU Leuven, Kasteelpark Arenberg 44, box 2450, B-3001 Heverlee,

Belgium

<sup>§</sup> KU Leuven Centre for Surface Chemistry and Catalysis, Kasteelpark Arenberg 23, box 2461,

B-3001 Heverlee, Belgium

\* Corresponding author – Tel: +3216321637 – Fax: +3216321998 – e-mail:

johan.martens@biw.kuleuven.be

### 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  $\alpha$ -Sb<sub>2</sub>O<sub>3</sub> (senarmontite) towards 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 ( $\alpha$ -Sb<sub>2</sub>O<sub>3</sub>), ammonium heptamolybdate and ammonium vanadate. The MHD treated mixed oxide prepared from suspensions of Sb<sub>2</sub>O<sub>3</sub> 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.

**Key words:** senarmontite; magneto hydrodynamic (MDH) synthesis; Mo-V-Sb mixed oxide; isobutane partial oxidation, methacrolein.

# 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<sub>4</sub> is selective to acrylonitrile in propane ammoxidation [8], while its performance can be improved by addition of Mo and Nb promoters. Mo-V-Sb<sup>IV</sup> 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 VSbO4 phase and is initiated by H-abstraction in an acid-base concerted mechanism involving a Lewis acid site on a V atom and a

MHD - Magneto Hydrodynamic; HD - Hydrodynamic

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  $\alpha$ -Sb<sub>2</sub>O<sub>4</sub> (cervantite) and low amounts of molybdenum oxides can be explained by the stabilization and exposure of selective (100) faces of the microcrystalline molybdenum oxide, while in absence of cervantite the non-selective (010) crystal faces of MoO<sub>x</sub> are more abundant [14]. However, at high concentrations of molybdenum, increasingly sized MoO<sub>3</sub> crystals again preferentially expose non-selective (010) 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  $Mo_1V_1Sb_{10}O_x$  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  $\alpha$ -Sb<sub>2</sub>O<sub>3</sub> 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.  $\alpha$ -Bi2O3), 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  $6.0 \cdot 10^4$ . 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<sub>8</sub>V<sub>2</sub>Sb<sub>90</sub>O<sub>x</sub> 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).

Composition	$Sb_2O_3(g)$	$(NH_4)_3Mo_7O_{24} \cdot 4H_2O(g)$	$NH_4VO_3(g)$	Volume (mL)
$Mo_{12}V_3Sb_{85}O_x$	4.8180	0.8242	0.1367	210
$Mo_8V_2Sb_{90}O_x$	5.1014	0.5497	0.0912	210
$Mo_4V_1Sb_{95}O_x$	5.3850	0.2752	0.0462	210
$Mo_2V_{0.5}Sb_{97.5}O_x$	5.5265	0.1373	0.0229	210

Table 1: Precursor quantities and water volume in Mo-V-Sb mixed oxide synthesis with varying composition via the slurry type synthesis [5] and the MHD approach.

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 sub 2.2), was pelletized to a fraction between 125 en 250  $\mu$ m 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, California, 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  $\mu$ m film thickness (Varian, Palo Alto, California, USA), connected to a methanizer and a flame ionization detector (FID) and (ii) a home-made 3 m, 1/8 inch internal diameter column filled with 80-100 mesh molecular sieve 5A 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<sub>a1</sub> 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<sub>2</sub> 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<sub> $\alpha$ </sub> radiation (10 kV, 22 mA). Charge compensation was achieved by an electron flood gun adjusted at 8 eV and placing a nickel grid 3.0 mm above the sample. Pass energy for the analyzer was 50 eV, while the spot size was 1000 µm in diameter, corresponding to a FWHM (full width at half maximum) of 1.1 eV for the Au 4f7/2 band of a gold standard.

# **3** Results & Discussion

### 3.1 Magneto hydrodynamic modification of senarmontite

Freshly prepared senarmontite suspensions were recirculated in a closed loop for 30 minutes through a slit-shaped restriction in presence and absence of a magnetic field. After separation, the sediment was dried at 65 °C. Powder XRD patterns recorded in ambient atmosphere for senarmontite particles before and after MHD and HD treatment were nearly identical (Figure S1, supporting information), thereby showing that the MHD treatment did not alter the bulk crystalline phase. SEM imaging of samples before and after MHD treatment (Figure 1) also did not reveal significant changes. Laser diffraction confirmed that particle size and distribution of the senarmontite particles remained similar, with a maximum around 4  $\mu$ m before and after (magneto-) hydrodynamic treatment. (Figure 2). The absence of morphological changes was also confirmed by the nearly identical specific surface area determined for both HD and MHD treated samples (BET area, ±0.9 m<sup>2</sup>g<sup>-1</sup>).



Figure 1: SEM pictures of untreated senarmontite powder (a) and senarmontite recirculated for 30 min through a MHD device (0.33T) at 5 L/min (b).

DSC-TGA analysis in air and in a 90 %  $O_2$  atmosphere, however, revealed a clear influence of the MHD treatment on the oxidation behavior of the crystals (Figure 3). TGA in air of the MHD sample revealed significantly suppressed sublimation. Analysis in 90 %  $O_2$  atmosphere

demonstrates an increased oxygen uptake for samples after MHD treatment as compared to HD treatment (Figure 4).



Figure 2: Volume fraction distribution (G(dH) of particle size (dH) of untreated senarmonite powder (a) ; senarmontite recirculated for 30 min through the (magneto-) hydrodynamic device at 5 L/min in presence (b) and in absence of the magnetic field (c).

These observations can be rationalized from the known chemistry of the antimony oxides. In its oxides, antimony occurs in different oxidation states (e.g. Sb<sub>2</sub>O<sub>3</sub>, Sb<sub>2</sub>O<sub>4</sub>, and Sb<sub>2</sub>O<sub>5</sub>) and allotropes. For Sb<sub>2</sub>O<sub>3</sub>, three enantiotropic Sb<sub>2</sub>O<sub>3</sub> phases can be distinguished, *viz.* the low temperature cubic form senarmontite ( $\alpha$ -Sb<sub>2</sub>O<sub>3</sub>), the orthorhombic valentinite ( $\beta$ -Sb<sub>2</sub>O<sub>3</sub>), and at high pressure, high temperature orthorhombic  $\gamma$ -Sb<sub>2</sub>O<sub>3</sub> [21,28]. The phase transition of senarmontite ( $\alpha$ -Sb<sub>2</sub>O<sub>3</sub>) to valentinite ( $\beta$ -Sb<sub>2</sub>O<sub>3</sub>) has been widely investigated [29–36]. For pure Sb<sub>2</sub>O<sub>3</sub>, this transformation can be observed between 615 and 645°C, depending on sample origin and mechanical pre-treatment [21]. Decrease of the transition temperature of  $\alpha$ -Sb<sub>2</sub>O<sub>3</sub> to  $\beta$ -Sb<sub>2</sub>O<sub>3</sub> down to about 570 °C has been reported in presence of significant amounts of sulfide [29] or of

water, either surface bound or as bulk[21]. This phase transition has been described as a multistage event where a partial dehydroxylation step is followed by an endothermic stage due to the liberation of chemisorbed and/or physisorbed water at elevated temperature [21].

Oxidation of  $Sb^{III}_{2}O_3$  to cervantite ( $Sb^{IV}_{2}O_4$ ) is strongly dependent on the allotrope and the oxygen partial pressure. In air, the onset of the oxidation of valentinite to cervantite is observed at 410 °C [21]. For senarmontite, the oxidation starts at 531 °C, following an initial sublimation step at 465 °C [21]. The difference in oxidation temperature between the two phases has been explained by the crystallographic similarity between the orthorhombic structures of valentinite and cervantite. The coherent linking of cervantite to the original valentinite matrix substantially reduces the energy of surface-nucleation of the former [32]. Previously reported observations indicate a sublimation controlled oxidation of the molecular crystal senarmontite ( $\alpha$ -Sb<sub>2</sub>O<sub>3</sub>) [21], first sublimating to valentinite, which offers low-energy nucleation sites for oxidation into cervantite [33,34]. This sublimation/oxidation mechanism significantly complicates the determination of the exact oxidation temperatures for  $\alpha$ -Sb<sub>2</sub>O<sub>3</sub> phases, and even makes the possibility of direct transformation of senarmontite to cervantite doubtful. Asides the occurrence of sublimation prior to oxidation, presence of oxidizing agents also encumbers exact determination of a possible transition temperature of senarmontite to cervantite. In argon for example, cervantite formation has been observed at 615 °C, revealing the influence of chemisorbed and/or physically adsorbed water as oxidizing agent [21]. This observation has been interpreted as indication that variations in oxidation temperature are related to water bound in the sample or to variation of the oxygen partial pressure in the local atmosphere at the particle surface [21].



Figure 3: DSC and TGA (upper and lower part) of senarmontite powders circulated through a (magneto-) hydrodynamic device at 5 L/min for 30 min: with magnets mounted (MHD treatment) (a, c) and without magnets (HD treatment) (b, d). TGA and DSC were performed in air with a heating rate of 4  $^{\circ}$ C/min. The inset shows a zoomed in section of trace a and b between 560 and 580 $^{\circ}$ C.

Detailed analysis of the thermal behavior of the sediments in air (Figure 3) shows a pronounced weight loss starting around 500 °C, followed by an increase in sample weight associated by a strong exothermic peak in the DSC trace. The initial weight loss can be ascribed to sublimation, typically preceding the exothermic oxidation of senarmontite to cervantite [21]. As shown by

TGA, the magnetic treatment significantly decreased the amount of sublimation before the start of the oxidation (Figure 3, C), indicated by an increase in sample weight. DSC in air (Figure 3, A,B) showed the exothermic oxidation peak appearing about 10 °C earlier for the magnetically treated sample as compared to samples experiencing HD treatment only (without magnetic field). Evaluating the thermal behavior in a 90 % oxygen atmosphere, the difference in oxidation temperature between HD and MHD treated samples decreased from 10 to 2 °C (Figure 4B). Although the higher oxygen concentration decreased the difference in oxidation temperature, the magnetically treated particles still showed a 5 % higher oxygen uptake (Figure 4A).



Figure 4: TGA of samples circulated during 30 min through the (M)HD device at 5 L/min. (a) Two experiments with magnets mounted (MHD treatment); (b) two experiments without magnets (HD treatment). TGA was performed in 90 %  $O_2$  with heating rate of 4 °C/min (TA Q500). The inset (B) shows a zoomed in section between 500 and 520 °C

In view of the different sublimation and oxidation behavior of senarmontite and valentinite, the observed reduction of sublimation and the lower oxidation temperature of senarmontite samples after MHD treatment, was interpreted as a strong indication for either a partial conversion of senarmontite into valentinite during the magnetic treatment, or a significant de-stabilization of the senarmontite structure. As the presence of valentinite could not be confirmed by P-XRD, partial conversion of senarmontite would be limited to the formation of a surface-fraction of nano-sized crystalline or amorphous Sb<sub>2</sub>O<sub>3</sub> with a structure potentially resembling valentinite.

### 3.2 Magnetic field-assisted synthesis of Mo-V-Sb mixed oxide catalysts

Non-porous Mo-V-Sb mixed oxide catalysts with a homogeneous bulk composition have been successfully used as catalysts for the oxidation of isobutane [5,13,17–20]. Among these catalysts, high throughput synthesis and combinatorial screening methods indicated  $Mo_8V_2Sb_{90}O_x$  as optimal composition for the selective partial oxidation of isobutane [17–20]. Indeed, the  $Mo_8V_2Sb_{90}O_x$  mixed oxide prepared via a sol-gel procedure resulted in increased isobutene selectivity at the expense of  $CO_x$ . The methacrolein selectivity was almost equal to that of a slurry type reference catalyst [18–20] prepared using the method of Shishido et al. [5,13].

Since the MHD effects on senarmontite oxidation were interpreted as a surface modification and the catalytic action of dense mixed oxides is also limited to the surface, MHD pretreatment was evaluated as an alternative route for synthesis of mixed oxide catalysts. Optimal composition of the synthesis mixture was evaluated by MHD pretreatment of a suspension of senarmontite particles in an aqueous solution containing dissolved  $(NH_4)_3Mo_7O_{24}\cdot 4H_2O$  and  $NH_4VO_3$  salts. Respecting a Mo/V ratio of 4/1, senarmontite suspensions with a total elemental composition  $Mo_{12}V_3Sb_{85}O_x$ ,  $Mo_8V_2Sb_{90}O_x$ ,  $Mo_4V_1Sb_{95}O_x$  and  $Mo_2V_{0.5}Sb_{97.5}O_x$  were recirculated in the MHD

system. After MHD pretreatment, the precipitates were separated from the supernatant solutions, dried and calcined according to a reference method (see sub 2.2) [5].

Comparison of the catalytic activity of the resulting solids showed that overall, isobutane conversion and reaction yield towards methacrolein,  $CO_x$ , and isobutene increased with increasing Mo(V)/Sb ratios (Figure 5). However, Mo<sub>8</sub>V<sub>2</sub>Sb<sub>90</sub>O<sub>x</sub> showed a similar methacrolein yield in combination with an increased isobutene and decreased CO<sub>x</sub> yield as compared to Mo<sub>12</sub>V<sub>3</sub>Sb<sub>85</sub>O<sub>x</sub>. Therefore, Mo<sub>8</sub>V<sub>2</sub>Sb<sub>90</sub>O<sub>x</sub> was considered to be the optimal composition. The optimal elemental composition of the synthesis suspension (Mo<sub>8</sub>V<sub>2</sub>Sb<sub>90</sub>O<sub>x</sub>) matches the optimum bulk composition as identified by Paul *et al.* for acid-catalyzed sol-gel catalysts [18].

Performance of the MHD catalyst with the optimal elemental composition ( $Mo_8V_2Sb_{90}O_x$ ) of the synthesis suspension was compared with a similar catalyst prepared using the reference slurry type synthesis [5,13] (Figure 6). While the isobutane conversion and  $CO_x$  yield versus temperature were much higher for the slurry type catalyst, the yield of desired products (isobutene and methacrolein) for the MHD catalyst was very similar. Because of the consistent suppression of overoxidation and  $CO_2$  formation, the MHD catalyst was considered superior as compared to its slurry type counterpart. This is also evident form the product selectivities shown in Figure S2 (supporting information).



Figure 5: Isobutane conversion, methacrolein selectivity and methacrolein, isobutene and  $CO_x$  yield *versus* temperature for MHD synthesized catalysts with composition  $Mo_2V_{0.5}Sb_{97}O_x$  (•),  $Mo_4V_1Sb_{95}O_x$  (•),  $Mo_8V_2Sb_{90}O_x$  (•) and  $Mo_{12}V_3Sb_{85}O_x$  (•) (See Table 1). Two samples were analyzed for each catalyst at each temperature.



Figure 6: Isobutane conversion, methacrolein selectivity and methacrolein, isobutene and  $CO_x$ , yield *versus* temperature for  $Mo_8V_2Sb_{90}O_x$  catalysts synthesized using MHD pretreatment ( $\blacksquare$ ) and slurry type method ( $\bullet$ ). Two samples were analyzed for each catalyst at each temperature.

The impact of the magnetic field during MHD synthesis was evaluated unambiguously by comparing the performance of MHD synthesized catalyst  $Mo_8V_2Sb_{90}O_x$  with materials resulting from an identical synthesis suspension, treated in absence of the magnetic field, but with the same flow restriction (HD treatment).

XRD patterns for the mixed oxides phases prepared in presence and absence of the magnetic field were recorded before calcination (Figure S4, supporting information). Both patterns were highly similar and contained diffraction lines from senarmontite only. The profile of the reflections of the two samples appeared similar, with a line width in the order of magnitude of the diffractometer resolution. For this reason no further attempt was made to derive particle size and strain from the collected diffraction data. Similar to the observations for pure senarmontite, laser diffraction did not indicate significant differences in particle size distribution for HD and MHD treated catalysts.

While MHD and HD catalysts effected a very similar conversion versus temperature, the MHD catalyst showed higher methacrolein and isobutene yields in combination with a lower  $CO_x$  yield (Figure 7). The HD catalyst exhibited an undesirable high  $CO_x$  selectivity, especially at low conversions, while the isobutene selectivity followed the opposite trend (Figure S5, supporting information). Note the performance of the catalyst obtained after magnetic pre-treatment which is higher than any previously reported results [5,17]. Indeed, a methacrolein selectivity of 40 % is amongst the highest values reported in literature for Mo-V-Sb mixed oxides in the partial oxidation of isobutane.



Figure 7: Isobutane conversion, methacrolein selectivity and methacrolein, isobutene and  $CO_x$  yield *versus* temperature for two  $Mo_8V_2Sb_{90}O_x$  catalysts and a senarmontite ( $\blacktriangle$ ) sample.  $Mo_8V_2Sb_{90}O_x$  catalysts were synthesized using MHD conditions ( $\blacksquare$ ) and HD conditions ( $\bullet$ ) respectively. Two samples were analyzed for each catalyst at each temperature.

Figures 5 and 6 indicate the  $CO_x$  yield as the macroscopic parameter showing the highest sensitivity towards any modification in catalyst synthesis (e.g. slurry vs. MHD, variation in the synthesis composition, etc.). The highly similar  $CO_x$  yields for different MHD synthesized  $Mo_8V_2Sb_{90}O_x$  samples are therefore a direct demonstration of the robustness and reproducibility of this catalytic system (Figure S6, supporting information). Catalyst stability towards deactivation is demonstrated by the comparison of consecutive catalytic runs with a single MHD synthesized  $Mo_8V_2Sb_{90}O_x$  sample indicating a small increase in methacrolein selectivity, while isobutane conversion decreased (Figure S3, supporting information).

XPS revealed that Sb and Mo were completely oxidized after calcination, while the amount of V was too low to distinguish any difference in oxidation state. As shown in Table 2, the Sb/O ratio was lower in materials prepared in presence of the magnetic field. This observation was also confirmed by TGA (Figure 8), showing a significantly higher weight gain upon oxidation for the MHD treated material, as compared to the HD treated variant. According to the Sb/V and Sb/Mo atomic ratios, Mo and V are inclined to settle at the surface instead of penetrating into  $\alpha$ -Sb<sub>2</sub>O<sub>3</sub> particles (Table 2). The V and Mo content of the samples was however too low to detect phases containing these elements (Figure S4, supporting information). In view of the MHD induced surface alteration of senarmontite (supra), it can be expected that the surface sites for HD and MHD treated oxide will be different. This will affect the local interaction of the vanadate and molybdate ions with the surface hydroxyls and can be speculated to induce a difference in the surface complexes formed during synthesis. This could explain the differences in Sb/O and Sb/V ratios as observed by XPS for respectively HD and MHD treated oxides and hence could provide a partial explanation for the MHD effect on catalyst synthesis.

Table 2: Metal-oxygen and metal-metal ratios from XPS on  $Mo_8V_2Sb_{90}O_x$  catalysts synthesized by circulation of the precursors in presence and in absence of the field

Ratio	magnetically treated catalyst	catalyst treated without magnetic field
Sb/O	0.41	0.43
Sb/V	24.90	19.78
Sb/Mo	4.71	4.91
Mo/V	5.28	4.03



Figure 8: TGA of  $Mo_8V_2Sb_{90}O_x$  catalysts synthesized by circulation of the precursors in presence (a,—) and in absence of a magnetic field of 0.33 T (b,---) for 30 min at 5 L/min. Measurement conditions: 100 mL/min  $O_2:N_2$  of 90:10 vol%, 23 mg sample, heating rate of 10 °C/min.

An increased oxygen uptake at the  $Sb^{V}$  sites has however been suggested by Shishido *et al.* as a factor accelerating the mechanism for propane activation [13]. Since propene is an important intermediate in the catalytic reaction mechanism for selective oxidation of propane with Mo-V-Sb mixed oxide catalysts, the formation of isobutene with high selectivity in the partial oxidation

of isobutane with Mo-V-Sb mixed oxide catalysts is an indication that the oxidative dehydrogenation for propane and isobutane should be similar. Because this reaction step occurs on a fully oxidized VSbO4 catalyst surface, the combination of a higher oxygen uptake during calcination with both increased isobutene and methacrolein selectivity was interpreted as confirmation that the formation of isobutene is indeed the first step in the selective oxidation of isobutane to methacrolein.

### **4** Conclusions

A peculiar effect of weak magnetic fields during hydrodynamic treatment of senarmontite suspension was observed to lead to significantly changed oxidation behavior. Comparing magneto hydrodynamic (MHD) with pure hydrodynamic (HD) treatment of an aqueous suspension of senarmontite, the MHD treatment resulted in a decreased sublimation and a faster and higher oxygen uptake during oxidation in air. This effect, though still unexplained, was successfully applied to synthesize superior mixed oxide catalysts. Mo-V-Sb oxide catalysts were prepared using MHD synthesis with an aqueous senarmontite suspension and dissolved (NH<sub>4</sub>)<sub>3</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O and NH<sub>4</sub>VO<sub>3</sub>. With a methacrolein selectivity of 40 %, the performance of the MHD synthesized catalysts for the partial oxidation of isobutane was higher than any previously reported in literature. The increased methacrolein selectivity was achieved in combination with a decreased  $CO_x$  selectivity and increased isobutene selectivity. These results indicate magneto hydrodynamic synthesis as a simple, time-efficient and cheap alternative to the preparation of mixed oxide catalysts via slurry type and sol-gel syntheses. Molecular scale surface analysis and modeling of the MHD catalysts should be the subject of further investigation as this will add key mechanistic information on the action of the magnetic field in MHD synthesis.

## **5** Acknowledgements

E.B. thanks FWO Vlaanderen for a fellowship as Postdoctoraal Onderzoeker. J.E. acknowledges financial support by the "Institute for the Promotion of Innovation through Science and Technology in Flanders (IWT-Vlaanderen)". The Flemish government is acknowledged for long-term structural funding (Methusalem) and the Belgian government for financing interuniversity poles of attraction (IAP-PAI). This work was part of a KU Leuven Interdisciplinary Research Program (IDO). Prof. dr. ir. Gaigneaux, (Unité de catalyse et chimie des matériaux divisés, Université catholique de Louvain) is kindly acknowledged for providing access to XPS.

# **6** References

- [1] J.F. Brazdil, Top. Catal. 38 (2006) 289–294.
- [2] C. Zhang, C. Catlow, J. Catal. 259 (2008) 17–25.
- [3] H. Zhang, K. Sun, Z. Feng, P. Ying, C. Li, Appl. Catal., A 305 (2006) 110–119.
- [4] H. Matsumura, K. Okumura, T.I. Shimamura, T. Miyake, T. Suzuki, J. Mol. Catal. A: Chem. 250 (2006) 122–130.
- [5] T. Shishido, A. Inoue, T. Konishi, I. Matsuura, K. Takehira, Catal. Lett. 68 (2000) 215– 221.
- [6] D.J. Stewart, O. Knop, C. Ayasse, F.W.D. Woodhams, Can. J. Chem. 50 (1972) 690–700.
- [7] J.B. Stelzer, J. Caro, M. Fait, Catal. Commun. 6 (2005) 1–5.
- [8] M.O. Guerrero-Pérez, J.N. Al-Saeedi, V. V. Guliants, M.A. Bañares, Appl. Catal., A 260 (2004) 93–99.
- [9] P. Botella, E. García-González, A. Dejoz, J., L. Nieto, M., Vázquez, J. González-Calbet, J. Catal. 225 (2004) 428–438.
- [10] K. Oshihara, Y. Nakamura, M. Sakuma, W. Ueda, Catal. Today 71 (2001) 153–159.
- [11] W. Ueda, Y. Endo, N. Watanabe, Top. Catal. 38 (2006) 261–268.
- [12] V.H. Rane, U. Rodemerck, M. Baerns, J. Mol. Catal. A: Chem. 245 (2006) 161–166.

- [13] T. Shishido, T. Konishi, I. Matsuura, Y. Wang, K. Takaki, K. Takehira, Catal. Today 71 (2001) 77–82.
- [14] E.M. Gaigneaux, P. Ruiz, E.. Wolf, B. Delmon, Appl. Surf. Sci. 121-122 (1997) 552–557.
- [15] E.K. Novakova, J.C. Védrine, E.G. Derouane, J. Catal. 211 (2002) 226–234.
- [16] J. Al-Saeedi, V. Guliants, Appl. Catal., A 237 (2002) 111–120.
- [17] J.S. Paul, R. Janssens, J.F.M. Denayer, G. V Baron, P.A. Jacobs, J. Comb. Chem. 7 (2005) 407–13.
- [18] J.S. Paul, M.H. Groothaert, C.E.A. Kirschhock, O.I. Lebedev, P.A. Jacobs, W.F. Maier, Catal. Today 91-92 (2004) 265–269.
- [19] J.S. Paul, P.A. Jacobs, P.W. Weiss, W.F. Maier, Appl. Catal., A 265 (2004) 185–193.
- [20] J.S. Paul, J. Urschey, P.A. Jacobs, W.F. Maier, F. Verpoort, J. Catal. 220 (2003) 136–145.
- [21] R.G. Orman, D. Holland, J. Solid State Chem. 180 (2007) 2587–2596.
- [22] G. Semin, J. Mol. Struct. 403 (1997) 253–255.
- [23] G.K. Semin, A.A. Boguslavsky, Chem. Phys. Lett. 251 (1996) 250–251.
- [24] B. Stuyven, G. Vanbutsele, J. Nuyens, J. Vermant, J.A. Martens, Chem. Eng. Sci. 64 (2009) 1904–1906.
- [25] B. Stuyven, Q. Chen, W. Van De Moortel, H. Lipkens, B. Caerts, A. Aerts, L. Giebeler, B. Van Eerdenbrugh, P. Augustijns, G. Van Den Mooter, J. Van Humbeeck, J. Vanacken, V. V Moshchalkov, J. Vermant, J.A. Martens, Chem. Commun. 0 (2009) 47–49.
- [26] S. Kerkhofs, H. Lipkens, F. Velghe, P. Verlooy, J.A. Martens, J. Food Eng. 106 (2011) 35–39.
- [27] J. Emmerich, E. Breynaert, C.E.A. Kirschhock, J.A. Martens, Catal. Today 192 (2012) 63–66.
- [28] D. Orosel, R.E. Dinnebier, V. a Blatov, M. Jansen, Acta Crystallogr., Sect. B: Struct. Sci 68 (2012) 1–7.
- [29] E.J. Roberts, F. Fenwick, J. Am. Chem. Soc. 50 (1928) 2125–2147.
- [30] C.A. Cody, L. DiCarlo, R.K. Darlington, Inorg. Chem. 18 (1979) 1572–1576.
- [31] S.E. Golunski, T.G. Nevell, M.I. Pope, Thermochim. Acta 51 (1981) 153–168.

- [32] V.G. Trofimov, A.I. Sheinkman, G. V. Kleshchev, Sov. Phys. J. 16 (1973) 413–415.
- [33] P.W. Centers, J. Solid State Chem. 72 (1988) 303–308.
- [34] P.S. Gopalakrishnan, H. Manohar, J. Solid State Chem. 16 (1976) 301–306.
- [35] S.E. Golunski, D. Jackson, Appl. Catal. 48 (1989) 123–135.
- [36] W.B. White, F. Dachille, R. Roy, Z. Kristallogr. 125 (1967) 450–458.