



Taking advantage of a priori unwanted catalysts modifications



E. Arendt, E.M. Gaigneaux*

Institute of Condensed Matter and Nanosciences (IMCN), Division MOlecules, Solids and Reactivity (MOST), Université catholique de Louvain, Croix du Sud 2, L7.05.17, 1348 Louvain-la-Neuve, Belgium

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ABSTRACT

A catalyst experiences numerous physico-chemical changes during its life. Often these changes are a priori regarded as 'unwanted' in terms of catalytic performance. However, understanding the details of these transformations offers the opportunity to control them. By distinguishing which changes do contribute to deteriorate the catalytic performance, vs. those that bring improved catalytic behaviours, it becomes possible to channel the system towards specific modifications. Along this strategy, a priori unwanted modifications of the catalysts become beneficial when induced and exploited in suitable conditions. This paper revisits examples wherein such an approach was fruitful: (i) MoO₃ + α-Sb₂O₄ mixtures and (ii) Re–Sb–O compounds, explored in the oxidation of isobutene to methacrolein, (iii) γ-MnO₂ explored in the total oxidation of methanethiol, and (iv) (NH₄)₆P₂Mo₁₈O₆₂ polyoxometalate explored in the oxidative dehydrogenation of 2-butanol to methyl-ethyl-ketone.

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1. Introduction

A catalyst is defined as a material that enhances the rate and selectivity of a chemical reaction and that is cyclically regenerated during the catalytic process. Thus, although a catalyst might undergo temporary modifications in the course of a cycle (e.g., atoms reorganization, superficial reduction, etc.), these are in principle perfectly recovered at the end of the cycle. Precisely, the catalyst starting a cycle, and the catalyst having just performed a cycle, should be identical, with consequently stable catalyst's characteristics and performance with time-on-stream [1].

However, catalytic cycles are in many cases non-ideal. In such cases, the catalyst's state differs between the starting and ending points of the cycle. Accumulating along the successive cycles, initially tiny differences may lead to macroscopic modifications of the catalysts. In such cases, a deactivation of the catalyst is frequently observed, resulting from, e.g., poisoning, fouling, thermal degradation, gas or liquid phase leaching of active species, and attrition [1]. A complete elimination of catalyst deactivation is merely possible. Nevertheless, it is worth envisaging the possibility to take advantage of the modifications of the catalysts. In this spirit, this paper

explores whether a good understanding and control of the modification mechanism would allow minimizing the rate of performance decay, and eventually lead to improved performance.

Modifications of catalysts are, in some specific situations, already known to be beneficial for the catalytic activity. For instance, structural changes undergone by the vanadium–phosphorus oxide (VPO) catalyst in the oxidation of *n*-butane to maleic anhydride directly impact on their catalytic performance [2]. Precisely, the distribution of the oxygen groups and the oxidation state of vanadium dictate the performance, whereas they change during the activation of the catalyst in a way depending on temperature, O₂/butane ratio, flow rate, and water content in the gas atmosphere [3,4]. Hence, Gai and Kourtakis exploited this understanding to demonstrate that active surface defects can be created only in a specific reducing atmosphere applied during the activation period [5]. Another example is the modification of CsH₂PMo₁₂O₄₀ during the oxidation of methacrolein to methacrylic acid [6]. The working catalyst undergoes a migration of Mo, together with the destruction of the Keggin units and the formation of MoO₃. MoO₃ being less active, the phenomenon could thus be foreseen as bringing some deactivation. However, 'free' cationic Mo oxospecies resulting from the Keggin decomposition in the intracrystalline porous system actually corresponds to the truly active species of the catalyst. Thus, the a priori unwanted Keggin decomposition actually induces a beneficial effect on both the activity and selectivity [6].

* Corresponding author. Tel.: +32 10 47 36 65; fax: +32 10 47 36 49.
E-mail address: eric.gaigneaux@uclouvain.be (E.M. Gaigneaux).

The objective of this contribution is twofold. We wish (i) to further report examples confirming that some catalysts are beneficially modified during the catalytic processes, and (ii) to show that, in some cases, it is possible to purposely induce catalysts modifications, sometimes a priori unwanted, with at the end a real advantage on the performance. More precisely, the idea is to illustrate the concept of purposely elaborating catalysts, initially less active but prone to get modified, and using them under conditions favouring the modifications. The target is to obtain better performance as compared to those of classical, initially more active and stable, catalysts.

For this purpose, we revisit the performance and behaviours of four catalytic systems all being chosen in the field of catalytic oxidation on oxide catalysts. These are (i) $\text{MoO}_3 + \alpha\text{-Sb}_2\text{O}_4$ mixtures [7–11], and (ii) Re–Sb–O mixed phases [12,13] in the partial oxidation of isobutene to methacrolein. Then, are addressed (iii) $\gamma\text{-MnO}_2$ in the oxidation of methanethiol, a representative sulfur-containing volatile organic compound [14,15], and (iv) $(\text{NH}_4)_6\text{P}_2\text{Mo}_{18}\text{O}_{62}$ Dawson polyoxometalate in the oxidative dehydrogenation (ODH) of 2-butanol to methyl-ethyl-ketone [16,17].

2. Experimental

2.1. Catalyst preparation

Oriented MoO_3 crystallites (developing preferentially the (010) faces) were synthesized by recrystallization of a commercial powder of molybdenum trioxide (BDH Chemicals, 99.5+%) in a flow of pure O_2 (Air Liquide, 99.995%) at 873 K during 12 h [7,8]. Isotropic MoO_3 crystallites (developing as much as possible the (100) lateral faces) were prepared by decomposing $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ at 773 K in air during 20 h [8].

$\alpha\text{-Sb}_2\text{O}_4$ was obtained by calcination at 773 K in air of Sb_2O_3 (Aldrich, >99%) previously dispersed in concentrated nitric acid at 323 K during 1 h, evaporated under vacuum, washed with distilled water and dried in air at 383 K overnight [9].

Biphasic catalysts were prepared by interdispersion of powders, prepared as described above, in *n*-pentane (Aldrich, 98%, 100 mL of *n*-pentane for 1 g of powder) by mechanical and ultrasonic agitations, followed by evaporation under reduced pressure and drying at 353 K overnight [7–9]. Compositions of the mixtures are mentioned at the appropriate places in the text. The mechanical mixing procedure was checked not to lead to morphological or structural modifications of the compounds mixed together.

SbRe_2O_6 was synthesized by calcining a mixture of $\text{SbOReO}_4 \cdot 2\text{H}_2\text{O}$ (prepared by a hydrothermal method [12]) and metallic Re (Soekawa Chemicals, purity >99.99%) with a 9:5 molar ratio at 773 K during 3 days in an evacuated silica tube [12,13]. The black powder obtained in the centre of the tube was identified as pure SbRe_2O_6 by XRF and XRD.

$\gamma\text{-MnO}_2$ sample was provided by Erachem-Comilog Europe S. A. (Tertre, Belgium) and used as such [14,15]. $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ was purchased from Merck (Ref. 1.059999.1000) [14].

The Dawson $(\text{NH}_4)_6\text{P}_2\text{Mo}_{18}\text{O}_{62}$ compound was synthesized by a procedure inspired from [18]. The identity and purity of the samples were checked by FTIR, Raman, XPS and elemental analyses [16,17].

2.2. Catalysts characterizations

Scanning electron microscopy was achieved on a Hitachi S-570 microscope using 15 kV as accelerating voltage [7–10].

X-ray patterns were performed on a Kristalloflex Siemens D-5000 equipment in the continuous coupled $\theta/2\theta$ scan reflection mode using the $\text{K}\alpha$ radiation of Cu ($\lambda = 0.15418$ nm) for all samples

[6,15–17]. Only for Re–Sb–O samples, a Rigaku Miniflex goniometer was used [12,13].

In situ confocal laser Raman microscopy was done on a Jasco NRS2100 SA spectrometer equipped with an Ar+ laser ($\lambda = 514.5$ nm) and coupled with a liquid nitrogen cooled CCD detector with a resolution of 5 cm^{-1} [12,13].

DRIFT spectra were obtained with a Bruker EQUINOX55 spectrometer equipped with an air-cooled MIR source with KBr optics and a MCT detector [14]. Fourier transformed infra red spectra (FTIR) of Dawson samples were recorded in the transmission mode with the same spectrometer using a DTGS detector. The resolution was then 4 cm^{-1} . Wafers were prepared after diluting the sample in KBr (Janssens Chimica 99+%) by a weight factor of 100 [16,17].

2.3. Catalytic activity measurements

Selective oxidation of isobutene was performed in a fixed bed reactor at 693 K [7–10]. The composition of the gas mixture was isobutene/ O_2 /He = 1/2/7 (vol.) (total flow = 30 mL min^{-1}). The mass of catalyst tested was 0.5 g. The activity was measured during 3 h, after which the catalysts were cooled down in the reactant stream at 7.5 K min^{-1} . Concentrations in reactants and products were measured by on line gas chromatography. For the Re–Sb–O compound, 0.15 g of catalyst powder were tested at 673 K in a total flow of 40 mL min^{-1} [12,13].

The oxidation of methanethiol was performed in a fixed-bed flow microreactor [14,15]. The reaction feed was a 100 mL min^{-1} flow of a mixture of 250 vppm methanethiol (Indugas, 5000 vppm in N_2) and 20 vol.% O_2 (Indugas, 99.995%) in N_2 (Indugas, 99.995%). The catalytic tests were performed with 0.1 g of catalyst, making that the VVH was around $102,000\text{ h}^{-1}$. Before reaction, the catalysts were heated in situ at the reaction temperature under a pure oxygen flow (50 mL min^{-1}). Then before measuring the conversion, the oxygen flow was maintained at the reaction temperature for 30 min. The reactant and the products of the incomplete oxidation were quantified by on line gas chromatography using a flame ionization detector.

For the reaction of 2-butanol, the concentration of 2-butanol (Sigma–Aldrich 99+%) in the reaction mixture was 2 vol.%, and the flow of He (Praxair 4.6) and O_2 (Praxair 4.5) was adjusted to keep the total gas flow constant at 70 mL min^{-1} . The mass of catalyst tested was 0.3 g. In all cases, concentrations of reactant and products were measured by on line gas chromatography [16,17].

3. Results and discussions

3.1. Reconstructions of oxides surfaces during oxidation reactions: the case of $\text{MoO}_3 + \alpha\text{-Sb}_2\text{O}_4$ in the oxidation of isobutene to methacrolein

Gaigneaux et al. investigated the catalytic performance of oriented (with crystals preferentially developing the (010) basal faces) and isotropic (with crystals developing in equal proportions the (010) basal and (100) lateral faces) MoO_3 in the oxidation of isobutene to methacrolein [7–10]. The data agree with the structural specificities of molybdenum trioxide [e.g., 19]. Namely isotropic MoO_3 is active and slightly selective to methacrolein, whereas oriented MoO_3 is merely active and does not yield methacrolein at all (Table 1). In addition to the simplicity of its preparation, the fact that isotropic MoO_3 consists of smaller crystals with a higher specific surface area, likely explains why it is the molybdenum trioxide material classically used in oxidation catalysis.

The mixture of isotropic MoO_3 with $\alpha\text{-Sb}_2\text{O}_4$ exhibits a synergetic improvement of the selectivity to methacrolein. No

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