

Review

Mixed-oxide catalysts with vanadium as the key element for gas-phase reactions

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ABSTRACT

This review deals with an analysis of the main structural and reactivity properties of mixed oxide systems containing vanadium oxide as the key component in catalysts for gas-phase reactions, mainly oxidations. Particular focus is placed on catalysts showing intrinsic bi-functional properties, where the combination of both acidic/basic properties and redox V-sites is a requisite for achieving optimal catalytic performance. For the selected catalytic systems, structure–reactivity correlations that have been proposed in many decades of literature were analysed, with the aim of shedding light on the molecular-level aspects of current processes and facilitating a more rational design of future catalysts.

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1. Introduction

The importance of vanadium as a component of mixed oxide catalysts is well illustrated in Table 1, which summarizes the most significant systems for gas-phase reactions, and their corresponding technology levels [1–7]. In this review, we briefly analyse the main structural and reactivity properties of these systems, and

discuss more in detail the peculiarities of selected examples. A special focus is placed on the role of vanadium in those systems showing intrinsic bi-functional properties, where the combination of both acidic/basic properties and redox V-sites is a requisite for achieving optimal catalytic performance.

2. Vanadium antimonate with rutile structure: an emblematic example for non-stoichiometry in mixed oxides

One of the most-studied systems based on V-containing mixed oxides is derived from V antimonate with rutile structure (Fig. 1); this compound is the main component of the catalyst for propane

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Table 1
Examples of V oxide-based mixed oxides and their catalytic application for gas-phase oxidations.

Mixed oxide	Formula of the main component	Reaction	Technology level
V/M/Sb/O	VSbO ₄ (Rutile structure) (M = Al, W, Sn, ...)	Propane ammoxidation to acrylonitrile	Demonstration
Mo/W/V/O	M ₅ O ₁₄ (Tetragonal) (M = Mo, V, W)	Acrolein oxidation to acrylic acid	Industrial
Mo/V/Te/(Sb)/Nb/O	(Te ₂ O)M ₂₀ O ₅₇ (Orthorhombic) (M = Mo, V, Nb)	Propane ammoxidation to acrylonitrile; Propane oxidation to acrylic acid;	Pilot; Pilot;
V/P/O	(VO) ₂ P ₂ O ₇	Ethane oxidehydrogenation to ethylene	Research
V/P/Mo/O	A ₄ Mo ₁₁ VPMoO ₄₀ (Keggin-type POM) (A = H ⁺ , Cs ⁺ , etc.)	<i>n</i> -Butane oxidation to acrylonitrile Methacrolein oxidation to methacrylic acid; Isobutane oxidation to methacrylic acid;	Industrial; Industrial; Research (pilot);
V/Mg/O	Mg ₂ V ₂ O ₇	Propane oxidation to acrylic acid	Research
W/V/O	A _n BO _x (Hexagonal bronzes) (A = Na ⁺ , Cs ⁺ , etc. and B = W, V, Mo, Nb)	Propane oxidehydrogenation to propylene Glycerol oxidehydrogenation to acrylic acid	Research Research

ammoxidation to acrylonitrile, which was formerly developed by Sohio (later BP and now Ineos), even though it has never been implemented at an industrial level [8–17]. Multi-element systems also containing other trivalent elements (e.g. Fe, Cr, Ga, and Al) have been the subject of several studies, with the aim of both underpinning structural peculiarities and improving the catalytic behaviour [18–44].

The formula of metal antimonates is MeSbO₄; however, the preparation of a truly stoichiometric compound is a difficult task. *Quasi*-VSbO₄ (see below) shows a great structural flexibility and can accommodate up to 1/8th of cation vacancies [45]: a phenomenon which is accompanied by changes in the oxidation state of V. The atomic ratio between Sb and V can also deviate remarkably from the stoichiometry, ranging from a 1:1 ratio up to a large excess of V. However, this does not involve the creation of extended structural defects, but more subtle structural changes in the long- and short-range order. Even though the method of preparation employed affects the nature of the mixed oxide, in general non-stoichiometry is a particular feature of these systems [46–50].

The composition V_{0.92}Sb_{0.92}O₄ (*quasi*-VSbO₄) has been reported for the catalyst having V/Sb atomic ratio 1:1 [49]. This cation-deficient structure, having 0.04 cationic positions unoccupied for each O ion, contains Sb⁵⁺, while vanadium is present both as V⁴⁺ and V³⁺. The electroneutrality is guaranteed for the composition V_{0.28}³⁺V_{0.64}⁴⁺Sb_{0.92}⁵⁺O₄ [51]. However, the ratio between V species can vary depending on the method of preparation, such as the

atmosphere and temperature of thermal treatment; for example, the preparation procedure will affect the number of cationic vacancies (for a V_{tot}/Sb ratio equal to 1.0) within the V_{1-y}Sb_{1-y}O₄ series, with y comprised between 0 (for the ideal stoichiometric compound containing V³⁺ only) and 0.11 [52].

Another possibility is that of having a ratio between Sb⁵⁺ and V other than 1.0. In the series with composition V_{0.9+y}Sb_{0.9}O₄ the number of vacant cation positions ranges from 0.2 (in V_{0.9}Sb_{0.9}O₄) to 0 (V_{1.1}Sb_{0.9}O₄, with full occupancy of the cation sites, and with vanadium present as V_{0.9}³⁺V_{0.2}⁴⁺) [38]. In this case, the V³⁺/V⁴⁺ ratio and the extent of cation site occupancy in the rutile structure are affected by the atmosphere of thermal treatment.

Berry et al. [46,47] described a compound of composition VSb_{1-y}O_{4-2y} in which y ≈ 0.1, which does not formally contain cation vacancies, and which is obtained when the catalyst is thermally treated with oxygen-impure nitrogen. In this mixed oxide, the ratio V³⁺/Sb⁵⁺ is equal to 1.0, and the solid solution is enriched with both V⁴⁺ and O²⁻ ions, which corresponds to a solid solution between stoichiometric VSbO₄ and VO₂ (both showing the rutile structure).

Cationic vacancies considerably affect the catalytic performance of rutile-type mixed oxides in propane ammoxidation [20,23,24,33,44,53,54]. For example, an increased concentration of cationic vacancies and isolated V⁴⁺ species in VSb(Fe)O systems, due to the introduction of increasing amounts of Fe in the lattice, led to a proportionally higher activity [44]. The formation of V⁴⁺ in

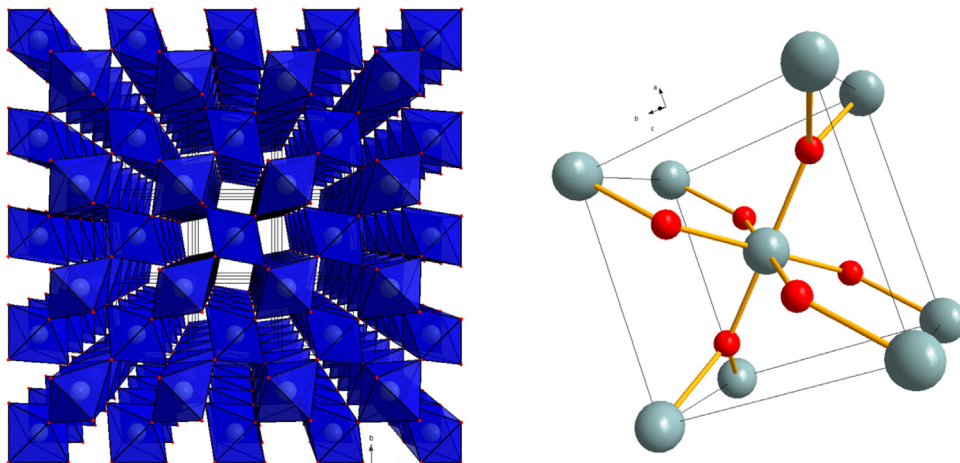


Fig. 1. Left: 3 × 3 × 3 representation. Right: the unit cell of rutile (O atoms are red).

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