

Oxidation of ethane to acetic acid by MoVO-based catalysts

M. Bouchard¹, M. Roussel¹, E. Bordes-Richard¹, K. Khalid²

¹: *Laboratoire de Catalyse de Lille, UMR CNRS 8010, USTL-ENSCL, 59655 Villeneuve d'Ascq Cedex, France*

²: *SABIC R&T, P.O. Box 42503, Riyadh, Saudi Arabia*

Introduction

Phases of the MoVO system are used as catalysts in several reactions of oxidation and more recently in the mild oxidation of propane to acrylic acid and ethane to acetic acid. Dopants are added to this system, and Nb seems to be preferred when ethane is oxidized to acetic acid and/or ethylene [1-5]. Merzouki et al. proposed that MoVNb catalysts could be made up of Mo₅O₁₄-type microdomains embedded in MoO₃ matrix [4]. A new study was undertaken. To catalysts based on MoV_{0.4} composition were added Nb and/or Pd. Their catalytic properties are analyzed in the light of some of their structural characteristics, and the above model is discussed.

Experimental

Catalysts (MoV, MoVNb, MoVPd, MoVNbPd) were prepared according to [6], from ammonium paramolybdate, ammonium metavanadate, and niobium oxalate and/or palladium chloride. After desiccation of the mixture, the resulting powder was calcined in air up to 350°C or 400°C. Solids were analyzed by XRD, Laser Raman Spectroscopy and XPS. Catalytic properties were measured using a conventional flow set-up with fixed-bed reactor fed with C₂H₆/O₂/N₂ = 40/6/54 at GHSV 3,600 h⁻¹ and operated at 260°C, effluents being analyzed by on-line GPC.

Results and discussion

Analyses performed on fresh catalysts show distinct differences according to the calcination temperature and to whether Nb is present or not. Orthorhombic α -MoO₃ is identified in catalysts calcined at T_c = 400°C as seen by its characteristic XRD lines and LRS bands at 992 (Mo=O) and 820 (Mo-O-Mo) cm⁻¹, but not at T_c = 350°C when Nb is present. In the absence of Nb and Pd, three phases are identified besides α -MoO₃ in MoV catalyst. The XRD pattern of Nb-containing samples is characteristic of a mixture of Mo₅O₁₄-type structure (which is known to accommodate cations like V and Nb) and α -MoO₃ nanocrystallites. Such a pattern

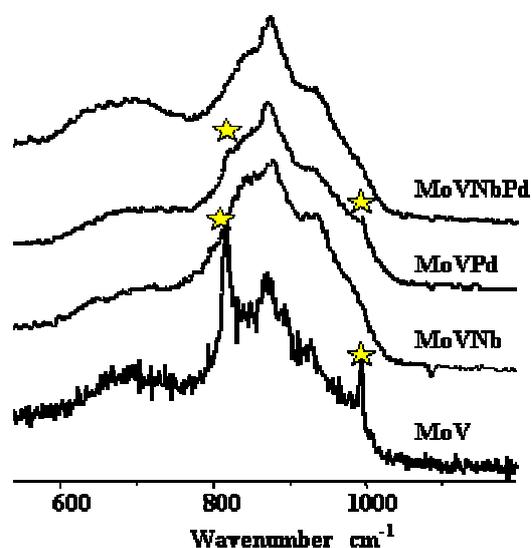


Fig. 1. Raman spectra of catalysts; ★ = MoO₃

has been already observed by other authors for similar compositions but with W in place of Nb and its occurrence related to high catalytic performance in propane oxidation to acrylic acid [7, 8]. Another characteristic pattern of Mo-O-V bonds is found by LRS when Nb is present (Figure 1) [9]. XPS experiments show that Mo and Nb (when present) are in their highest valence while both V(V) and V(IV) are found in fresh catalysts calcined at 350°C or 400°C.

In situ Raman spectroscopy was performed in a specially designed cell [10] at 25-475°C. When H₂ is fed the formation of MoO₂ is observed since 100°C in the abs-

ence of Nb while the pattern characteristic of Mo_5O_{14} -type is retained up to 250°C on MoVNbPd.

These results were confirmed by in situ HT-XRD performed in the same conditions. Thermal analyses were carried out in redox conditions at 400°C . Samples were heated quickly up to 400°C in nitrogen, then H_2/N_2 was allowed to flow. After reduction and sweeping with nitrogen, the reoxidation by air was observed. The rate of reoxidation is always at least ten times higher than the rate of reduction, as commonly observed with all Mo-based oxide catalysts. As it will be discussed, the role of Pd and Nb on reduction/reoxidation steps and on the deepness of reduction is different. Their combination results in an adjustment of the redox properties of the $\text{MoV}_{0.4}$ system which fits the trend exhibited by conversion of ethane (Figure 2). Since the most productive catalysts are made up from $(\text{Mo},\text{V},\text{Nb})_5\text{O}_{14}$ -type structure and α - MoO_3 nanocrystallites, the model (Figure 3) seems still topical.

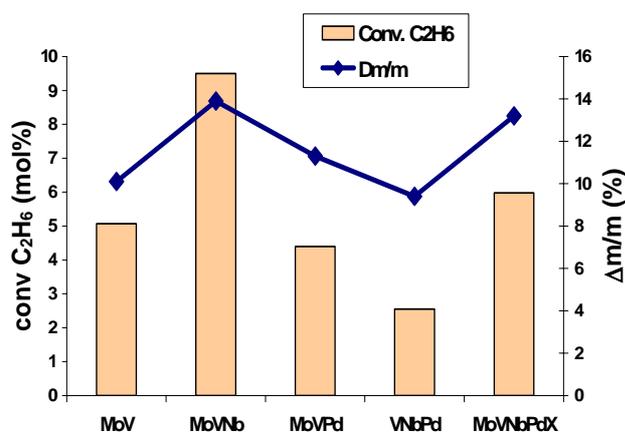


Fig. 2. Parallel trend between conversion of ethane and deepness of the reduction step ($\Delta m/m$, %) as measured in H_2 by TGA.

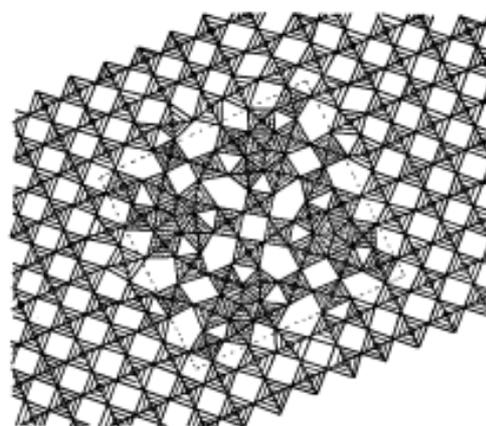


Figure 3. Idealized model of $(\text{Mo},\text{V},\text{Nb})_5\text{O}_{14}$ microdomain in α - MoO_3 (after [4]).

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