



Amoxidation of ethylene to acetonitrile over vanadium and molybdenum supported zeolite catalysts prepared by solid-state ion exchange

B. Rhimi^{a,*}, M. Mhamdi^{a,b}, A. Ghorbel^a, V. Narayana Kalevaru^c, A. Martin^c, M. Perez-Cadenas^d, A. Guerrero-Ruiz^d

^a Université de Tunis El Manar, Faculté des Sciences de Tunis, Laboratoire de Chimie des Matériaux et Catalyse, 2092 Tunis, Tunisia

^b Université de Tunis El Manar, Institut Supérieur des Technologies Médicales de Tunis, 9 Avenue du Docteur Zouhaier Essafi, 1006 Tunis, Tunisia

^c Leibniz-Institut für Katalyse e. V. an der Universität Rostock, Albert-Einstein-Str. 29a, D-18059 Rostock, Germany

^d Dpto. Inorganic and Technical Chemistry, Faculty of Sciences, UNED, 28040 Madrid, Spain

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ABSTRACT

This work reports on the investigation of the influence of the parent zeolite topology (MFI, MOR and USY) on the amoxidation of ethylene to acetonitrile over vanadium and molybdenum oxide supported zeolite catalysts. The physico-chemical properties were investigated by several characterization techniques such as XRD, N₂-adsorption, ²⁷Al MAS NMR, TEM, XPS, DR UV–vis, Raman and DRIFT spectroscopies and H₂-TPR. From the catalytic results, V and Mo oxide species in USY and MOR zeolites led to less active catalysts when compared to MFI structure. These results suggest that the catalytic performances depend strongly on the zeolite structure and thus, the size of the formed metal oxide particles. The catalytic activity and selectivity are controlled by the porous structure and the chemical state of V and Mo species. The extent of dispersion and reducibility of supported M–O_x (M=V or Mo) species are governed by the chemical identity of the support as detected by TPR analysis and optical absorption spectroscopy. The good catalytic performance of MFI-type zeolite might be related to the high dispersion of metal oxide species and to the internal pore space which permits an effective accessibility of the reactants.

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1. Introduction

Amoxidation of ethylene into acetonitrile has been the subject of great interest in recent years because acetonitrile is basically used as a solvent and as an educt in several organic and inorganic syntheses [1,2]. In addition the nitrile group can be easily converted by means of hydrogenation, hydration or hydrolysis reactions to amines, amides, imines and other functional groups which are very useful compounds in polymer and pharmaceutical industry [3]. Acetonitrile is typically obtained as a by-product during propylene amoxidation to acrylonitrile [4]. But recent developments have indicated the possibility of selective one-stage synthesis of acetonitrile from ethane and ethylene by amoxidation [5–7].

There is considerable interest in converting light alkanes directly to higher value organic chemicals because of the low cost and abundance of the alkanes. However, alkanes are chemically

stable, which poses a tremendous challenge to achieve a high selectivity in their conversions. As an alternative, many research groups [7,8] have reported that ethylene can be efficiently converted to acetonitrile by amoxidation since ethylene is a reactive hydrocarbon and a major intermediate product for the ethane amoxidation reaction.

Recent literature has focused on the design and development of active and selective catalysts that can allow the effective transformation of olefins into nitriles. Current commercial catalysts for nitrile production are based on metal oxides or supported metal oxides such as vanadium oxide, combined with other metal oxides like MoO₃ or WO₃. However, metal oxide-like systems were not found to be highly active in amoxidation of ethylene to acetonitrile. In the past few years, zeolites have been used as efficient support for catalysts in the amoxidation reaction. Recently, Li and Armor [6,7], Mies et al. [9] and Mhamdi et al. [10–13] found that Co/zeolite and Cr/zeolite based catalysts afford much better performance with a very high reaction rate and selectivity to acetonitrile than previously reported metal oxide catalysts.

* Corresponding author. Fax: +21671871666.

E-mail address: rhimi.baker@gmail.com (B. Rhimi).

It is well known that at low loading, transition metal ions (TMIs) in zeolites preferably occupy exchange sites and preferentially coordinate with the framework oxygen atoms. As a consequence TMIs are present in the form of isolated species after exchange, as Lewis-acid centers, with a high site density not usually achievable by bulk or supported metal oxides. However, metal oxide particles located at the zeolite external surface and/or in the void zeolite space can be formed during the ion exchange process and/or during subsequent calcination which exhibit different redox properties compared to the cationic species. In addition, it has been demonstrated that isolated and oligonuclear metal species in the zeolite channels are the active sites in ammoxidation of light hydrocarbons [14].

Molybdenum containing zeolite catalysts have been found to be effective in the conversion of methane into aromatic compounds such as benzene [15,16] and in ammoxidation of propane to acrylonitrile [17], and there is interest for optimizing these catalysts in terms of selectivity and activity. In recent years, more and more attention has been paid to the incorporation of various transition metals particularly the vanadium [18–20] to molybdenum-based parent catalysts in order to achieve more satisfactory catalytic performance. Besides the metal, the nature of support employed in terms of surface area, metal-support interaction and acid-basic sites influence the catalytic performance. It has been shown that the type of zeolite structure is an important factor affecting the activity of catalysts. The comparison between different kinds of zeolites as supports can be useful for understanding the nature of interaction existing between the support and the active site.

In view of the potential use of zeolites as a catalyst support, in the present study, a series of V-Mo-zeolite catalysts with different zeolite structures (MFI, MOR and USY) were prepared and characterized by several characterization techniques. The main objective was to analyze the effect of the zeolite topologies on the physicochemical properties of V and Mo exchanged solids and their catalytic behavior in the ammoxidation of ethylene into acetonitrile. To the best of our knowledge, there are only a few reports in the literature on the usage of bimetallic zeolite based catalysts for ammoxidation reactions in general and ethylene in particular. Against this background, the present study is aimed at exploring the potential of various bimetallic exchanged (V and Mo) zeolites based catalysts for the ammoxidation of ethylene to acetonitrile.

2. Experimental

2.1. Catalysts preparation

Parent zeolites: H-ZSM-5 (Si/Al = 15), NH₄-MOR (Si/Al = 10) and H-USY (Si/Al = 15) are commercial samples supplied by Zeolyst, Zeocat and Rhodia, respectively, that were used as support materials. Vanadium and molybdenum were supported onto zeolite by solid-state ion exchange method in two steps. At first, 1 g of zeolite and ammonium metavanadate NH₄VO₃ (98%, PROLABO) with a vanadium content of 2 wt% were finely ground and mixed in a mortar for 15 min at ambient conditions. The resulting mixture was then heated in a helium flow (30 mL/min) up to 500 °C (heating rate: 2 K/min) and left at 500 °C overnight (12 h). Then the obtained solid was finely ground and mixed with the molybdenum acetylacetonate precursor (98%, MERCK) in the molar ratio ((V + Mo)/Al = 1 in the case of ZSM-5 zeolite) and heated again for 12 h at 500 °C in a flow of helium. Finally the catalysts were calcined in oxygen for 1 h at 500 °C. The prepared V-Mo-Z catalysts are denoted as V_xMo_y-Z, where x means vanadium content (2 wt%), y is the (V + Mo)/Al molar ratio and Z is the parent zeolite (MOR, USY, ZSM-5). V₂-ZSM-5, Mo₁-ZSM-5 and V₂O₅/ZSM-5 solids serve as references in catalytic runs. V₂-ZSM-5 and Mo₁-ZSM-5 samples were prepared by mixing

in a mortar, i.e., 1 g of H-ZSM-5 and NH₄VO₃ (2 wt%) or molybdenum acetylacetonate (molar ratio Mo/Al = 1), followed by helium treatment at 500 °C for 12 h (30 cm³/min, heating rate 2 K/min). In addition, V₂O₅/ZSM-5 solid was also prepared by mixing in a mortar, i.e., 1 g of H-ZSM-5 and V₂O₅ (2 wt%; 99%, MERCK).

2.2. Catalysts characterization

The surface area of the catalyst samples and the adsorption/desorption isotherms were determined with a Micromeritics ASAP-2020 analyzer by nitrogen adsorption at -196 °C. X-ray diffraction (XRD) patterns were obtained on an X-ray Diffractometer from PANalytical using Cu-K α radiation. A step scan mode was applied at 0.2°/min and structural data for reference compounds were taken from the ASTM X-ray powder data files. The elemental analysis (Mo, V, Si, Al) of the catalysts was determined by inductively coupled plasma (ICP, Optima 3000XL, PerkinElmer). UV-vis spectra of Mo and V species were monitored on UV-vis spectrophotometer PerkinElmer Lambda 45 equipped with a diffuse reflectance attachment with an integrating sphere coated with BaSO₄ (DR UV-vis). BaSO₄ was chosen as diluent to minimize absorbance as well as used as baseline standard. FTIR spectra were recorded on a PerkinElmer (Spectrum BX) spectrometer in the wavenumber range 4000–400 cm⁻¹ using the KBr technique. Spectra were recorded in air using a 4 cm⁻¹ resolution. Raman spectra were obtained with a confocal Thermo Scientific DXR Raman device using a laser source at 532 nm. ²⁷Al MAS NMR spectra were recorded at 78.20609 MHz on a Bruker WB spectrometer using AlClO₃·6H₂O as reference. An overall 4096 free induction decays were accumulated. The excitation pulse and recycle time were 6 s and 0.06 s, respectively. DRIFTS experiments were carried out with a Bruker IFS 55 spectrometer equipped with a Thermo Spectra Tech reacting cell at a spectral resolution of 4 cm⁻¹ and accumulating 200 scans. Samples were treated in situ at 500 °C under helium (ramp: 5 K/min, flow: 30 cm³/min). H₂-TPR (temperature programmed reduction) analysis was performed with a Micromeritics Autochem 2910 Analyser using a quartz U-tube reactor and an on-line thermal conductivity detector (TCD) for gas analyses. The catalyst (70 mg) was dried at 500 °C for 1 h in air and reduced from 50 to 1000 °C (10 K/min) under 5% H₂/Ar flow. NH₃-TPD (temperature programmed desorption) analysis was performed with a Micromeritics Autochem 2910 analyzer. As the automatic NH₃-TPD program included a pretreatment in air, the sample (40 mg) was first exposed to an air flow (10 cm³/min) at 500 °C for 1 h, then saturated with flowing ammonia at 100 °C and flushed with helium at the same temperature. Finally, the temperature was ramped to 700 °C at a rate of 10 K/min. Quantitative analysis was performed by means of a TCD. Transmission electron microscopy (TEM) studies of the samples were performed using a JEOL JEM-2100 FX microscope at 200 kV, with a CCD ORIUS SC1000 (Model 832) camera and XEDS (OXFORD INCA) microanalysis system. The samples were prepared by grinding and ultrasonic dispersal in methanolic solution. X-ray photoelectron spectroscopy (XPS) was carried out with an Omicron spectrometer equipped with an EA-125 hemispherical electron multichannel analyzer and a source of X-ray provided by Mg filament (K α) having radiation energy of 1253.6 eV at 150 W and a pass energy of 50 eV. The samples (0.02 g) were slightly pressed into small pellets of 15 mm diameter and then mounted on the sample holder. Every sample was introduced into the chamber where they were degassed for 6–8 h, in order to achieve a dynamic vacuum below 10⁻⁸ Pa prior to analysis. Spectra were analyzed with CasaXPS software and RSF database by fitting after Shirley background correction.

Ammoxidation of ethylene was carried out in a fixed bed down flow micro reactor at ambient pressure. The amount of catalyst used was 0.05 g for all runs. In general, the inlet reactant composition was

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