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ScienceDirect
Journal of Catalysis 245 (2007) 369–380
JOURNAL OF CATALYSIS
www.elsevier.com/locate/jcat

Structural evolution of $H_4PVMo_{11}O_{40}\cdot xH_2O$ during calcination and isobutane oxidation: New insights into vanadium sites by a comprehensive in situ approach

A. Brückner [a,*,1], G. Scholz [b], D. Heidemann [b], M. Schneider [a], D. Herein [a], U. Bentrup [a], M. Kant [a]

[a] *Leibniz-Institut für Katalyse an der Universität Rostock e.V., Außenstelle Berlin, Richard-Willstätter-Str. 12, D-12489 Berlin, Germany*
[b] *Humboldt-Universität zu Berlin, Institut für Chemie, Brook-Tailor-Str. 2, 12489 Berlin, Germany*

Received 19 July 2006; revised 3 November 2006; accepted 6 November 2006

Dedicated to Prof. Dr. Bernhard Lücke on the occasion of his 70th birthday

Abstract

$H_4PVMo_{11}O_{40}\cdot 8H_2O$ was studied during thermal activation as well as during isobutane oxidation by simultaneous in situ-EPR/UV–vis/Raman spectroscopy, in situ-FTIR spectroscopy, and quasi-in situ-^1H and -^{51}V-MAS-NMR. In as-synthesized form, most V sites are pentavalent, octahedrally coordinated, and located within the intact Keggin anions. Stepwise dehydration in N_2 up to 350 °C leads to partial reduction and disintegration of the V sites from the Keggin units, followed by their condensation on the outer surface of the latter in square-pyramidal form. In water-free $H_4PVMo_{11}O_{40}$, only V^{5+} (not V^{4+}) is stable inside the Keggin unit. Thus, disintegration of V from the latter is favored by its reduction to the tetravalent state and thus depends on the redox properties of the atmosphere. Active sites in isobutane oxidation are most likely composed of single $O_4V^{4+/5+}{=}O$ species connected to Mo^{6+} via oxygen bridges. Partial deactivation occurs by formation of carbon-containing deposits.

Keywords: Heteropoly acid; In situ spectroscopy; EPR; Raman; FTIR; XRD; Solid state NMR; Selective oxidation

1. Introduction

Vanadium-containing polyoxometallates with Keggin-type structure, particularly those consisting of $[PVMo_{11}O_{40}]^{4-}$ units ($PVMo_{11}$), and their salts have been revealed to be promising catalysts for the selective oxidation of various hydrocarbons, for example, for the oxidation of methacrolein (MAC) to methacrylic acid (MAA) [1–3], the oxidative dehydrogenation of isobutyric acid to MAA [4–7], and the direct oxidation of isobutane to MAC and MAA [8,9].

Both $H_3PMo_{12}O_{40}\cdot xH_2O$ (PMo_{12}) and $H_4PVMo_{11}O_{40}\cdot xH_2O$ ($PVMo_{11}$), as well as their salts, have been subject of a number of spectroscopic studies performed during or after thermal dehydration in a flow of air or inert gas, as well as during or after exposure to different reactive gases such as methanol [10–12], ethanol [10], propene [13–15], methacrolein [2,3], and mixtures of these gases with oxygen. The main aim of all these studies was to elucidate the nature of the active phase formed from the as-synthesized compounds during thermal treatment and equilibration under various atmospheres. Despite numerous earlier studies, this issue remains controversial. In the case of PMo_{12}, certain authors assume that Mo ions are expelled from the complex anions, leaving behind so-called lacunary Keggin units with one or more Mo defects [2,13,15]. However, the connection of two additional Mo atoms (released by thermal decomposition and amorphization of a part of PMo_{12}) to the remaining intact Keggin units, followed by formation of a new $(MoO_x)_{0.5}PMo_{14}O_{42}$ phase, has also been discussed. The catalytic activity in the oxidation of MAC has been attributed to the latter phase, whereby no information about the role of the amorphous material was given [3].

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[*] Corresponding author. Fax: +49 30 6392 4454.
E-mail address: angelika.brueckner@catalysis.de (A. Brückner).

[1] Leibniz-Institut für Katalyse an der Universität Rostock e. V., Außenstelle Berlin, P.O. Box 96 11 56, D-12474 Berlin.

0021-9517/$ – see front matter © 2006 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcat.2006.11.004

In general, a higher catalytic performance in the selective oxidation of isobutane has been observed for $PVMo_{11}$ in comparison with its vanadium-free PMo_{12} counterpart [8]. This suggests that V might be part of the active site in $PVMo_{11}$. However, the structural evolution of those V sites during treatment in various atmospheres is uncertain. Quite a few papers have discussed the disintegration of V from the Keggin units and its transport into counterion positions between the remaining lacunary Keggin anions [4–6,9,11,12]. From in situ-XRD measurements, it was concluded that a vanadyl salt of the water-free heteropolyacid is formed during selective oxidation of isobutyric acid [5]. However, it has also been claimed that it is not the V, but rather the Mo ions that are disintegrated from the $PVMo_{11}$ Keggin unit and move into cation positions, forming a cubic $Mo_x[PVMo_{11-x}O_{40}]$ salt, which is believed to be the carrier of catalytic activity in propene oxidation [14]. In the ideal $H_4PVMo_{11}O_{40}{\cdot}xH_2O$ structure, with all metal atoms being part of the Keggin anion, Mo and V should exist in their highest oxidation states. However, in most real $PVMo_{11}$ materials, a certain amount of reduced VO^{2+} species is detected [4,12,16]. Moreover, XAS, UV–vis and EPR studies have shown that a marked reduction of Mo^{6+} and/or V^{5+} occurs under particular reaction conditions [11,12,14,15], the degree of which depends on the reducing agent. For example, methanol was found to be much more reducing than ethanol [10].

From ^{31}P ENDOR and HYSCORE measurements, it has been derived that reduced VO^{2+} species are not part of the Keggin anions, because the V^{4+}–P distance of 0.68 nm is too long [16]. It was concluded that VO^{2+} is located in the structural voids between the latter in the parent hydrated form and condenses on the surface of the Keggin units on dehydration. However, it remains an open question as to whether the V^{4+} detected under various reaction atmospheres arises from reduction of V^{5+} on disintegration from the Keggin units under these conditions or from reduction of V^{5+} that was never incorporated into the complex anions, even in the as-synthesized $PVMo_{11}$. As for V^{4+}, evidence for the incorporation of V^{5+} in the Keggin anions is not doubtless. Thus, an anisotropic ^{51}V-NMR signal with components at −314 and −971 ppm has been attributed to octahedral V^{5+} inside the Keggin anion of as-synthesized $PVMo_{11}$ [6]. It disappeared on calcination in air at 320 °C in favour of an isotropic line at −668 ppm assigned to tetrahedral V^{5+} outside the Keggin units, which was taken as an evidence for the disintegration of V^{5+} from the latter during calcination. Other attempts to identify V as part of the complex anion in $PVMo_{11}$ are based on IR measurements revealing a split band for the P–O stretching vibration in as-synthesized $PVMo_{11}$ that turned into a single band on calcination [9].

Given that vanadium is an initial constituent of the $PVMo_{11}$ Keggin anion and becomes disintegrated on thermal treatment/reduction, the stability of the latter will be crucially related to the reduction potential of the reaction mixture, which might differ markedly depending on the hydrocarbon. Thus, a generalization of the behaviour of $PVMo_{11}$ during selective oxidation of different hydrocarbons would be doubtful. As mentioned above, $PVMo_{11}$ belongs to the most effective catalysts for direct oxidation of isobutane to methacrolein and methacrylic acid but suffers from rapid deactivation [8,9]. This reaction is interesting from an industrial standpoint, because it is a one-step process based on an inexpensive feedstock and has negligible environmental impact. It could be an attractive alternative to the traditional acetone-cyanohydrin process, which comprises several steps and is environmentally harmful due to toxic raw materials, and the stoichiometric production of NH_4HSO_4 as an undesired side product. Against this background, it is surprising that almost no in situ studies have been reported on the behaviour of $PVMo_{11}$ under selective isobutane oxidation conditions, which might deviate from those of other hydrocarbons due to different reduction potentials, as mentioned above.

The aim of this work is to gain deeper insight into the structural evolution of V species being most likely part of the active site in $H_4PVMo_{11}O_{40}{\cdot}xH_2O$ in the partial oxidation of isobutane. Therefore, $PVMo_{11}$ was studied during the latter reaction as well as during activation in N_2 and air for the first time with the novel simultaneous in situ EPR/UV–vis/Raman/on line-GC technique [17], which provides information on structural changes of the catalyst by three spectroscopy measurements obtained simultaneously in a single experiment. In addition, in situ-FTIR spectroscopic investigations and ^{51}V- and ^{1}H-MAS-NMR studies of as-synthesized and calcined samples were performed to elucidate the active state of $PVMo_{11}$.

2. Experimental

$H_4PVMo_{11}O_{40}{\cdot}xH_2O$ was prepared from MoO_3, V_2O_5, and 85% phosphoric acid as described elsewhere [18]. Briefly, 22.3 g of MoO_3 and 1.3 g of V_2O_5 were added to 350 ml of deionized water, and the mixture was heated to reflux. Then 1.7 g of 85% phosphoric acid was added in three equal aliquots, followed by 150 ml of deionized water. After 15 h of reflux with vigorous stirring, the insoluble oxides had dissolved, and a deep-orange solution was formed. The liquid was evaporated, and a bright-orange solid was obtained. Thermal analysis (Netzsch STA 409; heating rate, 10 K/min; 50 ml/min N_2) revealed that the crystal water content was 8 H_2O. The water content was calculated from the mass loss during the first TG step between 100 and 250 °C, which is due to the release of crystal water.

For the in situ FTIR investigations, the sample was dispersed in ethanol and coated on an infrared transparent Si wafer (1 mm thick, 18 mm in diameter). During this manipulation, the orange colour of the sample remained unchanged, suggesting that the sample was not reduced in ethanol suspension. The wafer was placed in a heatable and evacuable IR cell with KBr windows, connected to a gas dosing/evacuation system, and heated in air or 20% isobutane/N_2 flow (40 ml/min) at a rate of 5 K/min. The spectra were recorded with a resolution of 2 cm^{-1} over 100 scans, using a Bruker IFS 66 spectrometer. Then the spectra of the pure Si wafer at appropriate temperatures were subtracted.

In situ EPR, UV–vis, and Raman spectra during calcination in N_2 or air flow and during treatment in a reactant atmosphere were recorded simultaneously as described in detail elsewhere [17]. Briefly, an UV–vis fibre optical sensor connected to an AVASPEC fibre optical UV–vis spectrometer