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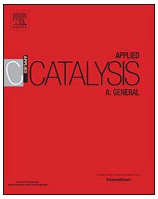

Feature Article

Effect of cobalt location in Keggin-type heteropoly catalysts on aerobic oxidation of cyclooctane: Experimental and theoretical study

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ABSTRACT

A combined experimental and theoretical study of the effect of the polyatom nature (W or Mo) and/or the location of the Co dopant within the heteropoly compound structure on the aerobic liquid phase oxidation of cyclooctane has been carried out. Compounds monosubstituted with Co, either in the cationic position, i.e., $CoHPW(Mo)_{12}O_{40}$, or within the Keggin anion, i.e., $TBA_4HPW(Mo)_{11}CoO_{39}$ (TBA = tetrabutylammonium) were synthesized and their identity confirmed by characterization with XRF, FTIR, and UV-vis. Oxidation of cyclooctane proceeded via autooxidation mechanism. Experimentally observed patterns of the catalytic behavior depended on the polyatom nature (W or Mo) and/or the location of the Co dopant within the heteropoly compound structure. In general, Mo-based catalysts proved more active than their tungsten counterparts, and location of Co within the Keggin unit more beneficial than addition of cobalt as a counter cation. DFT modeling of Co-substituted Keggin anions and calculations of free enthalpy for the elementary steps of key importance for the chain initiation and the chain propagation/branching provided rationale for the observed effects.

1. Introduction

The main reason which makes heteropoly compounds particularly attractive from the point of view of catalysis is the possibility of tailoring their acid-base and redox properties by an appropriate choice of chemical composition, both within the primary structure of the heteropolyanion, and the secondary structure involving compensating cations [1,2]. The most widely studied heteropoly compounds are based on Keggin anions $(XM_{12}O_{40})^{n-}$. The species consists of central XO_4 tetrahedron containing heteroatom X, surrounded by 12 MO_6 octahedra, where M is usually molybdenum or tungsten [3]. A wide selection of literature exists addressing the compositional versatility of heteropoly compounds (various combinations of X, M and the compensating cations) in relation to catalytic applications [1,2]. One of the aspects of interest is the role of the location of a transition metal center, other than Mo or W, in the heteropoly compound structure, i.e. either in the primary Keggin unit as an addendum center, or as a cation in the secondary structure. This issue has been investigated chiefly in relation to oxidation catalysis by the most studied vanadium-containing Keggin-type heteropoly oxometalates [e.g. 4–18], although no general conclusion as to the preference of a particular location of V dopant was offered. For instance, in oxidation of n-butane over V-containing 12-molybdophosphates, vanadium in the secondary structure resulted in a better selectivity at low conversion, while V centers inside the heteropolyanion were more selective at higher conversions [5]. Superior catalytic properties of Keggin-type molybdophosphates with V in the anion were observed for ethane to acetic acid oxidation [12] or ammoxidation of 2-methyl pyrazine and oxidation of methanol [17,18]. On the other hand, an opposite effect, pointing to the advantageous influence of vanadium in cationic positions, was reported for the partial oxidation of propane [14] and methacrolein [15]. This difference in opinions has been attributed to the ease of structural reconstruction of V-containing heteropoly compounds. In particular, it has been repeatedly demonstrated that V centers can be easily expulsed from the primary structure of the Keggin heteropoly vanadomolybdates to take a counter-cation position and/or form independent species [4–11,13,16,19].

In contrast to numerous studies on the vanadium distribution within the heteropoly catalyst structure, only very few works addressed this issue for other transition elements. The reports deal with the effect of Mn location in the Dawson type tungstophosphates on cycloalkenes oxidation [20], Cu location in 12-silicotungstate compounds on phenol

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hydroxylation [21] and Fe location in 12-molybdophosphates for selective oxidation of isobutane [22]. In both former cases substitution for the addendum atom resulted in a better catalytic performance. For Fe doped catalysts, a reconstruction of the catalysts associated with Fe migration was observed and eventually the catalyst in which Fe was initially in counter-cation positions gave better yield of methacrylic acid than the one obtained from precursor originally containing Fe inside the Keggin structure. Recently, it has been shown that the acidity of Keggin tungstophosphate compounds, and the related activity in anisole benzylation, can be enhanced by doping with niobium, the effect being more pronounced for Nb insertion into the primary structure, as opposed to the location of niobium in the counter cation position [23].

These few examples indicate that also in the case of transition metals other than vanadium, location of the dopant within the heteropoly compound structure has a significant bearing on the resulting catalytic properties. This prompted us to explore this field further, in order to provide more predictive power in designing effective polyoxometalate-based catalysts. The present paper describes our findings concerning the role of cobalt position in the structure of Keggin-type tungstophosphoric and molybdophosphoric compounds in determining their catalytic properties in aerobic oxidation of cyclooctane, a commonly investigated substrate in alkane functionalization involving carbon-hydrogen bond activation. The choice of cobalt has been dictated by its known ability to activate dioxygen [24]. In addition, the study provides insight into the function of the polyatom (Mo or W) in the cycloalkane oxidation process. Theoretical modeling, including first description of $PM_{11}CoO_{39}{}^{5-}$ (M = Mo, W) Keggin anions, has been employed to provide a deeper insight into the nature of the observed phenomena.

2. Experimental

2.1. Materials

Hydrates of $H_3PW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$, referred to as HPW_{12} and $HPMo_{12}$, respectively, were purchased from Sigma-Aldrich and used as received. The intended loading of cobalt in Co-containing heteropoly compounds corresponded to one Co center per one Keggin unit, irrespectively of the cobalt location.

The solids containing cobalt in the primary Keggin were prepared from HPW_{12} and $HPMo_{12}$, following the procedure described in the literature [25]. Obtained materials, of formulae $[(C_4H_9)_4N]_4HPW_{11}Co(CH_3CN)O_{39}$ and $[(C_4H_9)_4N]_4HPMo_{11}Co(CH_3CN)O_{39}$, are referred to as $TBAPW_{11}Co$ and $TBAPMo_{11}Co$, respectively. Catalysts containing cobalt in cationic positions of the secondary structure, represented by cobalt salts $CoHPW_{12}O_{40}$ (referred to as $CoHPW_{12}$) and $CoHPMo_{12}O_{40}$ (referred to as $CoHPMo_{12}$) were prepared according to the procedure described by Tsigdinos [26]. Details of syntheses are presented in Supplementary Materials.

2.2. Experimental methods

Chemical composition of the Keggin anions (W, Mo, P and Co) was determined by means of the X-ray fluorescence (XRF), with an Orbis Micro EDXRF spectrophotometer, using 30 kV radiation. Fourier transform infrared (FTIR) absorption spectra were recorded with a Nicolet 6700 spectrometer. Spectra of solid samples were recorded as KBr pellets in range of 4000–400 cm^{-1}. Spectra of acetonitrile solutions were recorded in attenuated total reflectance (ATR) mode using Smart Ark add on, in the range 4000–650 cm^{-1}. In a typical measurement 1 ml of sample solution was poured onto ATR holder with a 1000 μl Hamilton Gastight syringe. Ultraviolet-visible (UV–vis) absorption spectra of solutions were recorded with Perkin Elmer Lambda 35 double beam spectrophotometer, using quartz cells of 1 cm optical path. Spectra were recorded in 190–1100 nm range. X-ray diffraction patterns (XRD) were recorded with PANalytical X'Pert Pro powder diffractometer using CuK_α radiation.

Aerobic oxidation of cyclooctane was carried out in a homogeneous liquid phase, using acetonitrile as a catalyst solvent. The reaction was performed in a stainless steel batch reactor, under stirring at 700 rpm. The fixed amount of catalyst (corresponding to 2×10^{-6} mol of Keggin anions) dissolved in 1 ml of acetonitrile (0.02 mol) and 60 ml (0.44 mol) of cyclooctane were placed in the reactor. Subsequently the reactor was closed and the system purged with argon to remove air and provide inert atmosphere. The reactor was then disconnected from argon line and heated up to 120 °C. After thermostating the system at 120 °C for 1 h, air under the pressure of 10 atm was introduced into the reactor. The molar ratio of cyclooctane to oxygen was 6.5. After desired time the reaction was stopped by rapid cooling of the reactor in a cold water bath. The reaction mixture was analyzed using Agilent Technologies 6890N gas chromatograph. The content of cyclooctyl peroxide was determined by iodometric titration [27]. In tests checking on the radical character of the reaction, 0.2×10^{-3} mol of radical scavenger 2,6-bis(1,1-dimethylethyl)-4-methylphenol (BHT) was added to the reaction system. The reaction was studied in the kinetic region, which was confirmed in experiments with varying stirring speed.

2.3. Theoretical study

To study the properties of Co^{2+} cation located in heteropoly systems with various geometrical and chemical environments, the Density Functional Theory (DFT) implemented in program package Turbomole, version 6.4 [28] was used. Calculations were based on cluster model. In the calculations, exchange and correlation energies were calculated using the meta-GGA Becke-Perdew-Ernzerhof (PBE) functional [29]. All electron basis sets of def-TZVP quality [30,31] were employed for all atoms except transition metal ions (W, Mo) where pseudopotentials were used [32]. For all studied systems the calculations were performed for all possible spin states and all structures were optimized as a spin unrestricted open shell systems. The spin states with the lowest energies were chosen for further investigation, i.e., MULT1 for $Co(CH_3CN)_6{}^{2+}$, $PMo_{12}O_{40}{}^{3-}$, $PW_{12}O_{40}{}^{3-}$, MULT2 for $PMo_{11}CoO_{39}{}^{5-}$, MULT3 for $PW_{11}CoO_{39}{}^{4-}$, $PMo_{11}CoO_{39}{}^{4-}$, $PW_{11}CoO_{39}{}^{6-}$, $PMo_{11}CoO_{39}{}^{6-}$, $PW_{11}Co(CH_3CN)O_{39}{}^{4-}$, $PMo_{11}Co(CH_3CN)O_{39}{}^{4-}$, MULT4 for $PW_{11}CoO_{39}{}^{5-}$, $PW_{11}Co(CH_3CN)O_{39}{}^{5-}$, $PMo_{11}Co(CH_3CN)O_{39}{}^{5-}$. Geometry optimization was performed in accordance with quasi-Newton-Raphsod method [33]. Geometry was considered to be converged for the following conditions: a) the energy change between two optimization cycles drops below 10^{-6} a.u., b) the maximum displacement element drops below 10^{-3} a.u. and the maximum gradient element drops below 10^{-3} a.u. The influence of the solvent (CH_3CN, dielectric constant ε = 36.6) was taken into account by averaged solvent effect (COSMO-COnductor-like Screening Model) [34]. The studied structures were characterized by various electronic and geometric parameters (bond lengths, bond orders [35,36], energy and composition of frontier orbitals, and spin densities) and total and partial density of states spectra (calculated using AOMix program [37,38]). The harmonic frequencies from DFT optimization were utilized in the calculation of the free Gibbs energy (ΔG) for the studied reactions and/or interactions.

$$\Delta G(T) = Emin + \Delta g(T)$$

where:

Emin – energy calculated for minimum geometry

Δg(T) – thermal correction for the free energy, comprising the zero-point vibrational (ZPVE) and thermal vibrational energy corrections, rotational and translational corrections, and entropic contributions.

Geometries considered in theoretical calculations involved plenary Keggin anions $PW_{12}O_{40}{}^{3-}$ (abbreviated PW_{12}) or $PMo_{12}O_{40}{}^{3-}$ (abbreviated PMo_{12}), anions with Co^{2+} substituted within the primary Keggin structure, represented by the formula $PW_{11}CoO_{39}{}^{5-}$ (abbreviated $PW_{11}Co$) or $PMo_{11}CoO_{39}{}^{5-}$ (abbreviated $PMo_{11}Co$), and