

Partial oxidation of methane over modified Keggin-type polyoxotungstates



S. Mansouri^a, O. Benlounes^a, C. Rabia^b, R. Thouvenot^c, M.M. Bettahar^d, S. Hocine^{a,*}

^a Laboratoire de Chimie Appliquée et de Génie Chimique, Université Mouloud Mammeri - Tizi-Ouzou, BP.17 R.P, 1500 Tizi-Ouzou Algeria

^b Laboratoire de Chimie du Gaz Naturel, Faculté de Chimie, USTH, B.P 32, El-Alia, Bab-Ezzouar 16111, Alger, Algeria

^c Institut Parisien de Chimie Moléculaire, UMR 7201, Université Pierre et Marie Curie Equipe Polyoxométallates Case Courrier 42, 4 Place Jussieu, 75252 Paris Cedex 05, France

^d UMR CNRS 7565, IJB, Faculté des Sciences, Nancy Université, Boulevard des Aiguillettes BP 70239, 54506 Vandoeuvre-lès-Nancy, France

ARTICLE INFO

Article history:

Received 20 March 2013

Received in revised form 5 August 2013

Accepted 6 August 2013

Available online 22 August 2013

Keywords:

Methane
Methanol
Formaldehyde
Oxygenates
Partial oxidation
Polyoxometalates

ABSTRACT

Partial oxidation of methane by molecular oxygen and nitrous oxide was studied in the presence of catalytic amounts of the Keggin-type heteropolyoxometalates of general formula $[PW_{11}MO_{39}]^{(7-n)-}$ with $M = Co(II), Ni(II),$ and $Fe(III)$. The catalysts were prepared by refilling the vacant site of the lacunary precursor $K_7PW_{11}O_{39}$ by the metal additives and characterized by ^{31}P NMR, UV–vis and IR spectra, XRD, TGA/DTA and cyclic voltammetry. The oxidation reaction was performed at atmospheric pressure at 873 or 923 K. Reaction products observed were methanol, formaldehyde, carbon oxides and water. Most prominent results are the following: (i) selectivity to oxygenates as high as 48% (conversion 5%) was obtained; (ii) cobalt and iron doped polyoxometalates were the most active and selective catalysts; (iii) N_2O was more reactive and selective than O_2 . The activity rise was correlated with the increase of the oxidant character of the cluster metal. Kinetic study and catalyst behaviour suggested that reaction paths were different for nitrous oxide and molecular oxygen. For N_2O , methane would be oxidized by MO_2 centres to methoxy species, precursors of both methanol and formaldehyde. For O_2 , methane activation rather involves hydrogen abstraction by the lattice oxygen on $M = O$ centres to form metal-methyl species, the key-intermediates in the oxidation processes.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Catalytic oxidation of methane for the production of methanol or formaldehyde has received much attention in the recent decades [1–6]. Methanol is a key-intermediate in bulk and fine chemistry whereas methane constitutes one of the most abundant natural carbon resources [7–12]. Drawbacks for methane are its undesirable greenhouse gas properties and wastage. Also, in order to solve the twin problems of depletion of fossil fuels and global warming, catalytic oxidation of methane has been widely investigated by using homogeneous [13–16] and heterogeneous [17–21] catalysts under a variety of conditions. Oxidation of methane with biological enzymes has also been explored [22–25].

Many heterogeneous catalysts have been investigated for direct selective oxidation of methane to get high selectivity in C_1 -oxygenates [26–28]. However, the yield of C_1 -oxygenates still remains low, and CO and CO_2 are major products. Also there is a great need to develop better catalysts.

The main types of metal catalysts active for methane oxidation to C_1 -oxygenates have a degree of oxidation exceeding 3+. They include Pd, Mn, Co, Fe, V, Mo and Ga. Silica-supported V_2O_5 and MoO_3 were found to be among the most active and selective catalysts for partial oxidation of methane to formaldehyde [29–32] by using either N_2O [29,30] or molecular oxygen [31,32] as oxidants. The former is more active at low temperatures and the latter at high temperatures [33,34]. Silica-supported Fe_2O_3 is also claimed as a good catalyst for mild oxidation of methane [28,32–34].

The mechanism for partial oxidation of methane to methanol or formaldehyde over metal oxide catalysts have been investigated by many researchers [35–37]. However, despite extensive experimental [38–42] and theoretical [43–48] studies, the chemical processes involved is not entirely understood and still gives rise to controversy. Some studies suggest that methane is directly oxidized to formaldehyde and methanol, and then to CO and CO_2 through consecutive reactions [36,37,46,47]. Others propose the existence of parallel-consecutive scheme [48,49]. Methane oxidation on PdO is believed to follow a redox mechanism of Mars-van Krevelen type [50,51].

Transition-metal-substituted molybdophosphoric heteropolyanions ($PMo_{12-x}M_xO_{40}$, $M = Co, Zr$) are reported to be

* Corresponding author. Tel.: +213 559 631 634/26215232.

E-mail address: shocine.univ.to@yahoo.fr (S. Hocine).

active catalysts in the partial oxidation of methane [52–54]. However, these studies are relatively scarce. Therefore, in this work, CsPW_{12-x}M_xO₄₀ (M=Fe, Co, Ni) solids were evaluated as catalysts in the reaction of partial oxidation of methane to methanol and formaldehyde, using molecular oxygen and nitrous oxide as oxidants. The catalysts were characterized by X-ray diffraction (XRD), ¹⁸³W nuclear magnetic resonance (NMR), ultra violet–visible (UV–vis) and infra-red (IR) spectroscopy, thermal gravimetry analysis (TGA)/differential thermal analysis (DTA) and cyclic voltammetry. Reaction paths to methanol and formaldehyde formation are suggested based on the polyoxometallates reactivity and characteristics.

2. Experimental

2.1. Preparation of catalysts

The acidic potassium salt of [PW₁₁O₃₉]⁷⁻ (abbreviated PW₁₁), was prepared according to the literature method [54,55]. The lacunary heteropolycompounds modified with transition metal ions [PW₁₁O₃₉M]⁽⁷⁻ⁿ⁾⁻, [M=Ni²⁺, Co²⁺, or Fe³⁺, n = oxidation state of M] (denoted PW₁₁M), were obtained by addition of the metal nitrate according [56–58]. For the modified salts, an aqueous solution of the potassium salt K₇PW₁₁·xH₂O was treated with an aqueous solution of M(NO₃)_n under reflux. PW₁₁M samples were precipitated with caesium chloride. They were filtrated, washed with an ethanol/H₂O (1/1) mixture and dried at 353 K.

K₇[PW₁₁O₃₉] (PW₁₁). Elemental analysis: calc. (found) for K₇[PW₁₁O₃₉] (%): K, 7 (9.13); P, 1 (1.034); W, 68.2 (67.51).

Cs₄[PW₁₁O₃₉Fe] (PW₁₁Fe). Elemental analysis: calc. (found) for Cs₄[PW₁₁O₃₉Fe] (%): Cs, 3.90 (4.12); Fe, 1.01 (1.62); P, 0.97 (0.94); W, 57.2 (58.70).

Cs₅[PW₁₁O₃₉Co] (PW₁₁Co). Elemental analysis: calc. (found) for Cs₅[PW₁₁O₃₉Co] (%): Cs, 4.92 (5.22); Co, 1.57 (1.64); P, 0.86 (0.87).

Cs₅[PW₁₁O₃₉Ni] (PW₁₁Ni). Elemental analysis: calc. (found) for Cs₅[PW₁₁O₃₉Ni] (%): Cs, 4.95 (6.02); Ni, 1.67 (1.64); P, 0.87 (0.86); W, 53.2 (56.47).

2.2. Characterization

UV–vis spectra were recorded at 298 K on a UV–vis scanning spectrophotometer (Shimadzu UV-2100PC). A 2.5 mM reaction solution in acetonitrile of each catalyst was sampled, and the solution was diluted with 400 ml acetonitrile (0.5 mM). The absorption spectra were recorded with a Bio-rad FTS 60A spectrometer (spectral range = 4000–300 cm⁻¹) using the KBr pellet technique. Powder XRD data were obtained with a XR Fischer diffractometer using Cu K α radiation in the range 2 θ = 5–65°. Thermogravimetric analyses were performed with a Setaram LabSys 2000 instrument. The measurements were done in nitrogen using a platinum crucible. The heating rate was 5 °C/min and the sample mass was 50 mg.

2.3. Catalytic reaction

The reaction was conducted in a continuous fixed bed reactor at atmospheric pressure with a CH₄/O₂ or CH₄/N₂O mixture (molar ratio 2.5/1) at a flow rate of 2 l/h. The catalyst was pretreated in a flow of nitrogen at the reaction temperatures of 873 and 923 K with a flow rate of 1 l/h. After the pretreatment the gaseous reactants entered the reactor via three mass flow controllers. The products were analyzed by a gas chromatograph (Shimadzu 14B) equipped with thermal conductivity (TCD) and flame ionization (FID) detectors. Carbon monoxide, dioxide and water were analyzed on a Porapak Q column and the oxygenate products on Carbosphere column. The experimental data were recorded after 8 h of reaction.

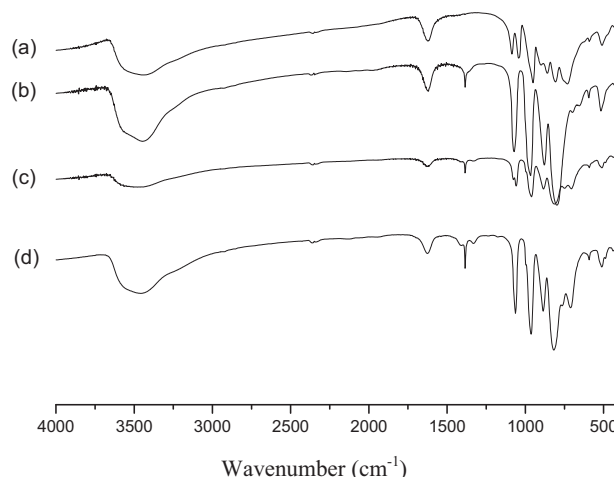


Fig. 1. IR spectra of heteropolytungstates: (a) PW₁₁, (b) PW₁₁Ni, (c) PW₁₁Co, and (d) PW₁₁Fe.

3. Results and discussion

3.1. Characterization of catalysts

The infrared spectra of polyoxometallates (Fig. 1) show strong absorption bands in the range 1100–700 cm⁻¹ region, assigned to W=O and W–O–W stretching vibrations, typical of the transition metal modified lacunary heteropolycompounds [59]. The $\nu_{as}(P-O)$ mode, observed in the 1110–1040 cm⁻¹ region, is the most informative band in the spectra of the tungstophosphates. The vibration of the P–O bonds of the central PO₄ tetrahedron gives rise to only one band, at 1080 cm⁻¹, in the spectrum of the parent Keggin anion, [PW₁₂O₄₀]³⁻ [60]. This band is split into two components (1085–1040 cm⁻¹) in the spectra of the lacunary PW₁₁ and of many PW₁₁M anions, due to the symmetry lowering of the PO₄ tetrahedron [61]. For the PW₁₁Co anions, the value of the ν_{PO_4} splitting ($\Delta\nu = 17$ cm⁻¹), $\Delta\nu$ is lower than that of [PW₁₁O₃₉]⁷⁻ ($\Delta\nu = 45$ cm⁻¹) (Table 1). For PW₁₁Fe and PW₁₁Ni filling the hole of the octahedral lacuna by the Ni or Fe cation restores the symmetry of the central tetrahedron, owing to the interaction between Ni or Fe and the available oxygen of the central PO₄ group (Oa).

In the Keggin structure, intense absorption bands at 200 and 260 nm are caused by charge-transfer of the terminal oxygen and bridge-oxygen to metal atoms, respectively (Fig. 2). For PW₁₁ and

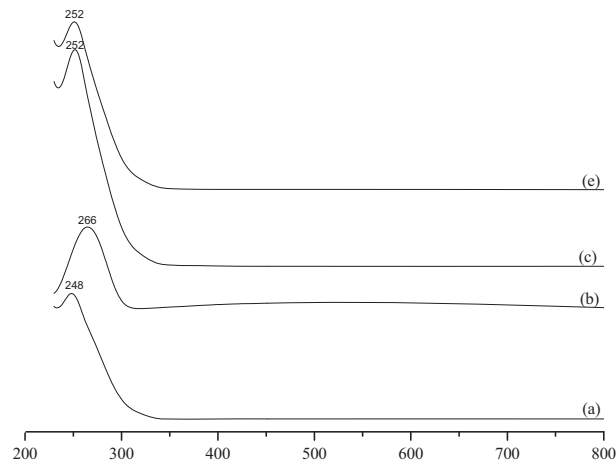


Fig. 2. UV spectra of heteropolytungstates: (a) PW₁₁, (b) PW₁₁Ni, (c) PW₁₁Co, and (d) PW₁₁Fe.

Download English Version:

<https://daneshyari.com/en/article/65670>

Download Persian Version:

<https://daneshyari.com/article/65670>

[Daneshyari.com](https://daneshyari.com)