



Impact of redox properties on dehydration of glycerol to acrolein over heteropolyacids assessed by operando-EPR spectroscopy

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ARTICLE INFO

Article history:

Received 8 February 2010

Received in revised form 7 April 2010

Accepted 19 April 2010

Available online 29 April 2010

Keywords:

Operando-EPR

Glycerol dehydration

Acrolein

Catalyst deactivation

Carbon deposits

ABSTRACT

$H_3PMo_{12}O_{40} \cdot xH_2O$ and $H_4PVMo_{11}O_{40} \cdot xH_2O$ with Keggin structure were supported on $SiO_2-Al_2O_3$ carriers with $Si/Al=0.21$ and 0.32 as well as on Al-MCM-41 ($Si/Al=10$), characterized and monitored by operando-EPR in the dehydration of glycerol to acrolein at 553 K using feed streams of glycerol/ $N_2/H_2O/O_2 = 1/14.1/36.8/0.68$ or $1/14.1/36.8/0$. Upon deposition on the supports, the Keggin anions are degraded into fragments containing about 3–6 metal ions. Both the presence of vanadium as well as small amounts of O_2 in the feed keeps the Mo species in a highly oxidized state. This diminishes slightly the acrolein selectivity but also the condensation degree of the carbon deposits which might favour catalyst stability.

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1. Introduction and objectives

To compensate for the foreseeable depletion of fossil resources, the exploitation of renewable feedstocks for the production of fuels is currently a hot topic in chemical industries. Thus, the production of biodiesel from vegetable oils increased rapidly in the last few years. Biodiesel is produced by transesterification of triglycerides being the main component of vegetable oils. In this process, 1 mol of glycerol is produced as by-product per mol of triglyceride, leading to a surplus of glycerol which in turn causes a price decline. Thus, the sale of glycerol is becoming the bottleneck of biodiesel production, which calls for sustainable and cost-effective alternatives of its use.

One promising opportunity is the acid-catalyzed dehydration of glycerol to acrolein, which is an important intermediate for the production of synthetic fibres, coatings and superabsorbers and is currently produced by partial oxidation of costly and increasingly scarce propylene. Thus, replacing propylene as feedstock for acrolein by cheap and abundant glycerol could be an attractive alternative. There have been several attempts in the past to use solid acids as catalysts for gas-phase dehydration of glycerol to acrolein, among them supported mineral acids [1], $ZnSO_4$ [2], zeolites [1,3], sulfated ZrO_2 and Nb_2O_5 [4]. Recently, heteropolyacids, $H_3[XY_{12}O_{40}] \cdot nH_2O$ ($X=Si, P; Y=W, Mo$) supported on alumina, silica-alumina [5,6], zirconia, titania [5] and active carbon [7] were

found to be promising catalysts for the gas-phase dehydration of glycerol with acrolein yields between 65% and 85%. However, certain zeolites and mesoporous MCM-based materials have also shown high catalytic performance. A recent review in this field has been published by Katryniok et al. [8]. They identified two key properties for high acrolein yields, namely high surface acidity and suitable pore structure.

However, the major drawback of almost all catalysts is their rather fast deactivation by coke deposition. It was found that this is favoured by small pore diameters due to steric limitations but also by high surface acidity which, on the other hand, is required for high acrolein selectivities [8]. From few previous studies it is suggested that co-injection of oxygen into the feed may suppress catalyst deactivation at least partially [9,10]. We anticipated that this undesired behavior can be at least partially suppressed by performing the reaction under oxidative conditions, which should be mild enough to prevent deep oxidation to CO_2 but sufficient to hinder the formation of highly condensed carbon deposits which block active sites.

Therefore, we followed two strategies: (1) introduction of Mo and V as redox-active elements in the heteropolyacid structure and (2) admixture of small amounts of oxygen to the feed. Moreover, the active heteropolyacid components have been supported on silica-alumina carriers of different Si/Al ratios, surface acidity and pore size. Long-term catalytic tests over 50 h and ex situ characterizations have been performed and described recently [11]. The aim of the present study is to derive relations between catalytic, structural and redox properties of $H_3PMo_{12}O_{40}$ and $H_4PVMo_{11}O_{40}$ dispersed on different supports as well as information on the

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nature of the carbon deposits formed in dependence on the feed composition. Therefore, we used operando-electron paramagnetic resonance (EPR) spectroscopy coupled with quantitative analysis of glycerol and acrolein in the effluent gas. Since both the transition metals as well as carbon may be paramagnetic, operando-EPR experiments can shine a light on the nature of carbon deposits and on the behavior of V and Mo ions in relation to acrolein selectivity.

2. Experimental

$\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot x\text{H}_2\text{O}$ was purchased from Merck. $\text{H}_4\text{PVMo}_{11}\text{O}_{40}\cdot x\text{H}_2\text{O}$ was prepared from MoO_3 , V_2O_5 and 85% phosphoric acid as described elsewhere [12,13]. Two commercial silica–alumina mixed oxides with Si/Al ratios of 0.21 (Siralox 20, Sasol) and 0.32 ($\text{Al}_2\text{O}_3/\text{SiO}_2 = 0.16$, Degussa) as well as Al–MCM-41 (Si/Al = 10) were used as supports. These supports were loaded with 20 wt.% of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (HPMo) or $\text{H}_4\text{PVMo}_{11}\text{O}_{40}$ (HPVMo), respectively, by wet impregnation, dried for 2 h at 393 K and finally calcined in flowing air at 623 K for 4 h. Thus prepared samples are labelled as HPMo/0.xx, HPVMo/0.xx or HPMo/MCM and HPVMo/MCM, respectively, in which 0.xx reflects the Si/Al ratio of the commercial silica–alumina supports.

Calcined catalysts were characterized for their BET surface area and average pore diameter by nitrogen adsorption at 77 K (Micromeritics ASAP 2020). Surface acidity was analyzed by transmission FTIR spectroscopy (Bruker IFS 66) of pyridine adsorbed at 373 K on self-supporting wafers after pretreatment in flowing air at 623 K, using the band areas at 1540 cm^{-1} for Brønsted and at 1450 cm^{-1} for Lewis sites [14]. This temperature should be high enough to remove the interstitial crystal water molecules from the heteropoly acid, but not the Brønsted sites in form of structural water [13,15]. UV–vis diffuse reflectance spectra of calcined catalysts were recorded by a Cary 400 spectrometer (Varian) in reflectance mode and converted into Kubelka–Munk functions $F(R)$.

EPR spectra in X-band ($\nu \approx 9.5\text{ GHz}$) were recorded with a cw-spectrometer ELEXSYS 500-10/12 (Bruker) using a microwave power of 6.3 mW, a modulation frequency of 100 kHz and modulation amplitudes of 0.1–0.5 mT. The magnetic field was measured with respect to the standard 2,2-diphenyl-1-picrylhydrazyl hydrate (DPPH). 125 mg of catalyst particles (sieve fraction of 0.315–0.355 mm) were loaded into a homemade quartz plug-flow reactor implemented in the rectangular cavity of the spectrometer [16]. Samples were heated with a rate of 10 K/min in flowing nitrogen (10 ml/min) to 553 K and kept at this temperature for 15 min, before admission of the reactant feed. 12.6 ml/min of pure N_2 or 4.8 vol.% O_2/N_2 were dosed using mass flow controllers (Bronkhorst) and 0.028 ml/min of a 10 wt.% glycerol/ H_2O solution was dosed using a HPLC pump connected to an evaporator. Thus, the molar ratio of the feed components was glycerol: O_2 : N_2 : H_2O = 1:0.68:14.1:36.8 or 1:0:14.1:36.8. Products were collected in a cold trap connected to the reactor outlet and analyzed off-line by a Shimadzu GC 17A equipped with a Chrompack FFAP capillary column. Reaction conditions were chosen such as to achieve almost complete glycerol conversion.

The total spin concentration of used catalysts was determined by measuring the spectra together with that of a spin standard (mechanical mixture of $\text{VOSO}_4/\text{K}_2\text{SO}_4$, 3.98×10^{20} spins/g) in a rectangular double cavity (Bruker) and comparing the total EPR signal intensities (double integrals). Computer simulation of EPR spectra was performed with the program SIM14S of Lozos et al. [17] using the spin Hamiltonian

$$H = \mu_B S g B_0 + S A I \quad (1)$$

Table 1

Pore and surface properties of pure supports and catalysts.

Sample	S_{BET} ($\text{m}^2\text{ g}^{-1}$)	Mean pore diameter (nm)	Brønsted sites ^b (a.u.)	Lewis sites ^c (a.u.)
Si/Al-0.21 ^a	349	8.34	2.2	8.8
HPMo/0.21	300	7.90	7.0	10.3
HPVMo/0.21	259	8.00	10.2	14.3
Si/Al-0.32 ^a	333	11.08	5.4	–
HPMo/0.32	235	11.27	4.9	3.3
HPVMo/0.32	206	11.46	7.8	6.7
Al–MCM-41 ^a	857	2.84	1.0	1.5
HPMo/MCM	611	2.75	3.7	6.7
HPVMo/MCM	408	2.81	4.2	8.4

^a Pure supports.

^b Derived by normalizing the FTIR band area at 1540 cm^{-1} on S_{BET} .

^c Derived by normalizing the FTIR band area at 1450 cm^{-1} on S_{BET} .

in which μ_B is the Bohr magneton, S is the electron spin operator, g is the g tensor, B_0 is the magnetic field vector, A is the hyperfine tensor and I is the nuclear spin operator.

3. Results and discussion

3.1. Properties of fresh catalysts

The BET surface area of the two silica–alumina supported heteropolyacids HPM/0.21 and HPM/0.32 ($M = \text{Mo}, \text{V}$) is markedly lower than that of the MCM-supported catalysts (Table 1). The mean pore diameter of the catalysts depends on the support as well and decreases in the order $\text{HPM}/0.32 > \text{HPM}/0.21 > \text{HPM}/\text{MCM}$. Comparison with the respective values of the pure supports indicates that there is no significant pore blocking upon depositing the heteropolyacids on the supports, although the BET surface decreases. The surface-specific relative amount of Brønsted and Lewis sites is highest for HPM/0.21 and lowest for HPM/MCM. Considering the same support, the V-containing heteropolyacids are slightly more acidic than those containing only Mo (Table 1). As expected, the pure supports contain Brønsted and Lewis sites as well, however, their concentration is lower in comparison to supported catalysts. Therefore, as shown in previous catalytic tests, bare acidic oxide supports show a certain performance in glycerol dehydration, too, although it revealed to be poor in comparison heteropolyacids supported on them [6].

Respective FTIR spectra of pyridine adsorbed on the supports and on the catalysts are shown in Fig. 1. While the band at 1450 cm^{-1} reflects all kinds of Lewis sites and has been used as a relative quantitative measure (Table 1), bands in the region around 1600 cm^{-1} provide information on the strength of the Lewis sites. In the pure supports only one band around 1619 cm^{-1} is seen, which arises from Al sites. In the supported catalysts, an additional band arises from slightly weaker Lewis sites at lower wavenumbers between 1614 and 1609 cm^{-1} , which must be ascribed to pyridine adsorbed on Mo and V sites. Comparison of the FTIR spectra of all catalysts in Fig. 1 suggests that the three catalysts do not differ much in the strength of the acid sites, since the band positions are very similar. The most obvious difference results from the number of the acid sites related to the surface area (Table 1). The relative number of Lewis sites and the respective FTIR spectrum of the bare Si/Al-0.32 support are not shown in Table 1 and Fig. 1 since the relevant spectral range below 1460 cm^{-1} is superimposed by a broad band of ammonium ions which obviously remain in the solid after synthesis. This band which, although much less predominant, is still seen in the supported catalyst (Fig. 1), makes a reliable quantification of the relative amount of Lewis sites impossible for the support Si–Al/0.32.

UV–vis–DR spectra of the supported heteropolyacids differ markedly from those of the unsupported heteropolyacids, already

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