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Dynamic redox properties of vanadium and copper in microporous supports during the selective oxidation of propene

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ABSTRACT

Vanadium(V) and copper(II) were co-deposited into the microporous neutral AlPO-5 and the acidic ZSM-5, obtaining VCu:AlPO-5 and VCu:ZSM-5. In this study we seek to investigate the effect of feed gas composition for the selective oxidation of propene applying C_3H_6/O_2 ratios from 4 to 0.25 over VCu:AlPO-5 and VCu:ZSM-5. The results from catalytic measurements were correlated with *in situ* X-ray Absorption Spectroscopy (XAS) to monitor metal speciation for different feeds. VCu:AlPO-5 produces acrolein over the whole feed composition range, reaching maximum yield (1.5%) for $C_3H_6/O_2 = 0.5$. *In situ* XAS reveal that when the major valence fractions present are the Cu(I)/Cu(II) and V(III)/VIV) redox pairs, the selectivity and activity is improved over VCu:AlPO-5. By comparison, VCu:ZSM-5 produce acrolein for $C_3H_6/O_2 = 1$ and 0.5 only, but with significantly lower yields (0.1% and 0.2%, respectively). At these conditions copper is mainly present as Cu(0), whereas vanadium exists as V(III)/V(IV). We believe activity is governed by the presence of available oxygen associated with a binuclear Cu/V complex in VCu:AlPO-5, not formed in the zeolite. Also, the activity is independent of copper valence state, indicating a possible Cu^0/VO_x interface is present in VCu:AlPO-5.

1. Introduction

Inorganic molecular sieve materials containing transition metal species are highly promising candidates for selective oxidation of linear hydrocarbons due to shape selective properties guiding reactant functionalisation on metal redox sites [1]. Microporous materials can promote reversibility and prevent sintering of the supported active metal, thus increasing catalyst lifetime [2–4]. We have previously reported on copper and vanadium containing AlPO-5 and ZSM-5 being more selective towards acrolein for the oxidation of propene than their monometallic counterparts. Our findings show that the reducibility of vanadium was significantly enhanced by the presence of copper, ascribed to a co-operative effect between vanadium and copper in VCu:AlPO-5 [5]. Secondly, when comparing the neutral AlPO-5 containing vanadium and copper with the acidic zeolite H-ZSM-5 (VCu:ZSM-5), the previous showed improved performance. In addition, sequential treatments between propene and oxygen revealed that VCu:AlPO-5 exclusively formed acrolein under anaerobic conditions. Copper and vanadium in VCu:AlPO-5 and VCu:ZSM-5 undergoes reduction to Cu(0) and V(III)/V(IV) by propene, and are subsequently re-oxidised by molecular oxygen. XAS suggested vanadium and copper are in close proximity in VCu:AlPO-5 under C_3H_6: 4 O_2 reaction conditions, being linked by bridging oxygens (Cu—O—V) which can partake in the Mars–van-Krevelen mechanism [6].

Zhao and Wachs [7] have investigated VO_x species on a range of different oxide supports typically present as isolated or polymeric VO_4 species. In their study various C_3H_6/O_2 ratios were examined to correlate the reducibility of the VO_x surface species with activity/selectivity towards acrolein formation. With increasing C_3H_6/O_2 ratio the reducible behaviour of the V(V) increased, and lead to a combination of V(IV)/V(III) species. Interestingly the acrolein selectivity was almost independent on the various C_3H_6/O_2 ratios, while increasing the O_2/C_3H_6 ratio lead to a rise in turnover frequency (TOF), indicating that the fully oxidised surface VO_4 species were more efficient in acrolein formation than the reduced V(IV)/V(III) fraction.

Copper functionalised on various supports such as SiO_2 and mesoporous SBA-15 can promote both acrolein and propene oxide (PO) [8–11]. There are, however, discrepancies in the literature as to which site is responsible for selectivity. Monnier and Hartley [12] stated that Cu(0) will readily oxidise during epoxidation reactions to Cu_2O and CuO, suggesting that metallic copper is not the active site. Belin et al. [8] studied $CuAu/SiO_2$ catalysts active and selective in production of acrolein from propene by co-feeding with H_2

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and O_2. They suggested the main active site to be copper based, as gold generally leads to PO formation, and EXAFS and XRD confirmed formation of CuO. The presence of gold influenced the performance of the catalyst suggesting that gold and copper were in proximity operating in synergism [8].

The objective of this study is to correlate the vanadium and copper speciation present in VCu:AlPO-5 and VCu:ZSM-5 at different C_3H_6/O_2 ratios with efficacy towards acrolein production. *In situ* XAS at both the Cu and V K-edge is employed to obtain valence fractions and metal surroundings during different C_3H_6/O_2 ratios, also assessing the catalytic behaviour during selective oxidation of propene in the various feed compositions.

2. Experimental

2.1. Catalyst preparation

Synthesis of AlPO-5 is described elsewhere [5]. The as-prepared AlPO-5 was calcined to 650 °C with a ramp rate of 1 °C/min and 17 h dwell time. The commercially available NH_4-ZSM-5 (Si:Al = 140, Zeolyst International) was calcined to 550 °C prior to ion exchange to yield H-ZSM-5.

Metal introduction was performed by a deposition procedure for AlPO-5 and conventional ion exchange for H-ZSM-5, where a solution of the tetravalent vanadyl ion (VO^{2+}, 0.03 M, 30 ml) and copper nitrate ($Cu(NO_3)_2$, 0.03 M, 30 ml) was added to calcined AlPO-5 (1 g) or H-ZSM-5 (1 g) during stirring. This is equivalent to 0.0009 + 0.0009 mol cation/g matrix. The pH was increased to 8.6 by the addition of ammonia (NH_3, 5 M). The suspensions were stirred for 24 h, followed by washing and drying (100 °C, 24 h). Samples were denoted VCu:AlPO-5, VCu:ZSM-5, respectively.

A fraction of the as-prepared samples were calcined in air to 500 °C with a ramp rate of 2.8 °C/min and a dwell time of 180 min.

2.2. Elemental analysis

Elemental analysis was performed on a high resolution Inductive Coupled Plasma Element II. The samples were pre-treated by dissolving in HNO_3 and HF.

2.3. Catalytic measurements

Catalytic measurements were performed using a tubular plug flow quartz reactor placed inside a tube furnace (Carbolite MTF 12/38/250) operating at atmospheric pressure. The products formed were monitored with a GC–MS (Agilent Technologies, 7890A GC, 5975C inert XL MSD) detecting products with retention times up to 15.5 min. The conversion of the feed components, selectivity and yield of reaction products, were calculated by integration of the peaks from the Flame Ionisation Detector (FID) and Mass Spectrometer (MS). Prior to the catalytic measurements the FID was calibrated for propene and acrolein and the MS detector was calibrated for carbon dioxide. Conversions were calculated from the following equation: $\text{Conv} = (1-(\text{Prop}_{\text{out}}/\text{Prop}_{\text{in}})) \times 100\%$. The different product selectivities (S_p) were calculated by amount of product formed divided by propene converted: $S_p = (\text{Product}/(\text{Prop}_{\text{in}}-\text{Prop}_{\text{out}})) \times 100\%$. Yield of acrolein was calculated from $Y_{\text{acr}} = (S_p \times \text{Conv})/100\%$. The catalyst (60 mg) consisting of sieved fractions (0.425–0.212 mm) was inserted into the reactor and kept in place by quartz wool on either side. The gas flows were controlled using Bronkhorst mass flow controllers, and a total flow of 20 ml/min was used for all experiments resulting in a weight hourly space velocity (WHSV) of 2 h^{-1}.

As-prepared samples were dehydrated to 450 °C in O_2/He (5%) with a ramp rate of 10°C/min prior to all catalytic measurements. First the catalysts were subjected to 4% C_3H_6/He at 450 °C for 20 min after dehydration, to ensure a fully reduced catalyst. Subsequently switching to a feed composition of 4 C_3H_6:1 O_2 (4% C_3H_6:1% O_2), with an injection done after 20 min when reaching steady state. The concentration of O_2 was increased after each injection, to study the product formation at different feed compositions. The various feed compositions used during the catalytic measurements for VCu:AlPO-5 and VCu:ZSM-5 at 450 °C are listed in Table 1. The catalytic measurements were performed as one experiment for each catalyst, and time frame and gas compositions are chosen based on our previous findings for these systems [6].

Table 1
Experimental details for the catalysis measurements at 450 °C employed for VCu:AlPO-5 and VCu:ZSM-5.

C_3H_6/O_2 ratio	Concentration of feed components (%)		WHSV (h^{-1})	Catalyst weight (mg)
	C_3H_6	O_2		
4	4	1	≈2	60
2	4	2		
1	2	2		
0.5	1	2		
0.25	1	4		

2.4. XAS data collection

Copper K-edge XAS data was collected at the Swiss-Norwegian Beamlines (SNBL, BM1B) at the European Synchrotron Radiation Facility (ESRF) in transmission mode. The data was collected in the multibunch filling mode, providing a maximum current of 200 mA and beam energy of 6 GeV. A bending magnet collects the white beam from the storage ring to the beamline. SNBL is equipped with a channel cut Si-1 1 1 double crystal monochromator. The monochromator was detuned 80% at the copper edge to supress higher harmonics. The incident and transmitted intensities (I_0 and I_t) were detected with ion chambers filled with, I_0 (17 cm) 96% N_2 + 4% Ar, and I_t (31 cm) 80% N_2 + 20% Ar. Copper references CuO, $Cu(OH)_2$ and Cu_2O were also collected *ex situ*. The XAS data were measured in Quick-XAS mode, with continuous step scan from 8800 eV to 9800 eV with a step size of 0.5 eV and counting time 150 ms.

The vanadium K-edge data was collected in fluorescence mode at beamline I811 on the MaxII-ring at MaxLab which offers electron beam energy of 1.5 GeV. I811 utilises light from a multiple wiggler insertion device, and the optical scheme consists of a vertical collimating first mirror, double crystal monochromator (S1 1 1) and a second focusing mirror. The monochromator was detuned 50% at the vanadium edge to supress higher harmonics. The ion chambers (30 cm) were filled with I_0 10% N_2 + 90% He (0.2 bar N_2 + 1.8 bar He), I_t (30 cm) 20% N_2 + 80% He (0.4 bar N_2 + 1.6 bar He). The fluorescence yield was collected using a passivated implanted planar silicon (PIPS) detector (Canberra, 10 cm diameter) with a titanium filter. The detector was positioned close to the sample to achieve the highest possible fluorescence signal. Vanadium was collected with an integration time of 0.08 s with scan time 180 s starting at energy 5373.76 eV to 5983.76 eV. Vanadium references V_2O_5, NH_4VO_3, Na_3VO_4, PbV_2O_6, V_2O_4 and $VOSO_4$ were diluted with boron nitride to mimic loading in the samples and also collected in fluorescence mode.

For all *in situ* measurements, the same conditions and setup were applied on both edges, hence sample weight, cell thickness and gas flow were kept constant for experiments at both the