The low temperature oxidative upgrading of short chain alkanes over Cu/ZSM-5 catalysts: the role of Cu speciation.

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Abstract: C_1–C_3 alkanes are partially oxidised with H_2O_2 at 50 °C over Cu/ZSM-5 catalysts prepared by chemical vapour impregnation (CVI). The undoped ZSM-5 support is itself able to catalyse selective oxidations, for example, methane to methanol, using mild reaction conditions and H_2O_2. Addition of Cu suppresses secondary reactions, affording methanol selectivities of up to 97 %. Characterisation studies attribute this to population of specific Cu sites below the level of total exchange (Cu/Al < 0.5). These species also show activity for radical- based methane oxidation, with productivities exceeding those of the parent zeolite supports. When tested for ethane and propane oxidation reactions, comparable trends are observed.

Keywords: Selective Oxidation • Alkanes • Cu/ZSM-5

1. Introduction

Natural gas is a potential bridging resource for society's transition away from a petroleum- dependent economy. Direct oxidation of methane to oxygenates would be a key step in achieving this. However, this is yet to be achieved under conditions which are both green and industrially viable. Whilst processes for upgrading methane to value- added products have been commercialised, a high C-H bond energy (439.6 kJ mol^{-1}) means that harsh conditions are often employed for its activation. Under such conditions however, further conversion of the desired products to deeper oxidation products such as CO_2 stymie industrial viability. Several routes for direct methane oxidation have been reported, with many involving non-environmentally benign chemistries, which spurns the current trend towards green chemical technologies.

2. Experimental

NH_4 ZSM-5 (Zeolyst) was calcined in a flow of air (550 °C, 20 °C min^{-1}, 3h) to yield H-ZSM-5. The proton form zeolite was then either; activated in static air prior to testing (550 °C, 20 °C, 3h), or impregnated with Cu via chemical vapour impregnation (CVI). The procedure for preparation of 2.5 wt% Cu/ZSM-5 through CVI is as follows; H-ZSM-5 was dried (2 h, 150 °C) under vacuum. Once dried, H-ZSM-5 (1.95 g) was added to a Schlenk flask and (Cu $(acac)_2$) (Sigma Aldrich, 99.9% purity, 0.206 g, 0.787 mmol) added. Following physical mixing, the dry mixture was heated to 140 °C under vacuum (ca. 10^{-3} mbar) for 1 h. The sample was then calcined (550 °C, 20 °C min^{-1}, 3h) in static air.

Catalyst performance was assessed in a 50 mL Teflon lined Parr autoclave reactor. Aqueous products were quantified via ^1H NMR using a TMS/ $CDCl_3$ internal standard. Gaseous products were quantified via GC-FID. For EPR radical trapping studies, 5,5-Dimethyl-1-pyrroline N-oxide (0.05 g, Sigma Aldrich, > 97%) was added to the aqueous phase and reactions carried out for 5 min.

3. Results and discussion

Cu/ZSM-5 catalysts prepared by CVI were tested for the oxidation of methane under mild aqueous conditions utilising hydrogen peroxide as the oxidant. In line with previous studies, a metal loading of 2.5 wt% Cu was employed [1], whilst the SiO_2/Al_2O_3 ratio was varied within the range of 23 – 280. Reaction data at t = 0.5 h are presented in Table 1. Of the catalysts tested, 2.5% Cu/ZSM-5 (SiO_2/Al_2O_3 = 23) showed relatively high activity, with 42.8 μmol products formed and 97.4 % selectivity towards methanol. This is compared with the previously reported 2.5 % Cu/ZSM-5 (30), which yielded 8.4 μmol products at 78.5 %

methanol selectivity. Further increasing the SiO_2/Al_2O_3 to 50 or 280 (at a fixed loading of 2.5 wt. % Cu) led to further decreases in catalyst activity.

Table 1 Catalytic data for methane oxidation catalysed by Cu/ZSM-5 of varied SiO_2/Al_2O_3 and Cu/Al ratios.

Entry	SiO_2/ Al_2O_3	% wt Cu	Cu/Al ratio	Total Product / µmol	Product / µmol				χ H_2O_2 / %	*S*(MeOH) / %
					MeOH	MeOOH	HCOOH	CO_2		
1	23	2.5	0.41	42.82	41.7	0.57	0	0.55	8.68	97.38
2	30	2.5	0.59	8.37	6.57	1.29	0	0.51	2.48	78.49
3	50	2.5	0.76	0.52	0.00	0.14	0	0.38	1.83	0.00
4	280	2.5	4.08	2.2	0.43	1.43	0	0.34	11.40	19.55

Test conditions; 27 mg catalyst, 0.5 h, P(CH_4) = 30 bar (0.03 mol), 50 °C, 1500 rpm, [H_2O_2] = 0.5 M (10 ml, 5000 µmol).

Characterisation of the catalysts in Table 1 via HRTEM, H_2-TPR, NH_3-TPD and DRIFTS showed the rate of methane oxidation to be independent of the size/ dispersion of supported Cu- oxide nanoparticles. Rather, enhanced rates of alkane oxidation and high selectivity towards 1° products were found to correlate with the degree of cation exchange, with a Cu/Al of < 0.5 favoured, as shown in Table 1. In probing ion exchanged Cu sites with NO, four IR- active stretching bands were observed (Fig. 1). These have previously been assigned to N-O-Cu^{2+} with exchanged divalent Cu^{2+} of; square pyramidal (AlO_4^- pair, 1915 cm^{-1}, *Cu-I* sites), square planar (single AlO_4^-, 1895 cm^{-1}, *Cu-II* sites), square pyramidal (AlO_4^- pair, 1921 cm^{-1})[2,3]. A band at 1811 cm^{-1} (monovalent Cu^+-NO species)) has also been reported and attributed to highly reducible Cu^{2+} sites.[2,3] Population of Cu^{2+} species associated with AlO_4^- pairs (1915 cm^{-1}) is favoured below total exchange (Cu/Al < 0.5). This correlates with enhanced catalytic activity and methanol selectivity in Table 1. EPR radical trapping studies (Fig. 2a) show that 2.5% Cu/ZSM-5 (23) produces a significant flux of ·OH radicals, whilst population of *Cu-II* sites correlates with suppression of this (Figs. 2b/2c). Comparable trends in reaction rates and selectivity were observed when the same Cu/ZSM-5 catalysts were tested for the partial oxidation of ethane and propane.

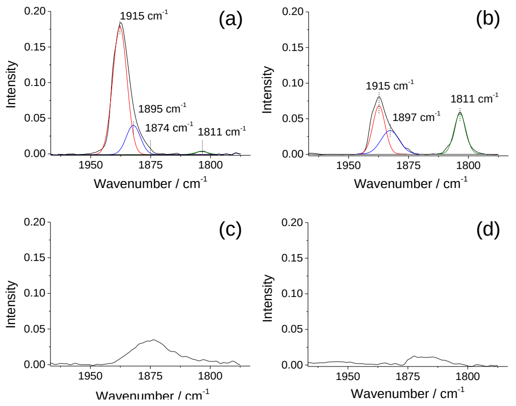

Figure 1. IR bands of NO adsorbed onto 2.5 wt% Cu/ZSM-5 of SiO_2/Al_2O_3 = (a) 23, (b) 30, (c) 50 and (d) 280.

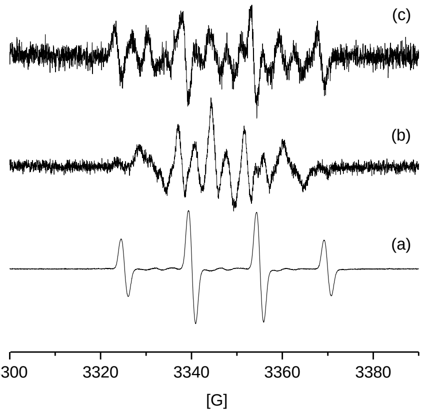

Figure 2. DMPO spin- trapping data obtained during methane oxidation catalysed by (a) 2.5 % Cu/ZSM-5 (23), (b) 2.5 % Cu/ZSM-5 (30) and (c) 2.5% Cu/ZSM-5 (280)

4. Conclusions

These data suggest that (i) ·OH are generated at and relatively stable over *Cu-I* sites and that either (ii) *Cu-I* species act as active sites for selective alkane oxidation or (iii) *Cu-I* sites propagate generation of ·OH, with alkane activation occurring on a secondary active site within the catalyst. Conversely, the previously reported DFT- derived mechanism for ZSM-5 catalysed methane oxidation with H_2O_2 involved a concerted, molecular active site with no input of oxygen based radicals.

References

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