Tailored Fe-ZSM-5 Catalyst Design for Aqueous Phase Methane Oxidation

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Abstract: Low temperature pathways are required to activate methane into methanol, which can be used as a precursor to many synthetically relevant organic molecules. Fe-ZSM-5 has been shown to catalyze this process at temperatures as low as 50 °C under aqueous conditions, utilizing H_2O_2 as a green oxidant. However, H_2O_2 is also prone to decomposition to water and oxygen and this hinders the efficiency of this catalyst for this reaction. This study considers the nature of the active Fe-sites by utilizing UV-vis and Resonance Raman spectroscopy and kinetic data for H_2O_2 decomposition in the absence of methane to determine the optimal composition of Fe-ZSM-5 for aqueous methane oxidation.

Keywords: Methane, oxidation, zeolite.

1. Introduction (11-point boldface)

Known reserves of natural gas are steadily increasing year on year,[1] however activation of the primary constituent methane, remains a major challenge. Due to the high bond strength of C-H ($\Delta H = 439.7$ kJ/ mol) methane valorization requires harsh and unfavorable conditions. There has been an increasing interest in low-temperature (< 100 °C) and direct strategies to methane activation. Aqueous-phase oxidation that utilises H_2O_2 as a benign and green oxidant has attracted attention from the research community. In particular, Fe-MFI materials has been shown to be active catalysts for low-temperature aqueous-phase oxidation of methane.[2] However, the efficiency of this reaction is reduced by decomposition of the oxidant:

$$H_2O_2 \rightarrow H_2O + \tfrac{1}{2} O_2$$

Using UV-Vis and Raman spectroscopy to get a better understanding of the sites that contribute to H_2O_2 decomposition, an optimal catalyst design to suppress peroxide decomposition.

2. Experimental (or Theoretical)

Fe-ZSM-5 materials were prepared by hydrothermal methods as previously reported by Hammond *et al.*[3] Hydrogen peroxide decomposition kinetic testing was carried out by charging a 100 mL two-necked round-bottom flask with 10 mL of 0.5 M H_2O_2 aqueous solution and placed in a thermostatically controlled oil bath set at 50 °C. The desired amount of catalyst (2.6 μmol Fe) was added to initiate the reaction. Aliquots (100 μL) were taken and H_2O_2 concentration was determined by acidified $Ce(SO_4)_2$ titration. TOF values (turnover frequency) were calculated as (mol H_2O_2 decomposed)/(mol Fe).(t).

3. Results and discussion

It has been previously shown that hydrothermally-synthesised Fe-ZSM-5 has greater activity per mol of Fe than Fe-Silicalite.[3] The presence of Al^{3+} in the framework facilitates the extraction of Fe^{3+} to extra framework positions. This increase, which is observed by UV-Vis spectroscopy (λ = 250 -350 nm) correlates to increase methane oxidation activity.[3] However, the proportion of Fe_2O_3 agglomerates observed in the UV-Vis spectrum (figure 1, $\lambda > 450$ nm) increases after heat-treatment during catalyst preparation. It is believed that these nanoclusters can increase the rate of hydrogen peroxide decomposition. UV resonance Raman spectroscopy (figure 2) also shows an increase in extra framework Fe^{3+} (512 cm^{-1}) along with an increased tetrahedral framework Fe species (1028 cm^{-1}) at higher Fe loadings.[4] These results correlate well with the kinetic data for catalysts with low Al contents (figure 3); as the proportion of Fe_2O_3 agglomerates increases, TOF values for H_2O_2 decomposition increases.

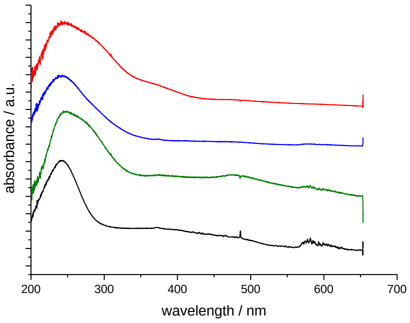

Figure 1 UV-Vis spectrum of 0.1 Fe-ZSM-5, Si/Al = 45 at various stages of the hydrothermal synthesis procedure. As synthesized = black; template free = green; NH_4^+ = blue; H^+ = red)

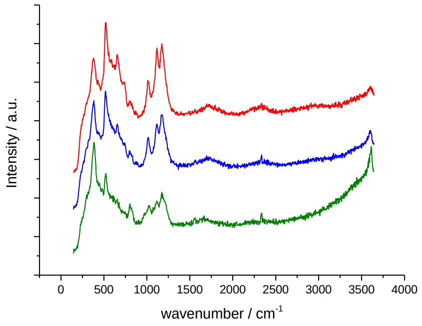

Figure 2 266 nm resonance Raman Spectroscopy of H^+ form of 0.1 wt % Fe = green; 0.25 wt % Fe = blue; and 0.5 wt % Fe = red at Si/ Al = 45

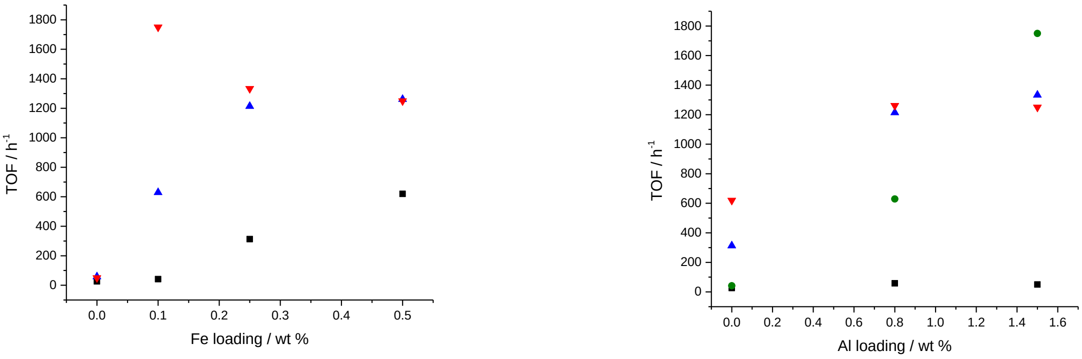

Figure 3 Left; TOF of various Fe-ZSM-5 at fixed Al content. Si/Al = 0, black square; Si/Al = 90, blue triangle; Si/Al = 45, red triangle). Right; TOF of various Fe-ZSM-5 at fixed Fe content. 0 wt % Fe = black square; 0.1 wt % Fe = green circle; 0.25 wt % Fe = blue triangle; 0.5 wt % Fe = red triangle

However, as the Al loading is increased to 1.5 wt % (Si/Al = 45, figure 3), the highest rate of decomposition of occurs at a Fe loading of 0.1 %. Even though the proportion of Fe_2O_3 nanoclusters is smallest for this composition. This would suggest that Bronsted acid sites may play a role in H_2O_2 decomposition along with Fe_2O_3 agglomerates.

4. Conclusions

It has been shown here that increased Al content in Fe-ZSM-5 results in higher activity for H_2O_2 decomposition, although it has yet to be determined the effect of Al content on the rate of methane oxidation. It is thought that an increased number of Bronsted acid may contribute to the decomposition pathway. To develop a better understanding of the species that are active for H_2O_2 decomposition, *in-situ* UV-Vis and Raman spectroscopy will be used to determine the change in speciation of Fe throughout the decomposition reaction. Considering the above, the aim is to design a catalyst that is intrinsically active for methane oxidation under aqueous conditions that suppresses H_2O_2 decomposition by determining the optimal Fe and Al loadings.

References

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