Characterisation of Carbonaceous Residues on the Pentasil Zeolite ZSM-5 following Reactivation: a Solid State ^{13}C N.M.R. Spectroscopic Study

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High resolution ^{13}C n.m.r. characterisation of carbonaceous residues present in the zeolite ZSM-5 following oxygen and ozone/oxygen reactivation has identified distinct species of which only the highly aromatic type can be linked to catalyst deactivation.

Zeolites are currently of considerable interest as catalysts for a number of industrially important reactions,[1] and most effort has been devoted to the elucidation of the structural[2] and mechanistic aspects[3] of their action. It is known that these catalysts are deactivated by deposition of carbonaceous material (coke), but the structural aspects of the carbonaceous deposits have received scant attention.[4,5] Such structural information is, of course, necessary for evaluating and improving long term catalyst stability. We have recently studied[6,7] methods (based on O_2 and O_3/O_2 mixtures) of catalyst reactivation; to our knowledge there have been no reported studies on the structure of coke following reactivation. We now report our initial studies using solid state ^{13}C cross polarisation–magic angle spinning (c.p.–m.a.s.) n.m.r. spectroscopy which demonstrate important differences between oxygen and ozone/oxygen reactivation.

Zeolite H-ZSM-5 (1 g, SiO_2/Al_2O_3 mol ratio = 35) was dried (N_2, 350 °C, 24 h) and treated with [^{13}C]MeOH (1 g, 90% ^{13}C, Amersham International) carried slowly (3 days) in a stream of dry N_2 over the zeolite in a Pyrex fixed bed reactor at 400 °C. Following methanol treatment the coked zeolite was heated in dry nitrogen for a further 12 h at 400 °C, before cooling, and finally dried *in vacuo* at 120 °C. Portions (0.33 g) of the coked zeolite were reactivated with either dry oxygen at 410 °C for 20 and 75 min or an ozone/oxygen mixture (O_3/O_2 = 5 mol %) at room temperature for 13 min. The carbon and hydrogen content of the samples was determined before and after reactivation by standard microanalytical techniques. Solid state ^{13}C (c.p.–m.a.s.) n.m.r. spectra of the coked and reactivated zeolites were obtained on a Bruker CXP-200 high power spectrometer with a contact time of 4 ms and a recycle time of 4 s. The sample rotor (boron nitride) was spun at 2.2 kHz and 30 000—60 000 spectra were accumulated before Fourier transformation. The empty rotor under these experimental conditions gave no detectable resonances in the range δ −150 to +340. Chemical shifts (δ) are quoted relative to an external Me_4Si standard.

The ^{13}C n.m.r. spectra (see Figure 1) exhibit five, (a—e), distinct resonances in the range δ 20—230 which are assigned[8] to (a): aliphatic (δ 0—50); (b): ether $\geqslant$C–O (δ 60—100); (c): aromatic (δ 100—150); and (d), (e): carbonyl C=O (δ >150) carbon environments. Following reactivation it is clear that significant amounts of carbon and hydrogen have been retained in the zeolite. We have previously shown[7] that coke retention is observed after extensive ozone/oxygen and oxygen reactivations of coked pentasil zeolites, but that this

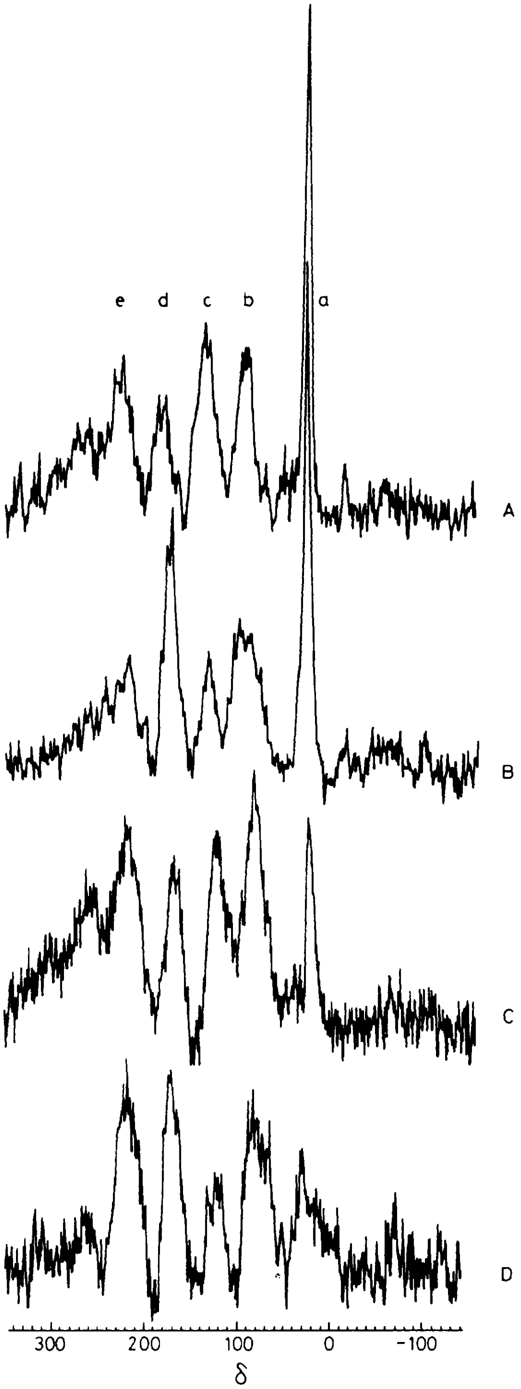

Figure 1. ^{13}C (c.p.–m.a.s.) N.m.r. spectra; A: coked ZSM-5 (C, 1.2%; H, 0.5%) 31 560 scans; B: sample A following ozone/oxygen reactivation, 13 min (C, 1.1%, H, 0.5%) 63 542 scans; C: sample A following oxygen reactivation, 410 °C, 20 min (C, 1.0%, H, 0.5%) 57 077 scans; D: sample A following oxygen reactivation, 410 °C, 75 min (C, 0.7%, H, 0.5%) 39 778 scans.

retained coke can be tolerated in the zeolite since these procedures restore the original catalyst activities. Furthermore, these studies indicated that ozone reactivation can lead to increased lifetime for methanol hydrocarbon conversions. The ^{13}C n.m.r. spectra of the ozone/oxygen and the oxygen reactivated zeolites show distinct differences in the residual carbon species following reactivation (see Figure 1). Ozone/oxygen reactivation clearly removes the aromatic residues preferentially, as the resonances at δ 100—150 are reduced relative to the other observed resonances. By comparison, oxygen reactivation does not appear to discriminate between aliphatic and aromatic residues and removes both. The most striking feature of oxygen reactivation is the progressive elimination of the aliphatic residues (δ 10—25) (see spectra C,D in Figure 1).

It is emphasised that low temperature ozone/oxygen reactivation does not lead to such extensive oxidation of the aliphatic residues. The coked and reactivated zeolites exhibit a significant concentration of ether and ketonic carbon environments which appear to be quite resistant to the reactivation procedures used. Some of these species may be involved in the anchoring of the carbonaceous residues to the zeolite structure *via* Al–O or Si–O linkages, since they are probably not physically adsorbed (the samples were heated under vacuum prior to the n.m.r. investigations). We consider the preferential removal of the aromatic carbons by the low temperature ozone/oxygen treatment to be due to localised attack at unsaturated centres leading to oxygenated fragments. The distinct broadening of the ether type resonance (δ 60—125) after ozone treatment lends support to this formulation.

Following low temperature ozone/oxygen activation the coke contains predominantly aliphatic, ether, and ketonic carbon environments, whilst following high temperature oxygen reactivation the coke mostly comprises ether and ketonic carbons. We have previously shown[7] that low temperature ozone/oxygen reactivation is as effective as high temperature oxygen reactivation in restoring catalyst activity and we now propose that catalyst deactivation is caused primarily by the build up of the highly aromatic type coke, whilst aliphatic, ether, and ketonic carbon species can be tolerated within the zeolite without significant deactivation.

This study has identified the existence of distinct aliphatic, aromatic, ether, and ketonic types of coke within the zeolite structure, and that of these only the aromatic type coke can be directly linked with catalyst deactivation.

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