Nitrous Oxide Reactivation of a Zeolite Y Catalyst for Hydrocarbon Cracking

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A novel method for total removal of carbonaceous deposits from a zeolite catalyst with restoration of activity for hexene cracking is described.

Zeolites are widely used as hydrocarbon cracking, oligomerisation, and isomerisation catalysts, and these reactions are usually accompanied by the deposition of highly carbonaceous material (coke) within the zeolite pore structure[1] which leads to a significant decrease in the observed reaction rates. Zeolite catalysts therefore require frequent reactivation to remove the chemically bound coke deposits and to restore their catalytic activity. The normal industrial procedure is simply to oxidize the coke to carbon oxides and water using oxygen at temperatures of 400—500 °C. We have recently proposed[2,3] a low temperature oxidation process using ozone–oxygen mixtures. This procedure can restore full catalyst activity (*e.g.* with zeolite ZSM-5 for methanol conversion to hydrocarbons) but only partially removes coke from the zeolite pores, and, in particular, preferentially removes carbon with aromatic functionality.[4] For some zeolitic applications, *e.g.* hydrocarbon cracking, it is essential to achieve rapid *total* removal of the coke. High temperature reactivation can achieve this but extensive reactivation periods may be required, thereby exposing the zeolite to high temperature water vapour for long periods which can lead to long-term deactivation due to de-alumination.[5] Identification of a procedure that reduces the reactivation timescale would alleviate this problem and this we have successfully addressed. We now report a reactivation procedure using N_2O that enables *rapid total* removal of carbonaceous deposits from a zeolitic framework.

Zeolite H-Y (2 g, Union Carbide LZY 82, H form) was reacted with hexene in a fixed bed Pyrex reactor[6] under suitable thermal control. Dry nitrogen gas, pre-saturated with hexene, was passed through the catalyst bed at 500 °C. Gaseous products were analysed by gas chromatography at regular intervals. The loss of activity of the catalyst was noted by the decrease in hexene conversion together with an increase in catalyst mass due to deposition of coke. After reaction for 6 h typically 18.0% by mass of carbon had been deposited and the activity had decreased by *ca.* 30%. Samples of this zeolite were then reactivated by substituting either pure O_2 or N_2O (flow rate 1 ml/s) for the N_2/C_6H_{12} reactant at

Table 1. Reactivation of zeolite H-Y.

Reactivation agent	Reactivation temp./°C	Reactivation time/h	Carbon/% by mass (±0.03)[a]
O_2	450	6	0.12
O_2	500	2.5	0.45
N_2O	450	6	0.00
N_2O	500	2.5	0.00

[a] Prior to reactivation the zeolite contained 18.0% C by mass.

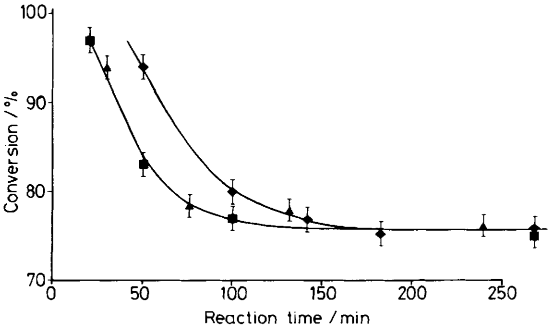

Figure 1. Catalytic activity for hexene cracking for (◆) fresh H-Y (calcined 500 °C, air, 2 h); (■) N_2O-regenerated H-Y (500 °C, 2.5 h); (▲) O_2-regenerated H-Y (450 °C, 6 h).

different reaction conditions and the relative reactivation efficacies are shown in Table 1. It is clear that N_2O removes *all* the carbonaceous deposit whereas O_2 treatment under comparable conditions leaves some residual coke deposit within the zeolite. Oxygen reactivation requires long reaction periods since use of a higher temperature, 500 °C, for a shorter time, 2.5 h, is not particularly effective. Following reactivation the catalytic activity for hexene cracking was evaluated and compared to that of the fresh catalyst (Figure 1). N_2O reactivation (2.5 h, 500 °C) was found to be as effective as an extended O_2 reactivation (6 h, 450 °C).

Five cycles of reaction followed by N_2O reactivation were carried out without any loss of activity. No major differences were observed in product selectivities between fresh zeolite H-Y and the O_2-reactivated or the N_2O-reactivated materials. Analysis by *X*-ray diffractometry and *X*-ray fluorescence of N_2O-reactivated zeolite H-Y showed that no significant changes in catalyst structure or composition had occurred. We can therefore conclude that N_2O reactivation provides a method for total removal of carbonaceous deposits that is more rapid in comparison to O_2 reactivation.

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