Ozone Reactivation of a Synthetic Zeolite Catalyst for Methanol Conversion

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A novel low-temperature method for removing carbonaceous deposits from a zeolite catalyst and restoring activity for methanol conversion into hydrocarbons is described.

There has recently been considerable interest both in the structural[1] aspects of pentasil-type zeolites and the mechanism[2] of their action as catalysts for the conversion of methanol into hydrocarbons. During the reaction deposition of carbon within the channels of the zeolite causes severe loss of activity, as indicated by lower conversion into non-oxygenated products.[3]

Although much effort has been applied to the understanding of the structure and reactivity of these catalysts, the regeneration of deactivated catalysts has received scant attention. A common method of reactivation is simply to oxidise the deposit to carbon oxides and water, using a catalyst bed temperature of 400—500 °C. Whilst such treatment does restore catalyst activity, it exposes the catalyst to water vapour

Table 1. Catalyst reactivation data.

Catalyst condition	New catalyst						Catalyst after reactivation									
							O_3–O_2[c] (192 °C)			O_2 (150 °C)	O_3–O_2[c] (150 °C)			O_2 (450 °C)		
Run number	1A	1B	1C	1D	1E	1F	2A	2B	2C	3	4A	4B	4C	5A	5B	5C
TOL (min)[a]	293	464	538	829	880	1154	145	456	974	54	830	867	978	250	1256	1580
LHSV (h^{-1})[b]	1.1	1.1	1.3	1.2	1.2	2.2	2.1	2.0	2.1	2.1	2.1	1.0	3.0	0.9	0.9	2.1
Temperature (°C)	370	370	371	370	370	372	369	371	370	370	369	379	370	370	366	368
MeOH Conversion (% mol/mol)	99.5	99.0	96.0	94.3	93.1	89.8	96.4	95.5	89.6	90.6	92.1	90.2	91.9	99.5	96.9	90.9
DME (% mass/mass)	0	0	0	0	0	83.0	0	0	78.0	85.0	0	0	86.0	0	0	83.0
Hydrocarbon selectivities (% mass/mass)																
C_1—C_6 gases	89.9	91.8	89.2	93.6	100.0	7.0	89.4	98.7	22.0	15.0	98.6	100.0	14.0	75.6	95.8	17.0
Benzene	0.6	0.5	0.5	0.2	—	—	0.1	—	—	—	0.1	—	—	0.8	0.2	—
Toluene	0.4	0.4	0.2	0.1	—	—	0.1	—	—	—	—	—	—	0.9	0.1	—
m + *p*-Xylene	3.8	2.9	2.3	1.3	—	—	1.6	0.2	—	—	0.3	—	—	8.0	0.9	—
o-Xylene	0.5	0.3	0.4	0.2	—	—	0.2	—	—	—	0.1	—	—	1.6	0.2	—
Mesitylene	2.3	1.7	2.4	1.4	—	—	1.8	0.2	—	—	0.2	—	—	5.7	1.1	—
Ethyl methyl benzene	1.4	1.3	1.4	1.4	—	—	2.3	0.3	—	—	0.3	—	—	9.3	0.4	—
Diethyl benzene	0.6	0.5	1.0	0.5	—	—	1.4	0.1	—	—	0.1	—	—	1.6	0.5	—
Durene	0.5	0.7	2.7	1.2	—	—	3.0	0.3	—	—	0.4	—	—	1.6	—	—

[a] Cumulative time on line to end of run. [b] LHSV = Volumetric flow rate of MeOH(l)/volume of catalyst used. [c] 4.8 mol % O_3.

at elevated temperatures and hydrothermal treatment is known to de-aluminate ammonium exchanged zeolitic frameworks.[4] Since it has been found that the catalytic activity is proportional to aluminium concentration[5] in the framework, it is therefore understandable that after many reactivation cycles an irreversible long-term degradation in catalyst activity is observed with these zeolites. To our knowledge, no reported studies have successfully addressed this important problem.

This communication reports on comparative studies of the activation efficacies at either high temperature, using pure oxygen gas, or at much lower temperatures, using oxygen gas containing 4.8 mol % ozone. This latter procedure avoids the exposure of the catalyst to high temperature water vapour.

Hydrocarbon conversions were performed in a Pyrex fixed-bed reactor containing 5.0 ml of active catalyst (previously characterised as of the type H-ZSM-5 by *X*-ray powder diffraction) under suitable thermal control, and dry nitrogen gas pre-saturated with methanol was passed through the reactor at a catalyst bed temperature of *ca.* 370 °C. Liquid products were collected in traps at ambient temperature and later analysed by gas chromatography, whilst gaseous products were similarly analysed on-line. For most experimental runs the gas flow-rate was adjusted to achieve an LHSV (liquid hourly space velocity) of 1.0—2.0 h^{-1}. The loss of activity of the catalyst was noted by an increase in concentration of MeOH and the appearance of dimethyl ether (DME) in the gas analyses (see Runs 1A—F, Table 1). When the relative concentrations of DME:light hydrocarbons (C_1—C_6 alkanes and alkenes) exceeded 2:1 in the gas stream leaving the reactor, reactivation was undertaken by substituting the MeOH–N_2 stream with either O_2 or O_3–O_2.

For those reactivations using ozone, the catalyst bed temperature was observed to rise rapidly from an initial 38 °C to a maximum of 120 °C within a few seconds of establishing the O_3–O_2 flow. This exothermic reaction was accompanied by the production of CO_2(g). After 12 min a decrease in temperature was observed and gradual heating to a maximum temperature of 192 °C was applied and maintained for 150 min. At this point, about half of the catalyst bed volume was observed to be free of carbonaceous material. The activity of the catalyst was then determined in the usual way (Run 2, Table 1). In further experiments it was found that ozone reactivation could be effected under even milder conditions, *viz.*, 150 °C for 80 min (Run 4, Table 1).

Attempted reactivation of the catalyst using pure oxygen gas under the same conditions as for the ozone experiments was found to be unsuccessful (Run 3, Table 1); no CO_2(g) was produced and no exothermic reaction took place.

Treatment with oxygen was found to reactivate the whole bed after several hours passage of oxygen gas at a catalyst bed temperature of 450 °C (Run 5, Table 1).

Only minor differences in the product selectivities of the catalyst after ozone and high temperature oxygen reactivation were observed. We can, therefore, conclude that ozone reactivation of approximately half the catalyst bed at less than 200 °C is a viable alternative when compared with an oxygen reactivation of the whole bed at 450 °C. Further studies on the optimisation of the low-temperature ozone treatment are currently in progress.

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