Regeneration of Pentasil Zeolite Catalysts using Ozone and Oxygen

Richard G. Copperthwaite, Graham J. Hutchings,* Peter Johnston and S. Walter Orchard

Department of Chemistry, University of the Witwatersrand, Johannesburg, 1 Jan Smuts Avenue, Johannesburg 2001, South Africa

A novel procedure for the removal of carbonaceous deposits from zeolites using ozone-enriched oxygen is described. Pentasil zeolites (SiO_2/Al_2O_3) mole ratios 35, 70) were studied and deactivated using methanol conversion to hydrocarbons and *o*-xylene isomerisation. Low temperature ozone reactivation was found to restore the catalyst activity for these reactions and hence can be considered as an alternative procedure to high temperature oxygen reactivation currently utilised industrially. Ozone reactivation was found to increase slightly the catalyst lifetime and also to reduce the initial methane yield when compared with oxygen reactivation.

In recent years there has been considerable interest in the pentasil type zeolites with respect to their structures¹ and their use as catalysts for methanol conversion to hydrocarbons² and hydrocarbon transformation reactions.³ During the reactions, deposition of carbonaceous material, usually referred to as 'coke', occurs within the channels of the zeolite and this causes severe loss of activity, as indicated by the low conversion of methanol to non-oxygenated products.⁴ The reactions of the pentasil zeolite ZSM-5 demonstrate shape selectivity and aromatic products $\ge C_{11}$ are not observed owing to the geometric limitations of the zeolite structure. This effect also minimises deposition of carbonaceous deposits by inhibiting the growth of the polymeric chains that are the precursors to these deposits.⁵ Although deposition of carbonaceous material is limited with ZSM-5 compared to other zeolites,⁴ periodic regeneration is required to maintain the catalyst activity at an acceptable level. These catalysts are usually reactivated by oxidising the deposit with air to carbon oxides and water, using a catalyst bed temperature of 400–500 °C. This treatment restores the catalytic activity, but exposes the zeolite to water vapour at elevated temperatures. Pentasil zeolites are usually in the acid form for hydrocarbon formation and conversion reactions, and are usually prepared by ammonium exchange of the sodium form of the zeolite and subsequent calcination at 500 °C. It is known that hydrothermal treatment of ammonium exchanged zeolites causes dealumination,⁶ and since catalytic activity is related to the aluminium concentration,⁷ it is not surprising that after many reactivation cycles an irreversible long-term degradation in catalyst activity is observed with these zeolites. In this study we describe an alternative low-temperature reactivation procedure, using ozone-oxygen mixtures, which effectively reduces exposure of the zeolite to water vapour at elevated temperatures during the reactivation treatment. In a recent communication⁸ we reported our initial findings and in this paper we exemplify and extend the general applicability of the method.

Zeolite Preparation

Experimental

The sodium form of the pentasil zeolite ZSM-5 was prepared according to the method of Howden⁹ with SiO_2/Al_2O_3 mole ratios of 35 and 70. The Na-ZSM-5 was converted to the protonated form (H-ZSM-5) by the following procedure: Na-ZSM-5 (100 g) was

Pentasil Zeolite Catalyst Regeneration



Fig. 1. Experimental apparatus. (1) Methanol or *o*-xylene loaders (Dreschel bottles); (2) Pyrex reactor and heating element; (3) heating controller; (4) cooled collection trap.

suspended, with stirring, in aqueous ammonium sulphate (1 mol dm⁻³, 1 dm³) for 30 min. The solid was recovered by filtration and washed with distilled water. The procedure was repeated twice and following the third treatment the zeolite was thoroughly washed with many portions of distilled water to ensure that it was free of sulphate ions. The ammonium-exchanged zeolite NH_4 -ZSM-5 was dried in air at 120 °C for 1 h and then calcined at 500 °C for 3 h to convert it to H-ZSM-5. It was then cooled and stored in a desiccator.

Catalyst Testing

Hydrocarbon conversion and formation reactions were carried out in a Pyrex fixed-bed reactor which is schematically shown in fig. 1. The Pyrex reactor had the advantage that the catalyst could be directly observed during use and reactivation. For the methanol conversion studies, dry nitrogen gas, pre-saturated with methanol at 50 °C, was passed through the reactor at a catalyst bed temperature of *ca*. 370 °C. The reactor effluent was cooled to 20 °C, the liquid products were collected in Pyrex traps and the residual gases were analysed on-line by gas chromatography using a flame ionisation detector (2 m × 5 mm porapak S column). The liquid products were subsequently analysed by off-line gas chromatography and were identified using g.c.-mass spectroscopy (VG Micromass 7070H with 50 m × 0.2 mm bonded OV1 capillary column). For most experimental runs the nitrogen flow was adjusted to achieve an l.h.s.v. (liquid hourly space velocity) of 1.2-3.0 h⁻¹. For the *o*-xylene isomerisation studies, dry nitrogen pre-loaded with *o*-xylene at 70 °C was used. The products were collected at 20 °C and analysed using n.m.r. spectroscopy. Only data with mass balances between 90–110% were utilised.

Catalyst reactivation was carried out by substituting the methanol (or *o*-xylene)– N_2 stream for oxygen or ozone-enriched oxygen. Ozone-enriched oxygen was prepared using a Fisher ozone generator (model 502).

Results

Ozone Reactivation of H-ZSM-5 Catalyst for Methanol Conversion, $SiO_2/Al_2O_3 = 35$

Methanol conversion to hydrocarbons was carried out using the synthetic zeolite H-ZSM-5 with SiO_2/Al_2O_3 mole ratio of 35 under a range of experimental conditions and the product distributions obtained are shown in table 1 (runs 1A–1D). Deactivation of the catalyst was indicated by a decrease in methanol conversion and the appearance of dimethyl ether (DME) in the products. In addition, it was observed that the catalyst particles rapidly discoloured during reaction owing to deposition of carbonaceous material. After run (1D), production of hydrocarbon products had largely ceased and the catalyst was reactivated using an ozone–oxygen gas mixture (O_3/O_2 mole ratio 0.043). Exposure of the coked catalyst to ozone at an initial temperature of 38 °C resulted in a rapid rise in temperature to 120 °C within 30 s of establishing the O_3/O_2 flow. This

m.	
16	
- 3.3	
×,	
0	
ä	
\simeq	
<u> </u>	
4	
-	
9	
2	
$\overline{}$	
\simeq	
\leq	
9	
0	
-	
<u> </u>	
. H	
S	
8	
~	
.=	
5	
2	
~	
2	
~	
н.	
>	
<u> </u>	
4	
d b	
led b	
nded b	
paded b	
loaded b	
nloaded b	
vnloaded b	
ownloaded b	
Jownloaded b	
Downloaded b	
. Downloaded b	
6. Downloaded b	
86. Downloaded b	
986. Downloaded b	
1986. Downloaded b	
y 1986. Downloaded b	
ry 1986. Downloaded b	
ary 1986. Downloaded b	
uary 1986. Downloaded b	
nuary 1986. Downloaded b	
anuary 1986. Downloaded b	
January 1986. Downloaded b	
1 January 1986. Downloaded b	
01 January 1986. Downloaded b	
101 January 1986. Downloaded b	
on 01 January 1986. Downloaded b	
on 01 January 1986. Downloaded b	
d on 01 January 1986. Downloaded b	
ed on 01 January 1986. Downloaded b	
hed on 01 January 1986. Downloaded b	
ished on 01 January 1986. Downloaded b	
lished on 01 January 1986. Downloaded b	
blished on 01 January 1986. Downloaded b	
ublished on 01 January 1986. Downloaded b	

Table 1. H-ZSM-5 catalyst reactivation data, $SiO_2/Al_2O_3 = 35$

G 🖁	SC	30	2.1	58	90.9		83.0		17.0	0	ass %.
r oxyg (450 °(158	6	3	6				8	5	otes ma
st afte vation	5 B	1256	0.0	366	96.9		0		95.8	4	% deno
cataly reacti	5 A	250	0.9	370	99.5		0		75.6	24.4	¹). ^c m/m ^c
zone 0 °C)	4C	978	3.0	370	91.9		86.0		14.0	0	used (dm ⁸
st after o ation (15	4B	867	1.0	379	90.2		0		100.0	0	catalyst
cataly reactiv	4A	830	2.1	369	92.1		0		98.6	1.4	volume of
catalyst after low-temperature oxygen reactivation (150 °C)	£	54	2.1	370	90.6		85.0		15.0	0	CH ₃ OH(dm ³ h ⁻¹)/
t after ne- ation °C)	2 B	974	2.1	370	89.6		78.0		22.0	0	low rate of
catalys ozo reactiv (192	2 A	145	2.1	369	96.4		0		89.4	10.6	lumetric f
	Ū	1154	2.2	372	89.8		83.0		17.0	0	.s.v. = vo
atalyst	IC	880	1.2	370	93.1		0		100.0	0	In. ^b l.h
new ca	1B	538	1.3	371	96.0		0	(% u	89.2	10.8	end of n
	1A	293	1.1	370	99.5		0	vities (m/	89.9	10.1	n line to e
catalyst condition	run number	TOL ^a /min	$1.h.s.v. (h^{-1})^b$	$T/^{C}$	MeOH conversion	(m/m%) ^c	DME (%)	hydrocarbon selectiv	C ₁ -C ₆ gases	C ₆ -C ₁₀ aromatics	^a Cumulative time o

R. G. Copperthwaite et al.

1009

Pentasil Zeolite Catalyst Regeneration

reactivation	ozone–oxygen 150 °C	oxygen 450 °C
component mass%		
CH	0.7	1.0
C ₂	7.8	6.9
C ₃	7.3	5.6
C [°]	11.2	13.6
C_5	1.5	1.1
Č,	1.5	0.3
DME	69.8	71.4

Table 2. Detailed composition of gas fraction, T = 371 °C, l.h.s.v. = 3 h⁻¹, catalyst H-ZSM-5, SiO₂/Al₂O₃ = 35

exothermic reaction was accompanied by the production of CO₂(g) and was always observed when ozone was utilised for catalyst regeneration. After 10-15 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, ca. half the catalyst bed appeared to be free of carbonaceous material and the particles at the top of the catalyst bed had returned to their original white colour. The activity of the catalyst for methanol conversion was then determined (run 2), which clearly demonstrated that the ozone treatment restored the catalyst activity. It was subsequently determined that reactivation could be achieved under milder conditions (O₃/O₂ mole ratio 0.066, 150 °C, 80 min) as shown in run 4. Attempted reactivation of the catalyst using pure oxygen gas under the same conditions as for the ozone treatments was unsuccessful (run 3); no $CO_2(g)$ production and no exothermic reaction being observed. Treatment with oxygen was, however, found to reactivate the whole bed after 6 h passage of oxygen at a bed temperature of 450 °C (run 5). Treatment with oxygen in this way removed carbonaceous material uniformly, but the catalyst did not return to its original colour and remained brown/grey. In further experiments it was found that CO₂(g) was not produced until a catalyst bed temperature of 360 °C was used, but to achieve an appreciable rate of reactivation, temperatures in the range 420-450 °C were necessary.

Differences in the product selectivities of the catalyst after ozone and high-temperature oxygen reactivation were observed. The catalyst following oxygen reactivation produced significantly more aromatic products, whereas the ozone reactivated catalyst produced correspondingly more C_1 - C_6 alkanes and alkenes. Detailed analyses of the gaseous products for ozone and oxygen reactivated catalysts are shown in table 2 for comparable reaction conditions. The ozone reactivated catalyst gave reduced methane and increased C_2 and C_3 hydrocarbon yields when compared to the oxygen reactivated material at the same methanol conversion and reaction time.

Ozone Reactivation of H-ZSM-5 Catalyst for Methanol Conversion $SiO_2/Al_2O_3 = 70$

H-ZSM-5 catalyst, with an SiO_2/Al_2O_3 mole ratio = 70, was used for methanol conversion and the product distributions are shown in table 3 (runs 6A–E). As noted previously for the H-ZSM-5 zeolite with $SiO_2/Al_2O_3 = 35$, deactivation was again observed under the experimental conditions, and when the production of hydrocarbon products was significantly reduced, the catalyst was reactivated with an ozone-oxygen mixture (O₃/O₂ mole ratio 0.05) at 150 °C for 90 min. An initial exothermic reaction was observed as before. The activity of the reactivated catalyst was then determined for methanol conversion (runs 7A–D) and it was again observed that low-temperature ozone treatment of the coked zeolite essentially restored the catalyst activity. After further on-line

catalyst condition		ne	w catalys			rea	after oz ctivation	one (150 °C)		rea	after oxy ctivation	/gen (450 °C)	
run number	6 A	6B	6C	6D	6E	TA	7B	7C	DT D	8A	8B	%C	8D
TOL ^a /min	06	195	415	675	923	135	325	525	732	120	243	401	658
MeOH conversion ^{b} (%)	100	100	92	51	32	6.66	99.1	75.9	53.6	6.66	99.7	83.3	53.6
hydrocarbon selectivities (mass %)												
ĊH,	5.5	4.7	8.6	11.1	9.2	5.8	9.2	10.1	11.5	7.3	7.7	9.5	10.7
C, t	18.0	22.6	38.2	41.3	58.8	33.6	32.7	40.4	48.6	27.9	42.2	43.4	51.1
C_{c}^{2}	33.3	40.0	31.5	31.3	20.2	30.8	30.3	29.4	24.1	25.7	23.2	27.6	24.5
Ċ	32.9	28.3	15.9	11.8	11.3	21.4	17.7	15.2	14.7	24.3	17.9	13.5	11.3
C,+	10.3	4.4	5.8	4.5	0.5	8.4	9.6	4.9	1.1	14.9	8.9	6.0	2.5
	mulative ti	me on lin	e to end o	of run. ^b	Methanol	conversi	on to hyd	Irocarbon	s only. ^c	> 95% 8	ilkenes.		

R. G. Copperthwaite et al.

0 h−1 371 °C 1 h s v F 5 Sin /AI O 4 ę 4 + + - 1--TCNI 5 L • 11 F



Fig. 2. Methanol conversion plotted against reaction time: ○, fresh catalyst; △, ozone-reactivated; □, oxygen-reactivated.

coking, the catalyst was reactivated with oxygen at 450 °C for 6 h and the subsequent activity for methanol conversion was determined (runs 8A–D). By using the catalyst under identical reaction conditions (T = 371 °C, 1.h.s.v. = 2 h⁻¹), the effect of the regeneration method on the catalyst lifetime with respect to methanol conversion was determined (fig. 2). Reactivation of the zeolite using low-temperature ozone resulted in a catalyst that remained active for slightly longer than the fresh catalyst, whereas high-temperature oxygen reactivation initially gave a slightly less active catalyst. This result was confirmed by determining the time on line when dimethyl ether first appeared in the reaction products, which under these reaction conditions was 360, 400 and 250 min for the fresh, ozone-reactivated and oxygen reactivated catalysts, respectively.

In addition to differences in catalyst activity, some differences were also observed in the product distribution. As the catalyst deactivated, the methane yield increased, whereas the C_3/C_2 mole ratio and the yield of C_5 + hydrocarbons decreased. The variations are considered to be caused by the decrease in methanol conversion and the deposition of carbonaceous material as the reaction time increases, and the increase in methane yield has been observed in previous studies.⁴ Fig. 3 shows the variation of the C_3/C_2 mole ratio with reaction time for these catalysts. The C_3/C_2 mole ratio initially observed with the fresh catalyst is > 1 for methanol conversions of 100%, but when the methanol conversion decreased to 92%, the C_3/C_2 mole ratio is significantly decreased. Reactivation with high-temperature oxygen restores the C_3/C_2 mole ratio to a value approaching that of the fresh catalyst and a similar decline is then observed as methanol conversion decreases. Low-temperature ozone regeneration does not restore the initial C_3/C_2 mole ratio and at high methanol conversions this catalyst gave higher yields of C_2 hydrocarbons compared to the fresh or oxygen-reactivated catalysts.

Fig. 4 shows how the methane selectivity varies with reaction time for these catalysts. Initially, higher methane yields are obtained with the oxygen reactivated material when compared to the fresh catalyst or ozone-reactivated catalyst. As reaction time increases

R. G. Copperthwaite et al.



Fig. 3. C_3/C_2 mole ratio plotted against reaction time: \bigcirc , fresh catalyst; \triangle , ozone-reactivated; \Box , oxygen-reactivated.

the methane selectivities observed for all three catalysts converge for reaction times > 600 min, at which point the methanol conversion has decreased to 50-60%.

Variation in the methanol l.h.s.v. also affected the initial product distribution for low-temperature ozone and high-temperature oxygen reactivated catalysts (table 4). As expected,¹⁰ increasing the methanol l.h.s.v. reduced the methanol conversion; however, ozone-reactivation always gave a slightly more active catalyst than did high-temperature oxygen reactivation. Selectivity differences were also observed at comparable methanol conversions, the most significant being the reduced methane yields observed after ozone-reactivation.

Ozone Reactivation of H-ZSM-5 Catalyst for o-Xylene Isomerisation, $SiO_2/Al_2O_3 = 70$

Following the previous methanol conversion experiments, the H-ZSM-5 catalyst, $SiO_2/Al_2O_3 = 70$, was reactivated with a high-temperature oxygen treatment (420 °C for 6 h) and *o*-xylene isomerisation to *p*-xylene was carried out at 400 °C with an *o*-xylene contact time of 1.5×10^{-4} s. The results are shown in table 5 (runs 9A–F). Owing to the short contact time, the *o*-xylene conversion observed was low (*ca*. 7%); this conversion gradually decreased further with reaction time, and carbonaceous material was deposited on the catalyst. The catalyst was then reactivated with a low-temperature treatment with an ozone–oxygen mixture (O_3/O_2 mole ratio = 0.06) at 150 °C for 90 min. The reactivated catalyst was tested for *o*-xylene isomerisation and the results are shown in table 5 (runs 10A and B). The low-temperature ozone reactivation essentially restores the catalytic isomerisation activity.



Fig. 4. Initial methane selectivities: \bigcirc , fresh catalyst; \triangle , ozone-reactivated; \Box , oxygen-reactivated.

Table 4.	Effect of	`variation in	methanol l.h.s.v.	on H-ZSM-5 catal	yst SiO _{2/}	$(Al_2O_3 = 70)$
----------	-----------	---------------	-------------------	------------------	-----------------------	------------------

catalyst	I	ozone eactivate	1	oxygen reactivated			
reaction time ^a /min	180	270	180	180	120	180	
MeOH l.h.s.v./h ⁻¹	1.2	2.0	3.0	1.2	2.0	3.0	
T/°C	371	371	371	371	371	371	
MeOH conversion $(\%)$	100.0	99.9	96.2	99.6	99.9	96.1	
hydrocarbon selectivity (m	ass %)						
C ₁	6.2	5.8	4.7	6.4	7.3	4.9	
C ₂	25.3	33.6	40.0	27.6	27.9	37.1	
$\overline{C_3}$	30.1	30.8	26.3	28.8	25.7	26.8	
C_4	29.2	21.4	20.3	28.3	24.3	20.8	
$C_5 +$	9.2	8.4	8.5	8.8	14.9	10.4	

^a Cumulative time on line at end of run.

Discussion

Visual inspection of the catalyst bed after the reactivation procedures indicated that high-temperature oxygen treatment uniformly removed carbonaceous material, whereas low-temperature ozone–oxygen treatment mainly removed the deposits from the top of the catalyst bed. It is known that ozone is thermally unstable at relatively low

1015

R. G. Copperthwaite et al.

catalyst			oxygen re	ozo reacti	one ivated			
run TOL ^a	9A 92	9 B 210	9C 403	9D 490	9E 658	9F 861	10A 105	10B 172
conversion (%)	7.4	7.4	6.4	6.2	5.7	5.4	7.5	7.3

Table 5. *o*-Xylene isomerisation, H-ZSM-5, $SiO_2/Al_2O_3 = 70$

^a Time on line at end of run: units are min. ^b No *m*-xylene was observed.

temperatures,¹¹ and it appears that most of the ozone is decomposed in the top part of the catalyst bed. This decomposition leads to reactive surface oxygen species¹² such as $O^-(ads)$, $O_2^-(ads)$ which react exothermically with the carbonaceous deposit to give $CO_2(g)$. Although with ozone treatment the carbonaceous deposits are removed only from the top part of the catalyst bed, the subsequent activity and lifetime of this material compare favourably with that of fresh catalyst and, in addition, are increased with respect to oxygen-regenerated material. We conclude that the whole catalyst bed has been partially reactivated and that the effect is not solely limited to the catalyst particles located at the top of the bed. A two-stage reactivation with ozone was also investigated in which the ozone–oxygen mixture was initially fed to the top and subsequently the bottom of the catalyst bed. This treatment did not significantly affect the observed catalyst lifetime or activity when compared with the usual ozone–oxygen low-temperature treatment. This evidence therefore supports the conclusion that the whole catalyst bed has essentially been partially reactivated by the low-temperature ozone–oxygen treatment.

Previous studies have investigated either the nature of the chemical precursors of the carbonaceous deposits,^{5, 13} or the relative rates of deactivation and the corresponding high-temperature oxygen reactivation for different zeolite structures.⁴ From these studies it was concluded that both paraffinic and aromatic chemical precursors participate equally in the function of these carbonaceous deposits. In addition, the pore structure of the zeolite was found to influence deactivation and reactivation markedly. ZSM-5 was considered to form carbonaceous deposits preferentially on the external crystallite surface, thus accounting for the reduced coking and deactivation rates observed compared to mordenite. Only limited studies have been carried out with respect to the structure of the carbonaceous deposits (coke) found on ZSM-5. Derouane⁴ has found that the coke is more graphitic in nature on ZSM-5 compared to that found on mordenite or offretite, and in a subsequent study¹⁴ using solid state ¹³C n.m.r. he showed that the coke consisted of alkyl aromatic compounds and the composition was highly dependent on the nature of the initial reactant. In addition, although these experiments were conducted using zeolites with relatively low contents of carbonaceous material, light products were observed trapped within the zeolitic structure as a consequence of pore blocking. Pore blocking, the process by which carbonaceous material is sequentially deposited within the zeolite, has been found to enhance the apparent molecular shape selectivity of ZSM-5 for *p*-xylene from toluene alkylation reactions.¹⁵ Hence, pore blocking can be considered to be one mechanism by which selectivity variations can be observed for zeolite catalysts with increasing reaction time. However, such selectivity differences could also be due to variation in the acidity of the active sites, and a reduction in the acidity of pentasil zeolites¹⁰ has been shown to reduce the formation of aromatic products. Derouane⁴ has shown, using ammonia adsorption, that carbonaceous deposits poison the strong and medium acid sites in ZSM-5. Hence, a combination of pore blocking and acid-site poisoning is probably responsible for the variations in selectivity

Pentasil Zeolite Catalyst Regeneration

sample	1^a	2 ^b	3 ^c
C (% by mass)	1.71	0.67	1.02
H (% by mass)	0.32	0.52	0.52
C/H atomic ratio	0.44	0.11	0.16

Table 6. Analysis of catalysts before and afterreactivation

^a Zeolite H-ZSM-5 (SiO₂/Al₂O₃ = 35) following reaction with methanol (l.h.s.v. = 2 h⁻¹, 371 °C, 6 h). ^b Sample 1 following reactivation with oxygen, 450 °C, 6 h. ^c Sample 1 following reactivation with ozone-oxygen mixture (O₃/O₂ mole ratio = 0.05), 150 °C, 1.5 h.

observed during the deactivation process (*i.e.* the increase in methane yield and a corresponding decrease in the C_2/C_3 mole ratio).

In the work reported here, a comparison of the C, H micro-analysis of deactivated (coked) zeolites after methanol conversion and the corresponding zeolite following high-temperature oxygen and low-temperature ozone treatment indicated that the reactivated material contained appreciable quantities of residual carbonaceous deposits (table 6). These reactivated zeolites gave essentially total methanol conversion when subsequently tested; therefore indicating that considerable quantities of carbonaceous residues can be tolerated within the zeolitic structure of ZSM-5 before deactivation is observed. However, these residual deposits could be expected to influence the subsequent product selectivity observed during the methanol conversion reaction, since it is apparent that the high-temperature oxygen treatment is more efficient for carbon removal than the low-temperature ozone treatment.

The significant difference for product selectivities between ozone- and oxygenreactivated zeolites in methanol conversion was the selectivity to methane at comparable conversions. The ozonised zeolites in general produced less methane and more light gases in the C_2-C_4 fraction, and consequently produced less C_5 + and aromatic products. The difference in methane yields was only significant for the initial reaction period following reactivation whereas a difference was always observed with the C_5 + yields. Hence, the two selectivity effects observed are not consistent through the reaction period and we suggest that this indicates that these effects have different origins and propose the following model.

It is known that methane yields increase with increased content of carbonaceous material in the catalyst structure and the observed differences in methane selectivity can be attributed primarily to different degrees of residual pore blocking following the reactivation procedures. As the reaction proceeds, carbonaceous material is deposited preferentially on the exterior of the crystallites⁴ and hence the effects of residual pore blocking should be a short-term effect. In this way the yield of methane from ozone-or oxygen-reactivated zeolite would be expected to become similar as the differences in pore blocking were minimised (fig. 4). However, the effect on the active sites present within the porous zeolite framework of the build-up of carbonaceous material on the crystallite exterior would not be expected to be as significant as those expected for residual pore blocking since $\geq 99\%$ of the active surface area is present within the zeolite crystallite.¹⁶ Any difference in the structure of the active site would then be expected to persist for a longer timescale and these differences, *e.g.* acidity and active site geometry, are proposed as the origin of the reproducible difference in C_5 + yields observed with ozone and oxygen regenerated material. Such a model would therefore be consistent with an

R. G. Copperthwaite et al.

1017

initial difference in methane selectivity together with a long-term difference in C_5 + yields. It is clear, however, that detailed structural studies are now required to investigate the observed selectivity differences more fully.

The results of this study indicate that low-temperature ozone reactivation of pentasil zeolites $(SiO_2/Al_2O_3 = 35, 70)$ essentially restores the catalytic activity for the two reactions studied and hence can be considered to be an alternative method to the well established high-temperature oxygen reactivation procedures currently used in industrial procedures. Zeolites, when used as catalysts, are usually involved in hydrocarbon synthesis or conversion reactions, and the deposition of carbonaceous materials is normally associated with catalyst deactivation for these processes. Hence low-temperature ozone reactivation could be expected to be generally applicable for removal of carbonaceous material in industrial catalytic processes.

We thank M. G. Howden and Dr D. M. Bibby for helpful discussions, and the National Institute for Coal Research, CSIR, Pretoria, for the g.c.-m.s. measurements.

References

- 1 C. A. Fyfe, G. C. Gobbi, J. Klinowski, J. M. Thomas and S. Ramdas, Nature (London), 1982, 296, 530.
- 2 C. D. Chang and A. J. Silvestri, J. Catal., 1977, 47, 249.
- 3 L. B. Young, S. A. Butler and W. W. Keading, J. Catal., 1982, 76, 418.
- 4 P. Dejaifve, A. Auroux, P. C. Gravelle, J. C. Vedrine, Z. Gabelica and E. G. Derouane, J. Catal., 1981, 70, 123.
- 5 D. E. Walsh and L. D. Rollman, J. Catal., 1979, 56, 195.
- 6 C. A. Fyfe, G. J. Kennedy, G. T. Kokotailo and G. T. De Schulter, J. Chem. Soc., Chem. Commun., 1984, 1093.
- 7 W. O. Haag, R. M. Lago and P. B. Weisz, Nature (London), 1984, 309, 589.
- 8 R. G. Copperthwaite, G. J. Hutchings, P. Johnston and S. W. Orchard, J. Chem. Soc., Chem. Commun., 1985, 664.
- 9 M. G. Howden, CSIR Report C Eng 413 (CSIR, Pretoria, South Africa, 1982).
- 10 C. D. Chang, C. T-W. Chu and R. F. Socha, J. Catal., 1984, 86, 289.
- 11 Kirk-Othmer, Encyclopedia of Chemical Technology (John Wiley, New York, 3rd edn, 1981), vol. 16, p.690.
- 12 M. Che and A. J. Tench, Adv. Catal., 1982, 31, 78.
- 13 D. F. Walsh and L. D. Rollman, J. Catal., 1977, 49, 369.
- 14 E. G. Derouane, J. P. Gilson and J. B. Nagy, Zeolites, 1982, 2, 42.
- 15 W. W. Kaeding, C. Chu, L. B. Young, B. Weinstein and S. A. Butler, J. Catal., 1981, 67, 159.
- 16 J. Dwyer, Chem. Ind., 1984, 258.

Paper 5/1318; Received 30th July, 1985