### Reactivation of Zeolite and Oxide Catalysts using Nitrous Oxide

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A novel procedure for the removal of carbonaceous deposits from catalysts using nitrous oxide is described. The general applicability of this method is demonstrated for zeolites H-Y and H-ZSM-5, acid-treated clinoptilolite and supported tungsten oxide as catalysts for hex-1-ene cracking and methanol conversion reactions. The method is particularly effective for acid-treated clinoptilolite as this material cannot be successfully reactivated using a standard oxygen method. Additionally with zeolite H-Y the procedure permits total removal of the carbonaceous deposits, which cannot be readily achieved using oxygen. For the catalysts investigated, nitrous oxide exhibited a marked variation in its reactivation activity (acid treated clinoptilolite > H-Y > H-ZSM-5 > 10 % WO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>), a feature which is not observed with the standard oxygen reactivation procedure. Studies of N<sub>2</sub>O decomposition of both coked and uncoked catalysts demonstrate that the main process occurring during N<sub>2</sub>O reactivation is the direct oxidation of the coke deposit by molecular N<sub>2</sub>O. The reactivation efficacy observed is expressed in terms of (a) the amount of coke deposited on the catalyst and (b) the structure of coke deposit which has been studied using solid-state <sup>13</sup>C magic-angle spinning nuclear magnetic resonance spectroscopy.

The successful operation of a heterogeneous catalyst on an industrial basis depends on a number of interlinked parameters,<sup>1</sup> and one which is of crucial economic importance is the useful catalyst lifetime. This is particularly important, since many industrial catalysts cannot be successfully reactivated, e.g. promoted fused Fe catalysts<sup>2</sup> for Fischer-Tropsch or ammonia synthesis fall into this category. Catalyst reactivation may not be possible owing, for example, to the loss of the active component during use (e.g. loss of Hg from acetylene hydrochlorination catalysts,<sup>3</sup> or the modifications of the structure of the catalysts caused by the reactivation procedure (e.g. sintering or loss of promoters). There is therefore an important requirement to understand fully this aspect of catalyst operation if future improvements are to be made. However, one class of catalyst, namely zeolites, can only be successfully operated industrially because they can be reactivated. Zeolites have found widescale operation in the petrochemical and fuels industries since their introduction as catalysts for fluid catalytic cracking<sup>4</sup> and more recently for the transformation and synthesis of hydrocarbons.<sup>5</sup> During use, deposition of carbonaceous materials, referred to as 'coke', occurs within the channels of the zeolite, and this is the primary cause of catalyst deactivation.<sup>6</sup> Zeolites are known to demonstrate shape selectivity, and this feature is thought to minimise the rate of coke deposition for some specific zeolites, e.g. ZSM- $5,^7$  but even then the effective working lifetime is only ca. 2–3 weeks for the methanol conversion reaction.<sup>8</sup> The rates and mechanisms of zeolite

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deactivation have received considerable attention in recent years, but the important process of reactivation has, in contrast, been little studied. For zeolites, reactivation is normally achieved by oxidising the deposit with air to carbon oxides and water, using a catalyst bed temperature of 400–500 °C. We have previously demonstrated that use of ozone<sup>9</sup> as an alternative oxidising agent can be highly effective at lower temperatures (150-190 °C), and we have further shown<sup>10</sup> that ozone preferentially reacts with the aromatic coke structures. Consequently this procedure could be useful for catalytic materials that are not stable at higher temperatures. However, for large-scale reactivation of catalytic pellets in a fixed bed the diffusion of ozone is found to be a singificant factor. and it is anticipated that this reactivation procedure will only be effective for fluidised catalyst beds. Additionally, ozone only removes some of the coke, ca. 40-50%, and this is not sufficient for some applications. In a recent communication<sup>12</sup> we reported our initial findings for a reactivation procedure based on N<sub>2</sub>O as oxidant which was shown to be more effective for total coke removal when compared with oxygen or ozone. In this paper we exemplify and extend the general applicability of this method, and discuss these results with respect to the rates of catalytic N<sub>2</sub>O decomposition on both fresh and coked catalysts.

#### Experimental

#### **Catalyst Preparation**

The sodium form of the pentasil zeolite ZSM-5 was prepared according to the method of Howden<sup>13</sup> with a  $SiO_2/Al_2O_3$  mole ratio of 35. The Na-ZSM-5 was converted into the protonated form (H-ZSM-5) using a method previously described<sup>9</sup> which involves a total of three separate ammonium-ion exchange and calcination treatments. Samples of partially exchanged ZSM-5 were also retained for catalytic testing.

Clinoptilolite was obtained as a natural zeolite from Zululand, South Africa, and contained 75–80 mass % clinoptilolite with minor amounts of quartz, cristobalite and potassium feldspar (composition: Si/Al ratio = 5.0, Fe 0.83 %, Ca 0.98 %, Na 0.88 %, K 3.03 %, surface area =  $21 \text{ m}^2 \text{ g}^{-1}$ ). Natural clinoptilolite (100 g) was treated with aqueous HCl (2 mol dm<sup>-3</sup>, 1 dm<sup>3</sup>) for 8 h at 75 °C to convert the zeolite into the acid form. This procedure was repeated three times, following which the zeolite was recovered by filtration, washed with distilled water, dried in air (120 °C, 3 h) and calcined (400 °C, 16 h). The composition of the acid-treated clinoptilolite was as follows: Si/Al ratio = 9.5, Fe 0.67 %, Ca 0.30 %, Na 0.05 %, K 1.37 %, surface area =  $85 \text{ m}^2 \text{ g}^{-1}$ .

Zeolite H-Y (Union Carbide, LZY82, H form) was calcined (500 °C, 2 h) prior to use (Si/Al ratio = 1.46, surface area = 675 m<sup>2</sup> g<sup>-1</sup>).

Tungsten oxide (10%) supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was prepared from ammonium metatungstate according to the method of Maitra *et al.*<sup>14</sup> using adsorption from an aqueous solution (pH 6.5, 25 °C, 8 h). After this procedure the sample was dried (120 °C, 8 h, air) and calcined for 16 h. Following calcination the catalyst was found to be amorphous by X-ray diffractometry, in agreement with previous studies.<sup>14</sup>

The calcined  $10 \% WO_3/Al_2O_3$ , acid-treated clinoptilolite and H-ZSM-5 were pelleted, without addition of binder, and sieved to give particles (0.5–1.0 mm) for use in the catalytic reactor.

#### **Catalyst Testing and Reactivation**

Catalysts were tested for methanol conversion and hex-1-ene cracking using procedures and equipment previously described,<sup>9</sup> except that reagents were fed to a heated vaporiser using calibrated peristaltic or syringe pumps which afforded improved control of

reactant feedrate. Catalyst reactivation was carried out by substituting the methanol (or hex-1-ene)– $N_2$  stream for oxygen or nitrous oxide (flow rate 1 cm<sup>3</sup> s<sup>-1</sup>).

 $N_2O$  decomposition was studied over both the fresh and deactivated catalysts in a fixed-bed Pyrex glass reactor. The extent of decomposition was determined by on line gas chromatography using a thermal-conductivity detector.

#### Structure of Coke Deposits

Solid-state <sup>13</sup>C (c.p. – M.A.S.) n.m.r. spectra of coked and partially reactivated zeolite H-Y were obtained using a Bruker AM300 spectrometer with a contact time of 1 ms and a recycle time of 4 s. The rotor (alumina) was spun at 5.0 kHz and 900–5900 spectra were accumulated prior to Fourier transformation. The rotors containing uncoked zeolite under the conditions specified gave no detectable resonances in the range  $\delta$ -150 to 340 ppm.

#### **Results and Discussion**

#### Nitrous Oxide Reactivation of H-Y Catalyst for Hex-1-ene Cracking

Zeolite H-Y was reacted with hex-1-ene at 500 °C and liquid hourly space velocity  $0.38 \text{ h}^{-1}$ , and the product distributions are given in table 1 (runs 1 A–1 E). Reaction with hex-1-ene was selected as we have previously shown that this reactant leads to rapid catalyst deactivation. Deactivation of the catalyst was indicated by a decrease in hex-1-ene conversion together with an increase in mass due to the 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 the deactivated zeolite were then reactivated by substituting either  $O_2$  or  $N_2O$  for the  $N_2$ -hex-1-ene feed at 450 °C for 6 h and 500 °C for 2.5 h. The relative rates of coke removal for these procedures are shown in fig. 1. Initial carbon removal is far more rapid for oxygen than for  $N_2O$ . However, it is clear that N<sub>2</sub>O removes all the carbonaceous deposit, whereas the equivalent treatment with O2 always leaves some residual coke within the zeolite which is particularly resistant to oxygen. Hence to obtain virtually complete coke removal with oxygen requires long reaction periods. Moreover, increases in temperature are not particularly beneficial, e.g. O2 treatment at 500 °C for 2.5 h gives a residual carbon level of 0.45% by mass. Following reactivation the catalytic activity for hex-1-ene cracking was evaluated and compared to that of the fresh catalyst (table 1 and fig. 2). The data show that zeolite H-Y is rapidly deactivated by reaction with hex-1-ene and after ca. 100 min a steady conversion level of ca. 75% is achieved. Analysis of coke deposition with time-on-line indicates that the coke is mainly formed during this period of rapid decline in conversion, leading to a decrease in active surface area, presumably by pore blocking. It is clear that both the N<sub>2</sub>O and O<sub>2</sub> reactivation procedures studied in this work can restore the initial high hex-1-ene conversion, with  $N_2O$  reactivation (2.5 h, 500 °C) being more effective than an equivalent O<sub>2</sub> treatment; however, for both oxidants, the reaction time for which the initial high conversion is maintained is significantly shortened. This effect was enhanced by repeated reaction and reactivation cycles when, although the high initial activity was always restored, subsequent deactivation became more rapid. Since the reactivated zeolite contains very similar amounts of coke following either  $N_2O$  or  $O_2$  reactivation, this difference in initial decay rate is probably not due primarily to residual coke deposition. It is more likely that the use of high concentrations of oxidant during reactivation may cause hydrothermal reactions owing to the rapid initial coke oxidation, leading to a change in the nature and number of the active acid sites. Hence, whilst this study confirms that N<sub>2</sub>O is a possible alternative regeneration oxidant it is clear that the reactivation procedure requires considerable optimisation to ensure that the integrity and numbers of the acid sites are maintained.

			Table ]	I. Н-Ү с	atalyst re	activatio	n data f	or hex-	l-ene cr	acking					
catalyst condition:		ne	w cataly	yst			after N <sub>2</sub>	O react	ivation <sup>a</sup>			after O	2 reactiv	vation <sup>b</sup>	
run number:	1 A	1 B	1C	Ū	ΙE	2A	2B	2C	2D	2E	3A	3B	3C	3D	3 E
time on line <sup>c</sup> /min conversion <sup>d</sup> (%) selectivity (% hy mass)	50 94.7	98 80.3	142 77.5	268 75.7	360 78.8	20 96.5	100 76.7	182 75.2	237 75.2	360 77.9	40 93.5	90 79.1	147 72.8	240 76.1	360 79.0
CH4 CH4	0.03	0.08	0.08	0.09	0.06	0.1	0.1	0.1	0.1	0.4	0.07	0.07	0.08	0.08	0.06 0.8
C <sub>2</sub> H <sub>4</sub> C <sub>3</sub> H <sub>6</sub>	0.1	0.3	0.3	0.3	0.1	0.4	0.4	0.5	0.3	0.1	0.2	0.3	0.2	0.2	0.1
٢, ٣	17.1	21.4	21.5	19.5	14.8	25.3	22.0	20.8	16.0	15.6	20.8	17.0	12.2	12.5	16.1
<sup>ت</sup> ت	53.2	42.0	42.6	35.6	33.1	4.1	40.6	37.3	33.4	39.8	54.1	46.9	45.4	41.0	40.2
ບໍ່ເ	29.8	32.9 2.6	32.5 2 4	26.5 18.4	26.7 23.9	26.7 1 8	31.8 4 0	21.4 18.3	26.6 27.6	35.5 8 5	22.5 0.8	33.3 1 6	37.9 3 4	36.3 9 1	34.5 8 2
<sup>a</sup> $N_2^{o}O$ reactivation 500 °C isomerisation to other $C_6$	, 2.5 h, 1 products	cm <sup>3</sup> s <sup>-1</sup> .	<sup>b</sup> O <sub>2</sub> re le <b>2</b> . H-	activatic ZSM-5	on 500 °C catalyst r	, 2.5 h, 1 eactivatio	cm <sup>3</sup> s <sup>-1</sup> . on data	<sup>c</sup> Cum for met	ulative t hanol c	ime on lin onversion	le to end	of run.	<sup>d</sup> Conv	ersion e	xcludes
catalyst condition:		ne	w catal	yst			after N2	O react	ivation <sup>a</sup>	-		after O	2 reactiv	vation <sup>b</sup>	
run number:	1A	1B	IC	ID	ΙE	2A	2B	2C	2D	2E	3A	3B	3C	3D	3 E
time on line <sup>e</sup> /h	4	~	=	23	26	4	~	=	23	26	4	×	=	23	26
conversion (%) selectivity (% by mass)	100	100	8.66	94.9	86.2	100	98.3	94.3	59.8	48.3	0.66	7.76	95.2	80.3	57.1
CH4	0.5	0.4	0.7	0.7	0.3	0.8	0.6	0.4	1.1	1.3	0.8	0.9	0.7	0.9	1.4
$C_2 \dot{H}_4$	2.4	3.1	3.6	2.9	3.8	8.1	8.1	8.9	15.1	14.7	5.5	8.3	9.2	12.3	16.7
$C_{2}H_{6}$	0.3	0.1	0.3	0.3	0.1	0.3	0.2	0.1	0.1	0.1	0.3	0.2	0.1	0.1	0.1
C <sub>3</sub> H <sub>6</sub>	3.8	4.7	9.0 0	4.1	5.1	9.4	8.5	x) t	19.6	19.1	8.7	12.6 7 5	10.2	14.2	22.9
C.H.	10.1	4.5 1.4	8.2 16.0	0.0 م	0.8 2 0	C.01	0.0	7.7	9.1 9 2 1	0.1 0.01	8.8 75.0	0.0 7 8 6	5.5 71 7	2.5 157	7.1
ిం	9.5	7.4	0.0 0.6	4.7	4.6	13.3	10.3	9.1	8.7	2.6	12.0	16.5	13.0	9.2	8.5
ືບ	6.8	6.3	8.5	6.6	5.6	8.5	7.7	8.0	8.5	9.1	7.7	4.1	10.9	8.6	8.4
Ç,	46.4	59.2	49.0	58.6	74.6	23.7	42.4	49.1	31.3	34.9	31.2	31.9	31.9	31.3	27.0

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<sup>a</sup> N<sub>2</sub>O reactivation 450 °C, 6 h, 1 cm<sup>3</sup> s<sup>-1</sup>. <sup>b</sup> O<sub>2</sub> reactivation 450 °C, 6 h, 1 cm<sup>3</sup> s<sup>-1</sup>. <sup>c</sup> Cumulative time on line to end of run.

Reactivation of Catalysts using  $N_2O$ 

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Fig. 1. Rate of carbon mass loss on reactivation:  $\times$ ,  $O_2$ , 500 °C;  $\bigcirc$ ,  $O_2$ , 450 °C;  $\square$ ,  $N_2O$ , 500 °C;  $\triangle$ ,  $N_2O$ , 450 °C.



**Fig. 2.** Catalytic activity of H-Y for hex-1-ene cracking for:  $\triangle$ , fresh H-Y (calcined 500 °C, air, 2 h);  $\Box$ , N<sub>2</sub>O-reactivated H-Y (500 °C, 2.5 h), after one reaction cycle;  $\bigcirc$ , N<sub>2</sub>O-reactivated H-Y (500 °C, 2.5 h), after five reaction/reactivation cycles;  $\times$ , O<sub>2</sub>-reactivated H-Y (500 °C, 2.5 h); +, O<sub>2</sub>-reactivated H-Y (450 °C, 6 h).

Only minor differences in product selectivity are observed for catalyst reactivation using equivalent  $O_2$  or  $N_2O$  treatments, the most notable being that after  $O_2$  reactivation, formation of  $C_{7+}$  hydrocarbons (*i.e.* oligomerisation products) are decreased relative to those for fresh catalysts; however, this is not observed for  $N_2O$ . Also, for  $N_2O$ reactivation an increase in the  $CH_4$ ,  $C_2H_4$  and  $C_3$  yields are observed at the expense of  $C_4$  and  $C_5$  hydrocarbons. Since the zeolites following reactivation do not contain significant residual coke, it is unlikely that these small selectivity differences can be attributed to residual pore blocking, as has been observed for ozone reactivated



Fig. 3. <sup>13</sup>C c.p. m.a.s. n.m.r. spectra: (A) coked zeolite Y (C 13.2%) 900 scans; (B) sample a following O<sub>2</sub> reactivation 22 min, 500 °C (C = 1.2%) 5900 scans with TOSS suppression of spinning side bands; (C) sample A following N<sub>2</sub>O reactivation 32 min, 500 °C (C = 4.3%) 13663 scans.

zeolites.<sup>9</sup> The observed differences in selectivity probably reflect slight differences in the nature of the active sites for the various materials.

The structure of the carbonaceous deposits of coked and partially reactivated H-Y were investigated using solid-state m.a.s. n.m.r. A coked sample was obtained by reaction with hex-1-ene (non-<sup>13</sup>C-enriched) at 400 °C and liquid hourly space velocity 0.38 h<sup>-1</sup> for 4 h (13% by mass carbon). The <sup>13</sup>C n.m.r. spectrum of coked zeolite H-Y [fig. 3(A)] shows two distinct and prominent resonances in the range  $\delta = 20-230$  ppm, which can be assigned to aliphatic carbon ( $\delta = 0-50$ ) and aromatic carbon ( $\delta = 100-150$ ) environments, denoted (a) and (b), respectively.<sup>15</sup> This coke structure is significantly different from that produced by methanol conversion over H-ZSM-5,<sup>10</sup> when five distinct resonances were observed, and our findings are therefore in agreement with previous studies<sup>16</sup> showing that the composition of the coke is dependent on the structure of the feed reactant molecule. <sup>13</sup>C M.a.s. n.m.r. spectra were also obtained for partially reactivated H-Y using N<sub>2</sub>O and O<sub>2</sub> as oxidants [fig. 3(B) and 3(C)]. It is apparent that both N<sub>2</sub>O and O<sub>2</sub> preferentially remove aliphatic carbon environments. Hence N<sub>2</sub>O does not demonstrate any selectivity difference during reactivation when compared with O<sub>2</sub>,

whereas we have previously described such differences with  $O_3/O_2$  reactivation in a related publication.<sup>10</sup> From this study it can be seen that with both  $N_2O$  and  $O_2$ , the aromatic carbon environments are the most resistant to oxidation; however,  $N_2O$  removes all carbonaceous deposits, whereas oxygen is not so effective, and this indicates that, at least in part, different mechanisms are operating for these two oxidants.

#### Nitrous Oxide Reactivation of H-ZSM-5 Catalyst for Methanol Conversion

Methanol conversion into hydrocarbons was carried out using the synthetic pentasil zeolite H-ZSM-5, at 400 °C and methanol weight hourly space velocity (w.h.s.v.) 1.7 h<sup>-1</sup>, and the results are given in table 2 (runs 1 A-1 E). Following deactivation (*i.e.* after run 1E) the catalyst was reacted with N<sub>2</sub>O or O<sub>2</sub> at 450 °C and the reactivated catalysts were again assessed for the methanol conversion reaction (table 2). N<sub>2</sub>O reactivation restores complete catalyst activity and gives a slightly higher initial methanol conversion when compared with oxygen reactivated H-ZSM-5. However, it is also apparent that N<sub>2</sub>O reactivated H-ZSM-5 exhibits a shorter useful lifetime when compared with O<sub>2</sub> reactivated H-ZSM-5. Reactivation at 500 °C, compared with 450 °C, with N<sub>2</sub>O did not give any significant improvement and N<sub>2</sub>O reactivated H-ZSM-5.

# Nitrous Oxide Reactivation of an Acid-treated Clinoptilolite Catalyst for Methanol Conversion

Acid-treated clinoptilolite was used as a catalyst for methanol conversion at 400 °C and methanol w.h.s.v. = 0.1 h<sup>-1</sup>, and the hydrocarbon product distributions are given in table 3. Under these reaction conditions the methanol conversion decreased with reaction time owing to the deposition of carbonaceous material, which was found to occur at a rate of  $3 \text{ mg}_{\text{C}} \text{g}_{\text{catalyst}}^{-1} \text{ h}^{-1}$ . The deactivated clinoptilolite was reactivated with either N<sub>2</sub>O or O<sub>2</sub> and then re-examined as a catalyst for the methanol conversion reaction (table 3). N<sub>2</sub>O reactivation was found to be significantly more effective than the use of O<sub>2</sub> reactivation under comparable conditions, which is apparent from a comparison of the effective catalyst lifetimes for methanol conversion (fig. 4). O<sub>2</sub> reactivation does not restore the catalytic performance to that of the fresh Hclinoptilolite, whereas N<sub>2</sub>O reactivation gives improved catalytic performance. Neither N<sub>2</sub>O nor O<sub>2</sub> reactivation treatment significantly affects the product selectivity observed for methanol conversion.

# Nitrous Oxide Reactivation of a 10% $WO_3/\gamma Al_2O_3$ Catalyst for Dimethyl Ether Conversion

To demonstrate the applicability of nitrous oxide reactivation to catalysts other than zeolites, the procedure was investigated with supported tungsten oxide which has previously been cited as a catalyst for methanol or dimethyl ether conversion.<sup>17</sup> Results for the reaction of dimethyl ether over 10% WO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> (w.h.s.v. = 0.6 h<sup>-1</sup>, T = 400 °C, 4 h) are given in table 4. Deactivation of the catalyst was rapid, as shown by a decrease in dimethyl ether conversion from 99 to 18% in 190 min time on line, and, following reaction, the catalyst was then found to contain 13% by mass carbon. The deactivation catalyst was then reactivated using either N<sub>2</sub>O (500 °C, w.h.s.v. = 0.4 h<sup>-1</sup>, 10 h) or O<sub>2</sub> (400 °C, w.h.s.v. = 0.4 h<sup>-1</sup>, 4 h). These procedures fully restored catalyst activity, and no significant differences in product selectivities were observed (table 4). Use of shorter reactivation times with N<sub>2</sub>O, *e.g.* 4 h, proved to be ineffective, and to remove *ca.* 99% of the carbon deposit, reactivation for at least 10 h was required.

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	ú	sw catal	yst	$N_{2}O$	reactiva	ttion <sup>a</sup>	02	reactivat	ion <sup>b</sup>
ne <sup>c</sup> /min	120	240	360	120	240	360	120	240	360
1 (%) (%, hv mass)	96.5	95.1	63.7	99.4	98.4	6.99	96.3	83.9	35.4
(seaning void)	9.5	10.1	10.8	8.8	6.7	10.0	7.0	8.6	15.3
	21.0	20.0	19.8	21.4	17.0	21.0	19.1	18.5	21.4
	2.5	2.1	1.7	2.2	1.2	2.0	1.6	1.7	2.1
	27.4	24.3	28.0	25.1	27.5	29.4	29.5	30.2	27.6
	5.2	4.4	3.6	5.2	3.9	3.9	4.7	4.0	2.4
	32.5	28.7	31.6	30.3	31.4	33.3	34.2	34.2	30.0
	20.5	22.0	19.4	22.8	24.7	18.3	21.6	19.7	15.5
	9.6	13.0	10.0	12.6	14.2	11.2	13.9	13.3	9.7
	2.7	3.4	5.5	1.3	4.0	3.1	2.2	3.2	4.6
	1.2	0.6	1.1	0.6	0.7	0.9	0.4	0.6	1.3
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. 110110110	Ē	ew catal	yst	N <sub>2</sub> O	reactive	ttion <sup>a</sup>	$O_2$	reactivat	tion <sup>b</sup>
line°/min	40	105	190	50	120	200	40	130	180
n (%) / (% bv mass)	99.2	41.3	17.9	84.9	28.2	28.0	88.5	20.4	25.3
	41.5	63.9	77.3	36.8	53.1	61.9	36.2	67.6	71.3
	14.3	8.0	5.0	14.2	9.7	6.9	17.4	6.7	6.7
	8.3	6.3	4.8	10.5	8.0	6.6	11.0	5.3	6.1
	13.8	9.3	6.9	15.4	11.4	8.4	17.1	8.2	8.9
	6.2	5.7	1.2	12.2	12.7	10.6	7.6	3.6	1.2
	3.3	2.7	2.5	5.1	4.1	3.3	4.2	2.4	2.9
	12.6	4.l	2.3	5.8	1.0	2.3	6.5	6.2	2.9

<sup>a</sup>  $O_2$  reactivation 400 °C, w.h.s.v. = 0.4 h<sup>-1</sup>, 4 h <sup>b</sup> Cumulative time on line to end of run. <sup>c</sup>  $N_2O$  reactivation 500 °C, w.h.s.v. = 0.4 h<sup>-1</sup>, 10 h.

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Fig. 4. Catalytic activity of acid-treated clinoptilolite for methanol conversion: △, fresh acid-treated clinoptilolite; ○, following O₂ reactivation; □, following N₂O reactivation.

#### Nitrous Oxide Decomposition

Nitrous oxide decomposition has been widely studied as a test catalytic reaction for many years using oxide catalysts.<sup>18</sup> While the thermal decomposition of nitrous oxide is negligible in the temperature ranges used for reactivation (N<sub>2</sub>O decomposition 0.22–0.23% in temperature range 400–530 °C), a large number of oxides show significant activity in the temperature range of the reactivation studies reported in this paper. It is therefore possible that the role of N<sub>2</sub>O when used as an oxidant for catalyst reactivation is to provide a controlled supply of dioxygen or a monatomic oxygen species which then oxidises the coke. However, since N<sub>2</sub>O reactivation has been shown to effect total coke removal (which is not observed with O2 reactivation) it is considered that, at least in part, N<sub>2</sub>O oxidises coke deposits via a mechanistic pathway not observed with  $O_2$  oxidation. To investigate this aspect further  $N_2O$  decomposition was studied over samples of the unreacted catalysts and the results are shown in table 5. It is clear that the acid form of ZSM-5 was a highly active catalyst for N<sub>2</sub>O decomposition, whereas the acid form of zeolites Y and clinoptilolite were not particularly active. At 450 °C only 0.43 % decomposition of N<sub>2</sub>O was observed with zeolite Y, and yet with this zeolite a 5 h reactivation at this temperature completely removed all carbonaceous material from the zeolite (fig. 1). Such a degree of N<sub>2</sub>O decomposition is insufficient to provide sufficient oxygen if the reactivation process were solely to be based on oxygen as oxidant. For example, at 450 °C N<sub>2</sub>O decomposition can provide only 0.7% of the O<sub>2</sub> required for total coke removal from zeolite Y in 6 h treatment, and 2.5 h at 500 °C provides only 1.5% of the O<sub>2</sub> required. Further inspection of the data indicates that at the reactivation conditions utilised for all the catalysts N<sub>2</sub>O decomposition cannot account for the degree of coke removal observed. It is therefore concluded that N<sub>2</sub>O reactivation must operate via a mechanism involving the interaction of coke with molecular  $N_{2}O$ . From the data of fig. 1 it is apparent that such a process occurs at a slower rate than the oxidation of coke using dioxygen, but that this process effects complete coke removal.

The acid form of ZSM-5 demonstrates significantly higher  $N_2O$  decomposition when compared with the other catalyst samples, particularly at temperatures > 480 °C. This

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		ZS	M-5					
$T/^{\circ}C$	b	С	d	е	zeolite Y	clinoptilolite	$WO_3/Al_2O_3$	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>
400	0.17	0.24	0.25	0.35	0.10	0.21	0.27	0.23
450	0.18	1.1	1.6	2.5	0.43	0.2	0.87	0.52
480	0.23	4.2	6.0	8.4	0.75	0.53	1.9	
500	0.31	9.2	13.0	18.2	1.7	1.0	3.7	2.3
510	0.35	13.6	21.0	24.6	2.3	1.3	4.9	3.2
520	0.39	23.4	32.1	32.3	3.6	1.7	6.2	4.8
530	0.48	33.5	44.5	40.8	_	2.2	8.9	6.7

Table 5. N<sub>2</sub>O decomposition over fresh catalysts<sup>a</sup>

<sup>a</sup> % N<sub>2</sub>O decomposition, N<sub>2</sub>O g.h.s.v. = 3600 h<sup>-1</sup>, blank thermal decomposition when no catalyst present = 0.2% over whole temperature range. <sup>b</sup> ZSM-5 as prepared, 7.00% Na. <sup>c</sup> ZSM-5 after one  $(NH_4)_2SO_4$  treatment, 1.02% Na. <sup>d</sup> ZSM-5 after two  $(NH_4)_2SO_4$  treatments, 0.98% Na. <sup>e</sup> ZSM-5 after three  $(NH_4)_2SO_4$  treatments, 0.61% Na as used in reactivation studies.

catalyst: T/°C	ZSM-5 <sup>b</sup>	zeolite Y <sup>c</sup>	clinoptilolite <sup>d</sup>	WO <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub> <sup>e</sup>
350		1.0		0.5
400	1.9	2.3	0.7	1.7
450	3.2	8.9	1.4	4.5
480	14.8	20.4		15.4
500	32.4	42.4	34.4	47.1

**Table 6.**  $N_2O$  decomposition over coked catalysts<sup>*a*</sup>

<sup>a</sup> % N<sub>2</sub>O decomposition, N<sub>2</sub>O g.h.s.v. = 3600 h<sup>-1</sup>. <sup>b</sup> Following reaction with methanol, w.h.s.v. =  $1.74 h^{-1}$ , 26 h, 370 °C, 5.77 % C. <sup>c</sup> Following reaction with hex-1-ene, w.h.s.v. =  $1.0 h^{-1}$ , 6 h, 300 °C. 14.0 % C. <sup>a</sup> Reaction with methanol, w.h.s.v. = 0.1 h^{-1}, 6 h, 400 °C, 2.2 % C. <sup>e</sup> Following reaction with dimethyl ether, w.h.s.v. =  $0.6 h^{-1}$ , 4 h, 400 °C, 13.0 % C.

was investigated further and a range of samples containing increasing concentrations of Na were prepared. In general, catalytic activity at any temperature increased with decreasing Na concentration and, in particular, the as-prepared ZSM-5 was particularly inactive. It is therefore apparent that the strong Brönsted-acid sites present in ZSM-5 are responsible for the high activity in N<sub>2</sub>O decomposition. This effect of Na concentration on N<sub>2</sub>O decomposition has been recently observed with  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>,<sup>19</sup> and the present study demonstrates that this could be of more general significance.

To study the interaction of  $N_2O$  with coke deposits a range of  $N_2O$  decomposition experiments over coked catalysts samples were carried out (table 6). The decomposition of  $N_2O$  is enhanced for coked catalysts when compared with unreacted catalyst samples. This is particularly marked for low reaction temperatures (< 450 °C) when very little decomposition is noted for the unreacted catalysts. However, the effect is observed at all temperatures investigated and for coked  $WO_3/Al_2O_3$  and zeolite Y, substantial decomposition occurs which is not observed for the unreacted catalysts. Analysis of exit gases during reactivation, particularly the initial 10 min, confirmed that the oxygen from  $N_2O$  was reacted to form carbon oxides. This therefore confirms that reactivation with  $N_2O$  is effected *via* direct interaction of the coke deposits with  $N_2O$  and not *via* a mechanism involving decomposition at a catalytic site followed by reaction of the coke

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with the oxygen produced. Further supporting evidence comes from experiments in which N<sub>2</sub>O decomposition was studied in the absence of catalyst but with co-fed 'model reagents' for coke structures (*e.g.* anthracene or methyl- $\alpha$ -naphthyl ketone). Enhanced N<sub>2</sub>O decomposition was always noted in the presence of co-fed organic model compounds. For example, in the presence of low concentrations of gas-phase methyl- $\alpha$ -naphthyl ketone, N<sub>2</sub>O decomposition was increased to 0.28–0.33% in the temperature range 400–530 °C; and in the presence of gas phase anthracene N<sub>2</sub>O decomposition was increased to 0.36–0.39% in the temperature range 400–450 °C. The oxidation of organic molecules by N<sub>2</sub>O has been well studied,<sup>20–22</sup> and it is known to oxidise alkenes and alkynes with a wide range of substitution to corresponding carbonyl components. The reaction between alkenes and N<sub>2</sub>O is considered<sup>23</sup> to occur *via* a concerted 1,3-dipolar cycloaddition. Based on the comparison of N<sub>2</sub>O decomposition using coked and unreacted catalysts and the model reagent studies, it is clear that direct reaction between N<sub>2</sub>O and alkenoid groups or other unsaturated structures plays a significant role in the reactivation process observed.

From the limited range of catalysts investigated for hex-1-ene cracking and methanol conversion we have nevertheless demonstrated that  $N_2O$  exhibits a marked variation in its reactivation efficacy, and that total coke removal can only be effectively achieved with  $N_{2}O$ . For the catalysts studied, the regeneration efficacy is in the order clinoptilolite > ZSM-5  $\approx$  H-Y > 10% WO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>. Such a marked variation is not observed for oxygen reactivation, for which typically 4-6 h at 450-500 °C is required for effective coke removal for all catalysts studied. As detailed in the previous discussion the primary process occurring during reactivation can be considered to be the interaction of  $N_0$ with unsaturated centres in the coke deposits. Hence the reactivation efficacy can be related to two parameters: (a) the amount of coke and (b) the 'chemical structure' of the coke. There exists a broad correlation between the amount of coke and reactivation efficacy, but this does not explain the observation that zeolite Y is readily activated by N<sub>2</sub>O, whereas 10% WO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> requires a very long reactivation treatment, but both catalysts contain similar amounts of carbon deposited as coke. It is therefore considered that the structure of the coke, which is dependent on both the nature of the active sites and the three-dimensional pore structure of the catalyst, is an important factor for  $N_{2}O$  reactivation. Zeolites have been shown<sup>24</sup> to restrict the deposition of coke owing to shape selectivity, and it can therefore be expected that the average molecular mass of the coke deposits will be much lower for the zeolites compared to the non-shape-selective 10% WO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst. The more complex chemical nature of the coke deposits expected for 10% WO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> may account for the poor reactivation efficacy observed. Previous studies on the oxidation of organic compounds using N<sub>2</sub>O as oxidant have shown that aromatic hydrocarbons are resistant to oxidation. Hence the reactivation efficacy observed with the three zeolite catalysts for the two reactions studied may reflect the amount of aromatic structures present in the coke deposits. The studies using solidstate <sup>13</sup>C m.a.s. n.m.r. demonstrate that coke derived from methanol as a reactant contains proportionately less aromatic carbon environments<sup>10</sup> when compared with coke derived from hex-1-ene (fig. 3). Hence on this basis for zeolite Y used for hex-1-ene cracking N<sub>2</sub>O would be expected to have a poor reactivation efficacy, which is observed. The observation that clinoptilolite is readily reactivated by N<sub>2</sub>O is also mainly due to the two factors previously discussed. However, two further factors may also be important. First, clinoptilolite is a small-pore zeolite compared with ZSM-5, and the laydown of carbonaceous deposits in the smaller pores causes rapid deactivation owing to pore blocking. In this case the coke deposits may be more accessible to  $N_2O$  for reactivation. Secondly, clinoptilolite contains significant levels of iron as an impurity (0.84% Fe by mass). This impurity may be catalytically active for the production of radical species from  $N_{2}O$ , and hence may improve the reactivation efficacy of this oxidant.

The results of this study demonstrate the general applicability of the use of nitrous

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oxide as a reactivation reagent for the removal of carbonaceous residues from catalytic structures. When compared with the standard oxygen reactivation procedure it is apparent that for zeolite Y and acid-treated clinoptilolite,  $N_2O$  may offer considerable advantages either with respect to more effective coke removal or improved catalytic behaviour.

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