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SELECTIVE CATALYTIC REDUCTION OF NO_x OVER ACID-LEACHED MORDENITE CATALYSTS

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ABSTRACT

Selective catalytic reductions of NO, NO_2 and mixtures of NO and NO_2 over mordeninte catalysts were studied. The activity of mordenite catalysts with different Si/Al ratios, obtained through acid leaching, decreased with the Al content of the mordenite. The change in activity with temperature and acid leaching together with the changes in contents of Fe and Al indicate that Lewis acids are active sites. These Lewis acids could be either Fe ions or Lewis acids formed on dehydroxylation of Broensted acid sites. Activities of NO reduction on leached mordenites were correlated to the amount of adsorbed NO^+ measured by IR. The activity in the reduction of NO_x revealed a maximal conversion at a NO_2/NO_x ratio of 0.5, indicating that the oxidation of NO or the decomposition of NO_2 are the rate limiting step in the overall reduction.

INTRODUCTION

Mordenite, a zeolite with a high Si/Al ratio, is well suited for SCR reduction of NO_x (1,2). It has a structure of parallel main channels, from which side pockets lead to oval small channels parallel to the main ones. The crystal structure resists hydro-thermal breakdown as well as acid environment. These are important properties of mordenite when used as a catalyst in flue gas treatment.

Four coordinated aluminium to oxygen in the zeolite lattice creates a negative charge in the structure. The charge is balanced by counter ions, located in channels and pockets of the structure.

Active centers of the catalyst are believed to be acidic centers (Broensted- and/or Lewis acid sites) on the internal surface. The chemical character of the counter ions affects catalytic acitivty. H-substituted mordenite exchanged with transition metal ions such as Cu or Fe has shown good catalytic properties in SCR of NO_x with ammonia (2).

Investigation of the influence of NO_2/NO_x ratio on SCR with ammonia over V_2O_5/TiO_2-SiO_2 has shown that the activity of NO_x reduction is favoured by coexisting NO and NO_2 in the reaction system. Our resuls show, that the activity is strongly enhanced by a ratio of 0.5 especially in the temperature systems with NO_2/NO_x ratios equal or greater than 0.5. According to Tuenter et al. NO_x reduction NO_2/NO_x ratio of 0.5 the activity was much higher compared to NO reduction over an industrial V_2O_5-WO_3-TiO_2 catalyst.

Compared to a V_2O_5/SiO_2-TiO_2 catalyst, mordentie shows one order of magnitude lower rate of reaction for NO reduction with ammonia (2,6). The difference in catalytic activity increases as the temperature is decreased from 600 to 470 K. In oxidation of NO H-mordenite has a higher catalytic acitivity than the compared catalyst (7,8).

It is possible, that the relatively poor catalytic effect of H-mordenite in NO reduction with ammonia is caused by competitive adsorption between water and one of the nitrogen oxides. Mizumoto et al. have shown these effects in the reduction of NO with ammonia over Cu(II)NaY (9).

The purpose of this study is to examine the influence of the aluminium content in H-mordenite, changed by acid leaching, on the catalytic reduction of NO, NO_2 and NO_x with NH_3.

EXPERIMENTAL

Catalyst

The catalyst, a commercial H-mordenite "Zeolon 900 H" from Norton Ltd Zeolon 900 H, was leached by hydrochloric acid using two different methods. In the first method different extents of leaching were achieved by varying the acid concentration indexed SLx (x=molar conc). In the seconed 2M HCl was used to leach the catalyst for 1,2 or 3 periods of two hours each (indexed SLEx x=periods). These treatments gave seven catalysts with different Si/Al ratios.

TABLE 1

Catalyst characterization

Catalyst	Si	Al	Fe	d	SBET	Vpor
	(Weight % hydrous)			(nm)	(m^2 g^{-1})	(cm^3 g^{-1})
Z900H	31.0	5.58	0.50	0.19489	472.1	0.207
SL1	32.2	5.06	0.28	0.19477	493.0	0.211
SL5	31.3	4.64	0.25	0.19466	-----	-----
SLconc	32.0	4.64	0.23	0.19471	-----	-----
SLE1	32.2	4.56	0.23	0.19469	-----	-----
SLE2	32.4	3.97	0.16	0.19447	505.7	0.223
SLE3	34.0	3.31	0.09	0.19415	528.7	0.239

The catalysts were characterized by XRF, AAS, X-ray diffraction analysis, BET N_2 adsorption and NH_3 adsorption. A thorough description of catalyst preparation and characterization methods can be found in (8). A summary of catalysts and characteristics is presented in Table 1.

Method and reaction conditions

The catalytic properties of the mordenite samples were tested in a stationary flow reactor. The procedure and the equipment have been described in a previous article (6). To avoid formation of NH_4NO_3 and reaction of NH_3 in the NO_x-converter of the analysing equipment the sample flows were scrubbed to remove NH_3 (7). The reactions, which were investigated, were reduction with ammonia of NO, NO_2 and mixtures of NO and NO_2 at different NO/NO_x ratios. The conversions were measured as a function of temperature or NO/NO_x ratio.

The flue gas was simulated by mixing the components, measured by flowmeters from gas cylinders with each component in N_2 at known concentration. NO and total NO_x were analysed by a Beckman 955 chemiluminisence instrument before and after passage through the reactor. The catalyst samples (0.1-0.5 g with a particle size 0.71-0.85 mm) were subject to a gas load of 50-60 l (NTP) h^{-1} at a total pressure of 200 kPa unless otherwise stated. The reaction conditions were varied according to Table 2.

The effects of external mass transfer and channelling were shown not to influence the reaction rates of reduction of NO over a V_2O_5/SiO_2-TiO_2 catalyst (6). These experiments were performed at higher rates of reduction and smaller amounts of catalyst were used than in the case of reduction over mordenites. Consequently the influence of these effects is negligible in the reduction of NO_x over mordenites.

TABLE 2

Reaction conditions

	NO Red		NO_2 Red	NO_x Red	
NO (ppm)	110	600	--	45	330
NO_2 (ppm)	--	--	100	50	270
NH_3 (ppm)	150	800	150	150	800
O_2 (%)	2	2	2	2	2
TEMP (K)	550-620	420-670	390-670	550-650	410-670
NO_2/NO_x	0	0	1	0-1	0.45
Catalyst (g)	0.1	0.5	0.1	0.1	0.5
S.V. ($cm^3\ g^{-1}\ h^{-1}$)	500,000	100,000	500,000	500,000	100,000

A net production of NO_x was observed during preheating of NO_2+NH_3+O_2 in N_2 at temperatures exceeding 590 K. Tests with an empty reactor resulted in production of total NO_x amounting to 10% at 670 K. At the same time a change in NO_2/NO_x ratio from 1 to 0.8 was observed at the reactor inlet. It is believed, that partial reduction of NO_2 by ammonia produces NO.

$$5NO_2 + 2NH_3 \longrightarrow 7NO + 3H_2O$$

This reaction has previously been reported for reduction of NO_2 in the same experimental setup (7). The change in NO_2/NO_x ratio at the reactor inlet influences the overall rate only at temperatures higher than 620 K.

The NO_2 reduction experiments exhibited a hysteresis effect when they were performed at increasing or decreasing temperatures. Lower conversions were obtained, when data points were taken at increasing temperatures compared to points measured at decreasing temperatures. The hysteresis appeared below 550 K. The reason for this behaviour is believed to be the formation of unstable ammonium nitrate.

Mass transfer limitaions

In order to evaluate the extent of intraparticle mass transfer, NO-reduction was performed over Z900H at constant W/F_{NO}, but at two concentrations of NO (570 ppm and 110 ppm). NO conversions at 650 K were 95 and 62% at the first and the second concentration levels respectively. If the reaction order is lower than 1, which is the order of mass transfer rate, a decreased reactant concentration will give an increased mass transfer influence on the overall reaction rate (r_{obs}). An Arrhenius plot of the reaction rate at the two concentration levels with the rate constant (k_{obs}) derived from the expression for a first order reaction in an integral reactor, gives an overall activation energy (E_{obs}).

At mass transfer limited reaction conditions the effectiveness factor (η) approaches the value of the inverse Thieles module (for $\eta<0.1$). Under these circumstances the intrinsic activation energy (E_{intr}) can be derived, if η in the over all reaction rate expression is substituted by the inverse Thieles module (11).

The influence of the activation energies of diffusion (E_{diff}), and of reaction (E_{intr}) on E_{obs} is then given by:

$$E_{intr} = 2*E_{obs}-E_{diff}$$

At the lower concentration level (110 ppm NO_x and 150 ppm NH_3) η is assumed to be less than 0.1. If E_{diff} of CH_4 in mordenite (12), 7 kJ $mole^{-1}$, is used as an approximation for $E_{diff\ for\ NOx}$, the values for NO, NO_2 and NO_x reductions presented in Table 3 are obtained.

TABLE 3

Reduction	Rate (mole $g^{-1}h^{-1}$)	E_{obs} (kJ $mole^{-1}$)	E_{intr} (kJ $mole^{-1}$)	E_{obs} (kJ $mole^{-1}$)	Temperature (K)
NO	$1.0*10^{-7}$	31±2	55±4	58±3	500-600
NO_2	$3.6*10^{-7}$	41±7	75±14	----	530-620
NO_x(*)	$4.4*10^{-7}$	23±4	39±8	27±1	500-600

*NO_2/NO_x=0.45

No result of NO_2 reduction over 0.5 g Z900H is presented since 600 ppm concentration of NO_2 caused formation of NH_4NO_3 in the system. In reduction of NO the calculated E_{intr} is close to the value of E_{obs} from reaction over 0.5 g Z900H. This indicates that the influence of mass transfer is negligible in reductions of 600 ppm NO over 0.5 g Z900H and that the assumption of <0.1 is valid. As the rates of reduction for NO_2 and NO_x are faster than that of NO, η should be smaller. Therefore the calculated E_{intr} for reduction of NO_2 and NO_x should be proper estimations of the true activation energies as well.

RESULTS

The reduction of NO

Results presented here were obtained at experimental conditions as stated above as level 1 (0.5 g catalyst, 600 vppm NO, 750 vppm NH_3 and 2% O_2 in N_2).

Figure 1 shows the influence of temperature on the conversion of NO. The acitivity increases with temperature but decreases with increasing si/Al ratio.

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