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 $NO_x$ 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.

$$5NO_2 + 2NH_3 \longrightarrow 7NO + 3H_2O$$
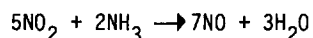
This reaction has previously been reported for reduction of $NO_2$ in the same experimental setup (7). The change in $NO_2/NO_x$ ratio at the reactor inlet influences the overall rate only at temperatures higher than 620 K.

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 ($\eta$) 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 $\eta$ 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 $NH_3$) $\eta$ 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 | $1.0*10^{-7}$ | $31\pm2$ | $55\pm4$ | $58\pm3$ | 500-600 |
| $NO_2$ | $3.6*10^{-7}$ | $41\pm7$ | $75\pm14$ | ---- | 530-620 |
| $NO_x(*)$ | $4.4*10^{-7}$ | $23\pm4$ | $39\pm8$ | $27\pm1$ | 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 $\eta$ <0.1 is valid. As the rates of reduction for $NO_2$ and $NO_x$ are faster than that of NO, $\eta$ 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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