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Selective catalytic reduction of NO_x with propene over CeO_2-ferrierite

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CeO_2-HFerrierite catalysts, prepared by physically mixing the components, showed very high conversions of NO under dry and wet conditions and excellent regeneration properties of the coked catalyst in the presence of water.

Increasingly stringent environmental legislation world-wide to reduce gaseous pollutants, especially nitrogen oxides, requires the development of new catalysts. Medium pore zeolites containing transition metal ions were found to be very active in such Selective Catalytic Reduction (SCR) reactions using various hydrocarbon reductants.[1] The major problems in using these catalysts are the deactivation caused by segregation of the active metal oxide from the framework and coke formation. The presence of water at higher temperatures also causes a decrease in catalytic activity due to dealumination. Only a few studies are reported on NO_x reduction using hydrocarbons in the absence of water over Ce based medium pore zeolite catalysts.[2–4] Mn_2O_3/Sn-ZSM-5, having high loadings of Sn, presumably present in the form of oxide, shows high NO_x conversions in the presence of water.[5] Here we present a system, made by simply mixing of small CeO_2 particles and the protonic form of zeolite ferrierite (HFER) which is a highly active catalyst for NO reduction with propene in the presence of water. The system showed attractive coke removal properties at low temperatures and was superior to a CeO_2-ZSM-5 catalyst having a similar pore structure. The excellent catalytic properties of the CeO_2-FER catalyst could be attributed to the high surface area of the oxidation component together with the unique pore structure and acidic environment of the zeolite. Conversions exceeding 60% at high space velocities over a broad temperature range make CeO_2-HFER a potential candidate for commercial applications.

K-FER (Si/Al = 9.2) and Na-ZSM-5 (Si/Al = 11) (TOSOH Corporation, Japan) were converted into the H-form by ion exchange with aqueous ammonium nitrate and calcination. 15wt% CeO_2 (surface area = 128 $m^2\ g^{-1}$) is physically mixed with HFER and HZSM-5 followed by calcination at 600 °C in air for 5 h. Selective catalytic reduction of NO_x was carried out in a tubular quartz reactor in the temperature range 150–600 °C. The synthetic exhaust gas mixture contained 1000 ppm NO, 1200 ppm C_3H_6, 10 vol% O_2, and balance N_2 (dry feed). 10 vol% H_2O is introduced into the above feed when desired (wet feed). The space velocity was 62 000 h^{-1}, assuming bulk density of ZSM-5 and FER to be 0.5 and 0.4 g cm^{-3}, respectively. The concentration of NO_x was monitored with a chemiluminescence detector, that of N_2O and propene using gas chromatography. The materials were characterised by NH_3-TPD for acidity, TGA for coke content, and chemical analysis for Si/Al ratio and CeO_2 content. N_2O was found to be below 6 ppm at all reaction temperatures.

Fig. 1 shows the conversion of NO_x at different reaction temperatures over CeO_2-HFER and CeO_2-HZSM-5 catalysts using propene as the reductant with and without water in the feed. The CeO_2-HFER system is highly active, with NO_x conversions reaching up to 85% at high space velocities of 62 000 h^{-1}. A broad temperature range where the NO_x conversion is $>60\%$ is obtained for the CeO_2-HFER catalysts especially when using wet feed. The conversion of NO_x over 15wt% CeO_2-HZSM-5 remained well below 60% and has a narrow temperature window. Contrary to many of the catalytic systems studied for SCR using hydrocarbon reductants, CeO_2-HFER catalysts showed very high conversions when the feed contained water. Such an increase is less pronounced for 15wt% CeO_2-HZSM-5 catalyst. Two- to four-fold higher NO_x conversion is observed at temperatures below 450 °C. For example on 15wt% CeO_2-HFER at 400 °C the NO_x conversion increased from 39 to 84% using dry and wet feed, respectively. In general the conversions decreased above 450 °C which is attributed to dominant direct oxidation of propene (Fig. 1(b)). In the first step of reaction NO is oxidised over CeO_2 to NO_2 which then is assumed to react with propene adsorbed on acid sites of HFER forming organic nitrogen containing compounds which finally decompose to N_2. The HFER itself has no oxidation function leading to poor activity. The lower conversion under dry conditions below 400 °C is due to the formation of coke (TGA, Fig. 1(b)) which blocks the access to the active sites of the zeolite. In the presence of water, there is a strong suppression of coke formation on the CeO_2-HFER catalyst as seen from TGA. Water also hinders the complete oxidation of propene at high temperatures resulting in improved conversions compared with conversions obtained using dry feed.

Ce-FER catalysts prepared by ion-exchange were also shown to be very active for NO reduction compared with other conventional catalysts reported in the literature.[6] The intrinsically high NO_x conversions over FER based catalysts using dry and wet feeds, compared to ZSM-5 based catalysts can be attributed to the unique 2-D pore structure and acidic environ-

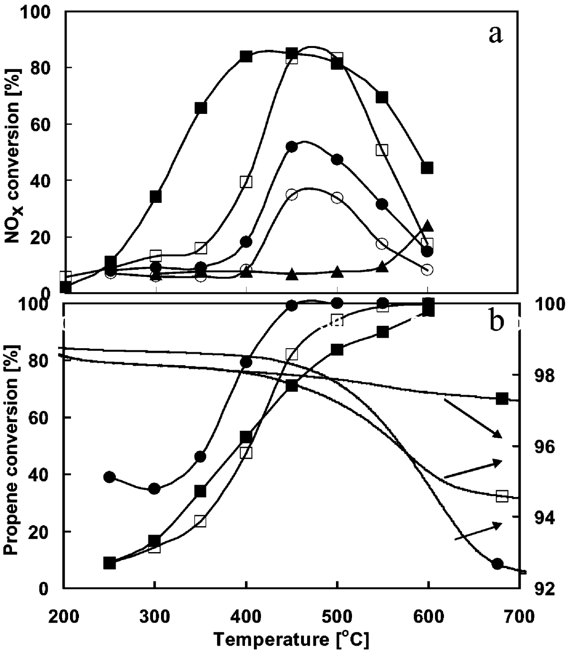

Fig. 1 NO_x conversion (a) and propene conversion (b) over CeO_2-zeolite catalysts. Open symbols–dry feed, closed symbols–wet feed: (□, ■) 15wt% CeO_2-HFER, (○, ●) 15wt%CeO_2-HZSM-5, (▲) HFER. In (b) also shown weight loss of catalysts in TGA after 5 h on stream at 350 °C.

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ment of the FER zeolite. NH_3-TPD showed only one desorption peak for HFER corresponding to strong acidity which may be responsible for the activation of propene. FER has 10-ring channels, where most of coke could reside, interconnected with 8-ring channels.[7] Pore blockage due to the formation of coke will have a large inhibiting effect[8] on the molecular diffusion in the large channels. Small molecules like propene could be less restricted due to the interconnecting 8–membered channels resulting in larger NO_x conversions. ZSM-5 has two interconnected, somewhat larger 10 ring channels resulting in larger intersections allowing severe coking.

Fig. 2(a) shows NO_x conversion under dry/wet cycles at 350 and 400 °C over 15wt% CeO_2-HFER and 400 °C over 15wt% CeO_2-HZSM-5 catalysts. Under dry conditions the conversion decreased with time on both catalysts. The conversion over the HFER based catalyst could be fully restored by switching to the feed containing 10 vol% water. On 15wt% CeO_2-HZSM-5, the conversion is just partly restored and remains low after the 2nd and 3rd recycle by adding water to the feed. Over 15wt% CeO_2-HFER catalyst under dry feed conditions the NO_x conversion decreased by more than half of the initial value at 350 and 400 °C due to coke formation. Even after repeated cycles of reaction with dry feed at both temperatures, which decreased the conversion, switching over to the feed containing water could restore the original conversion. The colour of 15wt% CeO_2-HFER catalyst was grey (no appreciable weight loss detected in TGA) at the end of dry/wet experiments of Fig. 2(a), whereas the colour of the 15wt% CeO_2-HZSM-5 catalyst remained black. This indicates that water is not only hindering the coke formation, as discussed, but is also helping to remove coke formed under dry conditions thereby regenerating HFER based catalysts. In Fig. 2(b) the NO_x conversion and NO_2 concentrations are monitored over 15wt% CeO_2-HFER at 350 °C under dry feed conditions. After 300 min the propene flow is switched off and one would expect the reduction of NO_x to stop and NO_2 concentration to reach a steady value immediately. However these steady values are reached only after 100 min of time on stream. This clearly shows that NO_2, which is formed over the catalyst, is reacting with the deposited coke. The regeneration of the catalyst can be seen from the high initial conversions after 600 min (Fig. 2(b)). 15wt% CeO_2-HZSM-5 also showed similar behaviour but it took much longer time to reach the steady values. Lower olefins like propene, butene and pentene are converted selectively into higher/branched olefins on HFER by isomerization or dimerization/cracking and oligomeric hydrocarbon fractions[9] are deposited on the active sites. Such less heavy hydrocarbon debris on FER is apparently more reactive towards NO_2 and water, thereby removing the coke blocking the active sites, and increasing NO_x conversions. HZSM-5 forms heavier hydrocarbon fractions, mainly paraffinic and aromatic in nature, which are difficult to volatilise by NO_2 and/or water.

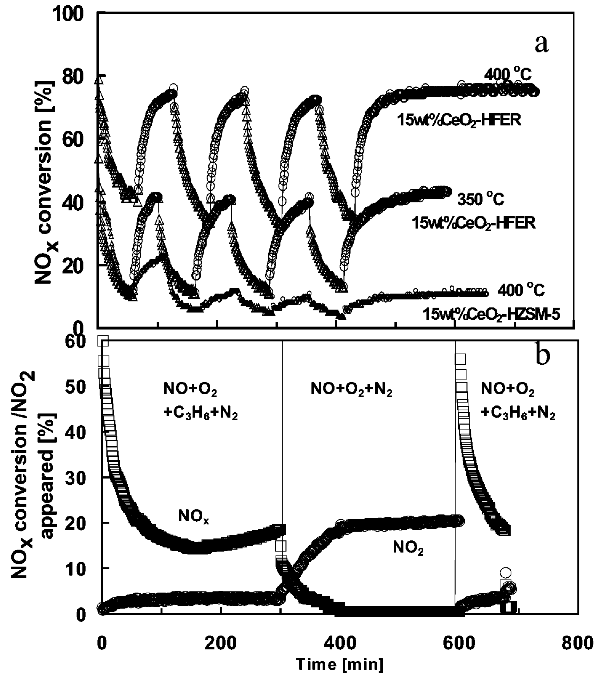

Fig. 2 NO_x conversion on 15wt% CeO_2-zeolite under (a) dry(△)/wet(○) cycles and (b) 15wt% CeO_2-HFER at 350 °C under conditions as indicated.

The long-term stability of the 15wt% CeO_2-HFER catalyst under hydrothermal conditions is shown in Fig. 3. The catalyst is tested for approximately 90 h at 400 °C. The conversion gradually decreased from 80 to 60% after 90 h of time on stream. The catalyst was heated twice at 600 °C for 2 h in air at different times on stream to remove any coke formed. However, the lost activity of the catalyst could not be recovered. This rules out coke formation as the cause of deactivation. The deactivation could be either due to the sintering of the dispersed CeO_2 particles or to dealumination of FER

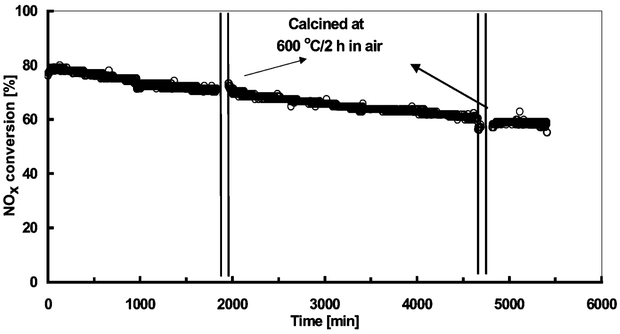

Fig. 3 NO_x conversion over 15wt% CeO_2-HFER with time on stream at 400 °C under wet conditions.

In conclusion the CeO_2-HFER catalyst prepared by a simple physical mixture method showed very high NO_x conversions of up to 85% especially at low temperatures under wet conditions. High NO_x conversions were obtained over a broad temperature range. The presence of H_2O in the exhaust gas mixture retards and removes coke formation and results in improved NO_x. 15wt% CeO_2-HFER has shown good long-term stability under hydrothermal conditions. These interesting properties could make HFER based materials potential catalysts in exhaust gas cleaning technology using hydrocarbons as reductant.

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