Titanium and vanadium silicalites as catalysts for the reduction of NO_x

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Titanium and vanadium silicalites with MFI structure are found to be active in the selective catalytic reduction (SCR) of NO with higher hydrocarbons; simultaneous incorporation of V and Ti in the framework provides an approach to modify the activity towards this reaction and demonstrates the use of a double oxidation function in molecular sieves for SCR of NO_x.

Abatement of NO_x generated from fuel combustion has been a focus of research due to demands for lower emissions of these pollutants. Ion-exchanged zeolites were perceived as suitable candidates for the selective reduction of NO_x despite certain disadvantages like sintering.[1,2] Inui *et al.* have demonstrated the activity of H-metallosilicates (M = Co, Cu, Fe, Ga and Mn) in $deNO_x$ using higher hydrocarbons.[3] Titanium and vanadium silicalites have occupied a distinct position in literature as they exhibit redox activity but do not have Brønsted acidic functions as in the case of H-zeolites.[4,5] Recently, we have reported that these materials are useful as catalysts in the production of hydrazine.[6] In spite of the considerable research activity on ion-exchanged and acidic zeolites in SCR that has been documented, so far, to our knowledge, there are no reports on the SCR activity of titanium and vanadium silicalites. In this communication, we report, for the first time, preliminary results obtained over Ti– and V–MFI silicalites for the reduction of NO using a hydrocarbon as reductant.

TS-1, VS-1 and VTS-1 were synthesized according to the rapid crystallization technique.[7] Since the presence of Na ions would have been detrimental to the incorporation of titanium in the framework, sodium silicate was replaced by tetraethylorthosilicate as the source of silica and sodium-free tetrapropylammonium hydroxide was used instead of tetrapropylammonium bromide.[8] The final mixture was a clear solution which enabled avoidance of the grinding procedure associated with the fast crystallization technique. The crystallization was otherwise carried out as reported earlier.[7] The crystallized samples were calcined at 540 °C, washed with 1 mol dm^{-3} NH_4OAc solution and recalcined before characterization and catalytic measurements. Samples were characterized using XRD, IR, UV–VIS, ICP-AAS, BET, EPR and SEM. Some physico-chemical characterization results for these materials are given in Table 1. Elemental analysis indicates that the Ti content in TS-1 is close to the substitutional limit (1.8% of T atoms) and higher than the V content in VS-1. The presence of even a minor amount of vanadium decreases the Ti lattice content. The as-prepared VS-1 sample is light blue indicating the presence of some V^{4+} which is oxidized to V^{5+} upon calcination.[4] This is also observed from EPR spectra of reduced and as-prepared samples which show a hyperfine splitting with $g_{\parallel}$, $A_{\parallel}$, $g_{\perp}$ and $A_{\perp}$ indicative of the isolated V^{4+} in distorted tetrahedral coordination.[4] Calcined samples do not show any EPR lines suggesting oxidation to V^{5+}. The XRD crystallinity of the samples was >90%. The N_2 BET specific surface area of the TS-1 and VTS-1 samples is within 10% of the reported value, whereas the slightly lower value of the VS-1 sample might indicate the presence of a small amount of amorphous material.[9] The same conclusion may be reached from the micropore volume measured by nitrogen physisorption.

Diffuse reflectance spectra of TS-1 and VTS-1 samples in the UV–VIS region showed a single strong charge-transfer transition centred at 213 nm which is assigned to an electronic transition localized on a structure containing most of the Ti ions in tetrahedral framework positions. The two transition bands observed with VS-1 are due to V=O groups in the vanadium molecular sieves. The UV–VIS band present at 330 nm for anatase was absent for Ti containing samples and the absence of transitions beyond 500 nm indicates the absence of extraframework vanadium species.[4]

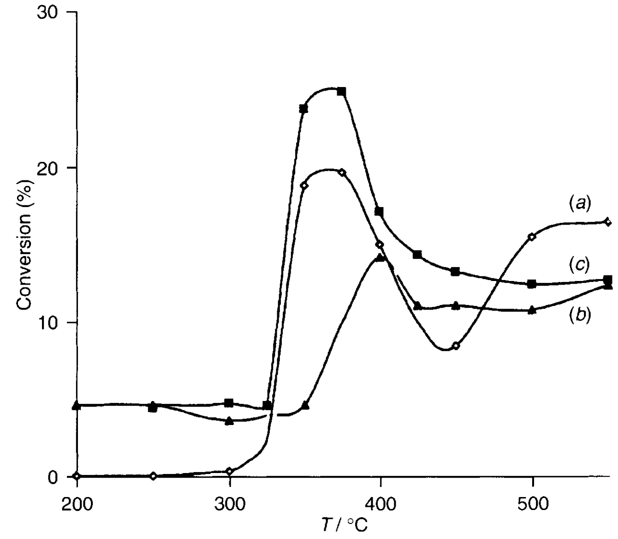

Fig. 1 Influence of temperature on the NO conversion over (*a*) TS-1, (*b*) VS-1 and (*c*) VTS-1 catalysts

Table 1 Physico-chemical characteristics of titanium and vanadium silicalites

Catalyst	Molar ratio Si/Ti	Molar ratio Si/V	Colour as-prepared	Colour calcined	IR_{960}/IR_{800}	N_2 surface area /m^2 g^{-1}	micropore volume /ml g^{-1}	EPR parameters, mT $g_{\parallel}$	$A_{\parallel}$	$g_{\perp}$	$A_{\perp}$
TS-1	55.6	—	white	white	0.59	410	0.143	—	—	—	—
VS-1	—	243.4	light bluish	white	0.10	322	0.106	2.23	17.45	2.03	5.79
VTS-1	74.9	224.6	white	white	0.84	356	0.154	2.23	17.34	2.06	6.09

Catalytic measurements were performed in a fixed bed downflow reactor. Details of the reaction procedure and analysis are reported elsewhere.[10] Typical reaction conditions were as follows: catalyst 2 g (15–24 mesh; 3 ml); GHSV: 30000 h^{-1}, feed composition: 1000 vppm NO, 1099 vppm *n*-octane and 10 vol% oxygen diluted in N_2.

Results of NO conversion over TS-1, VS-1 and VTS-1 catalysts are plotted in Fig. 1. Above 300 °C, TS-1 starts showing NO reduction activity, which rises exponentially and reaches a maximum between 350 and 375 °C. A similar trend has been observed for VTS-1; however, some activity was also observed at lower temperatures. VS-1 was found to possess activity at temperatures as low as 200 °C. The NO conversion follows the order: VTS-1 > TS-1 > VS-1. The maximum conversion for VS-1 was similar to that for silicalite-1, reported by Inui *et al.* under identical reaction conditions.[10] This is probably due to the low vanadium content of the sample. The higher activity observed for VTS-1 at the lower temperatures, compared to TS-1, may be assigned to the vanadium contribution in VTS-1. A difference was also observed in the activity maximum ($\Delta \approx +60$ °C) over VS-1 compared to VTS-1 and TS-1 which show similar maxima.

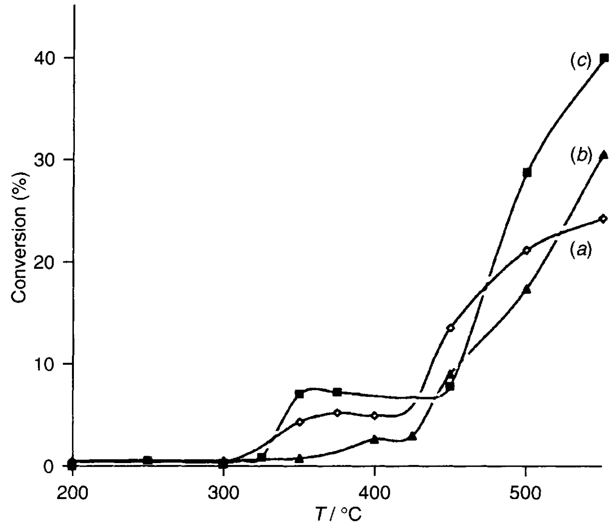

Fig. 2 CO_x formation from octane during the reduction of NO over Ti– and/or V–silicate catalysts curves (*a*) TS-1, (*b*) VS-1 and (*c*) VTS-1

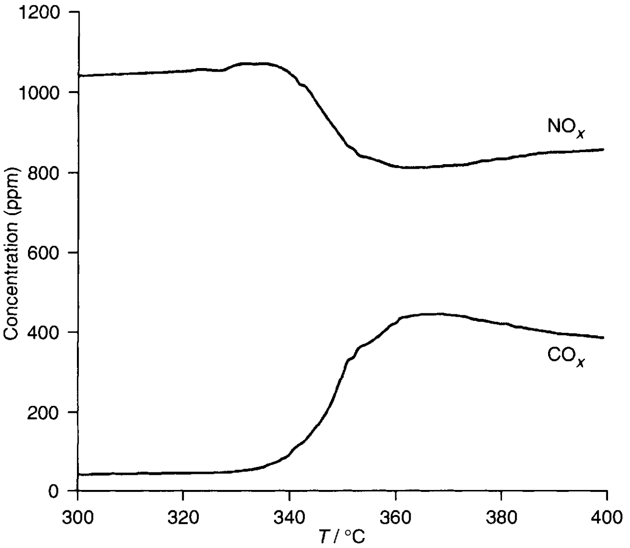

Fig. 3 Plot of concentration of NO_x and CO_x with increasing temperature over TS-1 catalyst

Fig. 2 shows the hydrocarbon conversion to CO + CO_2 (CO_x) *vs.* reaction temperature. No hydrocarbon conversion was observed below 300 °C. Above this temperature, the oxidation activity shows two inflection points, the first region below 450 °C shows a low degree of hydrocarbon conversion, while above this temperature the hydrocarbon conversion increases drastically with the reaction temperature. From the comparison of NO and hydrocarbon conversions,[5] it was observed that both NO_x and CO_x analysis show a maximum between 300 and 425 °C over TS-1, VS-1 and VTS-1. This clearly shows that the NO conversion reaches a maximum in this temperature range where the hydrocarbon oxidation by O_2 was low. Above 450 °C, a detrimental increase in hydrocarbon oxidation is associated with a decrease in NO conversion. This is further demonstrated by the results listed in Fig. 3, where the concentration NO and CO_x are plotted against temperature (measurements were performed at 1.5 °C intervals) over the TS-1 catalyst. The Figure shows that the NO concentration in the effluent gas decreases at the temperature where CO_x concentration in the reaction products increases. Thus, a linear correlation was observed for the NO and hydrocarbon conversions.

Lattice Ti^{4+} ions are known to be active in liquid-phase hydrocarbon oxidations with peroxides although they are not very active for combustion. Therefore the possibility of NO_2 being formed by the reaction of NO and O_2 as an intermediate is very high.[2] Titanium silicalites are also known to form various active sites including Ti–OH and Ti=O groups. Similar V–OH and V=O weak acid sites have been shown to play a role in the selective reduction of ammonia over V_2O_5/TiO_2 catalysts.[11]

In separate experiments we have found that VTS-1 catalysts at 375 °C did not show activity (< 3%) for the reduction of NO with propane, propene and pentane under similar reaction conditions. This may be due to the possibility that lower hydrocarbons have difficulty in forming stable carbenium ions.[2] It was also confirmed that the TS-1 did not have any redox activity by using TPR/TPO in reducing (H_2) and oxidizing (O_2) conditions.

It is observed that TS-1, VS-1 and VTS-1 possess activity for the reduction of NO_x with higher hydrocarbons. It is also observed that the simultaneous incorporation of V and Ti in the framework provides a means to improve the catalytic performance in this reaction, enlarging the temperature range which gives rise to the so-called window effect.[2]

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