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Abatement of N_2O in the selective catalytic reduction of NO_x on platinum zeolite catalysts upon promotion with vanadium

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The selectivity to N_2O during the selective catalytic reduction of NO_x on platinum-containing zeolite catalysts is reduced by incorporation of vanadium into the catalyst.

The selective catalytic reduction of nitrogen oxides by hydrocarbons is a promising process for the purification of exhaust gases from diesel-powered engines. Since the average temperature of diesel exhaust gases is well below 300 °C,[1] platinum-containing catalysts have proven to be efficient for this process owing to their low lightoff temperature. Another important advantage of platinum-containing catalysts is that they are comparatively insensitive to water in the exhaust gas.[2] However, a major drawback of these catalysts is that large portions of the nitrogen oxides are converted to nitrous oxide rather than to nitrogen. Nitrous oxide is highly undesirable, since it is a strong greenhouse gas and contributes to stratospheric ozone destruction.

In the past, several attempts were undertaken to overcome the N_2O problem with platinum-containing catalysts: Doumeki *et al.* reported that the selectivity to N_2 can be enhanced by using organoplatinum complexes such as $PtMe(OSiPh_3)(cod)$ instead of inorganic complexes as precursors for the preparation of Pt/SiO_2 or Pt/Al_2O_3 catalysts.[3] However, the N_2O selectivity remained as high as 65%. Wunsch *et al.* found that, upon adding CeO_2 to a Pt/ZSM-5 catalyst ($m_{CeO_2}/m_{Pt} \approx 4$), the maximum NO_x conversion increased from 48 to 59% without a change in temperature, whereas the selectivity to N_2O decreased from 62 to 54%.[4] More favourable results were reported by Seker and Gulari who observed an N_2O selectivity of only 17% on a Pt/alumina catalyst not prepared by the usual impregnation procedure but by a sol–gel process.[5] These results seem to be very promising, but further tests on the long-term and hydrothermal stability of the catalyst have yet to come. A totally different approach was followed by Burch and Ottery by changing the reductant: On a Pt/Al_2O_3 catalyst, no detectable amount of N_2O was formed with toluene as reducing agent at any temperature.[6] However, with this method one would be bound to toluene as reductant which is not a constituent of the exhaust gas stream.

We followed still another approach: in order to tune the activity and selectivity of platinum-containing catalysts we used a second metal as promoter. As depicted in Fig. 1, the selectivity to N_2O (S_{N_2O}) on platinum- and/or vanadium-containing H-ZSM-35 zeolites decreases considerably with increasing vanadium content of the catalyst. By contrast, the maximal NO_x conversion ($X_{NO_x,max}$) at T_{max} on Pt-V/H-ZSM-35 samples is similar to that on catalysts containing platinum only (Table 1). However, with increasing vanadium content of the samples, the temperature at the maximal NO_x conversion shifts to higher values. An explanation for this effect could be that the platinum is diluted by vanadium and, thus, the platinum clusters are smaller, facilitating effective NO_x reduction only at higher temperatures.

On catalysts containing platinum *and* vanadium, oscillations of the NO_x concentration with large amplitudes ($\Delta X_{NO_x,max}$[8]) tend to occur [Fig. 2(a), *cf.* ref. 9]. Owing to these oscillations, a precise determination of the selectivity to N_2O (*cf.* Fig. 1)

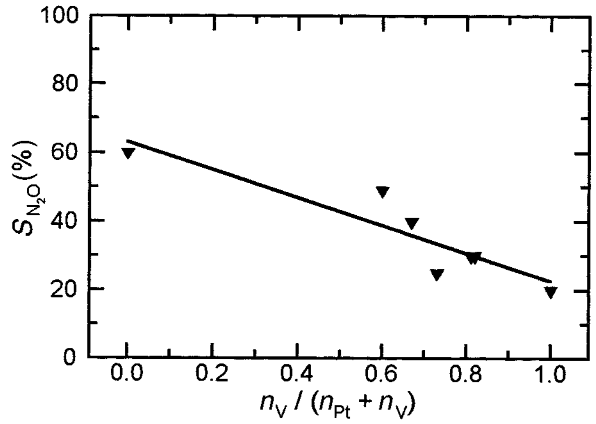

Fig. 1 Average selectivity to N_2O in the selective catalytic reduction of NO_x with propene as a function of the molar ratio $n_V/(n_{Pt} + n_V)$ of platinum- and/or vanadium-containing H-ZSM-35 zeolites.[7]

Table 1 Catalytic results on platinum- and/or vanadium-containing H-ZSM-35 samples

Catalyst	$X_{NO_x,max}$ (%)	$\Delta X_{NO_x,max}$ (%)	T_{max}/°C
1.0V/H-ZSM-35[a]	41	—	303
2.6Pt–3.1V/H-ZSM-35	81	19	215
0.9Pt–1.0V/H-ZSM-35	89	32	205
3.0Pt–2.2V/H-ZSM-35	82	21	212
1.9Pt–1.0V/H-ZSM-35	90	26	196
2.6Pt–1.0V/H-ZSM-35	97	40	177
2.7Pt/H–ZSM-35	85	—	165

[a] The numbers before the metals indicate the metal content in wt% in the dry catalyst.

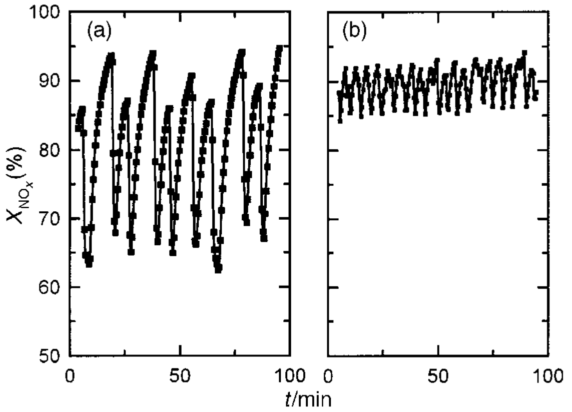

Fig. 2 NO_x conversion on (a) 0.2 g 2.6Pt–1.0V/H-ZSM-35, T_{cat} = 183 °C and (b) 0.2 g 2.6Pt–1.0V/H-ZSM-35 diluted with 0.7 g quartz, $T_{cat.}$ = 190 °C.

turns out to be difficult, because the N_2 concentration fluctuates considerably. Obviously, reaction, adsorption and desorption take place simultaneously and cannot be separated more properly, since the N_2O and N_2 concentrations change independently. First attempts to reduce the amplitude of the oscillations by diluting the catalyst with quartz sand are promising: for a mechanical mixture of the catalyst with quartz, the amplitude of the oscillations is strongly decreased, whereas the average NO_x conversion is even increased from 81 to 90% [Fig. 2(b)].

These observations prompted us to look in some detail into previously proposed reaction mechanisms. Burch *et al.* proposed that, on platinum, NO molecules are adsorbed in addition to N and O atoms resulting from NO dissociation.[10] The formation of N_2 can then be accounted for by recombination of two adsorbed N atoms, while the formation of N_2O is best interpreted in terms of the reaction of an adsorbed NO molecule with an N atom. We speculate that, in our system, most platinum atoms have vanadium atoms as next nearest neighbours. Owing to the higher affinity of vanadium for oxygen, the dissociation of NO could then be promoted resulting in a lower NO concentration on the surface and, hence, a lower selectivity to N_2O.

In conclusion, vanadium as a promoter is able to reduce considerably the selectivity to N_2O during the selective catalytic reduction of nitrogen oxides on platinum-containing zeolite catalysts. If the oscillations occurring on Pt–V/H-zeolites do not affect activity in real car exhausts or if the amplitudes can be strongly reduced by coating the catalyst onto monoliths in much the same way as this can be achieved by dilution with quartz, a major obstacle for the use of platinum catalysts in diesel exhaust gases could be overcome.

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8 Amplitude of the oscillations as difference between maximum and minimum NO_x conversion.

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