Role of the redox properties in the SCR of NO by NH_3 over V_2O_5–WO_3/TiO_2 catalysts

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The reactivity of ternary V_2O_5–WO_3/TiO_2 De-NO_x catalysts is investigated by transient and steady-state techniques, and results have been compared with those obtained over binary V_2O_5/TiO_2 samples having the same V_2O_5 loading. The results indicate that the reactivity of the ternary catalysts in the SCR reaction is higher than that of the vanadia–titania samples, and that at low temperatures the SCR reaction occurs via a redox mechanism that involves at first the participation of the catalyst lattice oxygen and then the reoxidation of the reduced sites by gas-phase oxygen. Accordingly, the higher reactivity of the ternary catalysts has been related to their superior redox properties.

Keywords: NO_x reduction; selective catalytic reduction; V_2O_5–WO_3/TiO_2 catalysts

1. Introduction

TiO_2-supported V_2O_5–WO_3 catalysts are extensively employed in the selective catalytic reduction (SCR) of NO_x with NH_3 from stationary sources [1,2]. In spite of their large diffusion in the SCR technology, aspects concerning the reactivity and the chemico-physical characteristics of the V_2O_5–WO_3/TiO_2 catalysts are still under debate [3–7].

The structural, morphological and physicochemical characteristics of model TiO_2-supported tungsta–vanadia samples have been recently investigated in our Labs [7,8]. It has been shown that the V and W surface species present in the case of the ternary catalysts are similar to those identified in the case of the binary V_2O_5/TiO_2 and WO_3/TiO_2 oxide systems, but a slight evidence for the presence of a mixed $W_xV_zO_y$ species has also been provided. This implies a structural interaction between the V and W centres over the TiO_2 surface.

Similar conclusions have been derived from EPR spectroscopy [7,8]: indeed different types of vanadyl species have been observed over the ternary and the binary V_2O_5/TiO_2 samples. In particular a deeper interaction of the vanadyl species with the TiO_2 matrix has been suggested in the case of the V_2O_5/TiO_2 samples.

EPR, UV–Vis and laser-Raman spectroscopies further indicated that strong electronic interactions exist between the V and W surface species and the TiO_2 support [7,8]. Indeed the V_2O_5/TiO_2 and the V_2O_5–WO_3/TiO_2 samples show a different behaviour upon outgassing, and the presence of tungsta increases the catalyst reducibility.

The reactivity of V_2O_5–WO_3/TiO_2 catalysts in the reduction of NO with NH_3 has also been investigated [7]. The results indicated that the V_2O_5–WO_3/TiO_2 catalysts are more reactive than the V_2O_5/TiO_2 and WO_3/TiO_2 samples with the same metal loadings since higher NO conversions are measured at lower temperatures. Calculations showed that the reactivity of the ternary catalysts cannot be explained by a simple additive model on the basis of the reactivity of the V and W atoms measured over the binary samples with the same metal loading: accordingly a synergism in the SCR reaction exists between the TiO_2-supported V and W surface species.

Different factors can be invoked to explain the higher reactivity of the ternary catalysts in the SCR reaction. The catalyst redox and/or acid properties have been claimed as the controlling factors for the De-NO_x reaction [3,5,9–14], but their role is still far from being completely clarified. To provide new insights in these aspects, the reactivity of V_2O_5–WO_3/TiO_2 model catalysts has been investigated in the reduction of NO by ammonia under steady-state and transient conditions (temperature-programmed desorption/reaction methods). Due to their unsteady-state nature, transient methods are particularly appealing to probe the role of the catalyst functions in the SCR reaction. Transient experiments have been performed both in the presence and in the absence of gas-phase O_2 to clarify the role of the catalyst lattice oxygen and of the gas-phase oxygen in the SCR reaction. Finally, the results obtained under transient conditions have been compared with data obtained under steady-state conditions.

2. Experimental

2.1. Catalyst preparation and characterisation

V_2O_5/TiO_2 ($V_2O_5 = 1.47\%$ w/w) and V_2O_5–WO_3/

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TiO_2 catalysts ($V_2O_5 = 1.47\%$ w/w, $WO_3 = 9\%$ w/w) were prepared by dry impregnation of TiO_2 and WO_3/TiO_2, respectively. A hot water solution of ammonium metavanadate and oxalic acid was used, followed by drying and calcination at 823 K [7,9].

Specific surface areas of 80 and 46 m^2/g have been measured by the BET method for the ternary and the binary sample, respectively. The W, V and (W + V) surface coverages (calculated as reported in ref. [7]) for the V_2O_5–WO_3/TiO_2 catalyst are 0.67, 0.12 and 0.79, respectively, whereas the V coverage in the case of the binary V_2O_5/TiO_2 sample is 0.21. Accordingly, the calculated coverages are lower than the theoretical monolayer. Further details on the chemico-physical characterisation of the samples used in this study can be found elsewhere [7–9].

2.2. *Reactivity measurements*

Transient and steady-state catalytic activity measurements were performed in a quartz tubular fixed bed microreactor (i.d. = 7 mm) loaded with 160 mg of catalyst (60–100 mesh). The outlet of the reactor was connected to a quadrupole mass detector (UTI model 100 C) for the analysis of the gases exiting the reactor.

Different sets of experiments have been performed: in a first set (temperature-programmed surface reaction, TPSR) the sample has been saturated with ammonia at 313 K, and then heated up to 773 K at 15 K/min under a flow of He + 800 ppm NO. These experiments have been undertaken to investigate the stability with temperature and the reactivity of preadsorbed ammonia with gaseous NO. In a different set of experiments (temperature-programmed reaction, TPR), after saturation with ammonia at 313 K the catalyst was heated under a flow of He + 800 ppm NH_3 + 800 ppm NO: accordingly these experiments allow the study of the reactivity of the catalysts also at high temperatures, that could not be analysed during TPSR experiments due to the depletion of adsorbed ammonia species. TPSR and TPR experiments were also performed with O_2 in the carrier gas stream (~ 1% v/v).

Steady-state catalytic activity experiments were performed with 800 ppm NO + 800 ppm NH_3 + 1% v/v O_2 in He. The total flow rate was always set at 60 Ncm^3/min.

Mass to charge ratios (m/e) of 17, 18, 28, 30, 32, 44 and 46 were selected to monitor the concentration of NH_3, H_2O, N_2, NO, O_2, N_2O and NO_2, respectively, after correction for the contribution of the fragmentation pattern of the various species. Further details on the experimental equipment and procedure can be found elsewhere [7,9].

3. Results and discussion

The reactivity of the catalysts under transient conditions and in the absence of oxygen has been investigated first. Figs. 1A and 1B report the NO conversion traces measured during the TPSR (traces a) and the TPR (traces b) experiments performed over the V_2O_5/TiO_2 and V_2O_5–WO_3/TiO_2 samples, respectively. The concentration traces of oxygen, present as impurity (< 30 ppm) into the gas stream, have also been reported in the figures.

In the case of the V_2O_5/TiO_2 sample (fig. 1A), during both the TPSR and the TPR run (traces a and b, respectively) NO is converted starting from 420 K. The NO conversion increases with temperature during the TPR experiment, whereas in the case of the TPSR experiment the NO consumption shows a maximum near 610 K and then decreases due to the complete consumption of adsorbed ammonia. A correspondent evolution of N_2 and of water (not reported in the figure) are observed, indicative of the occurrence of a genuine SCR process. Impurity oxygen is consumed above 500 K, and the ori-

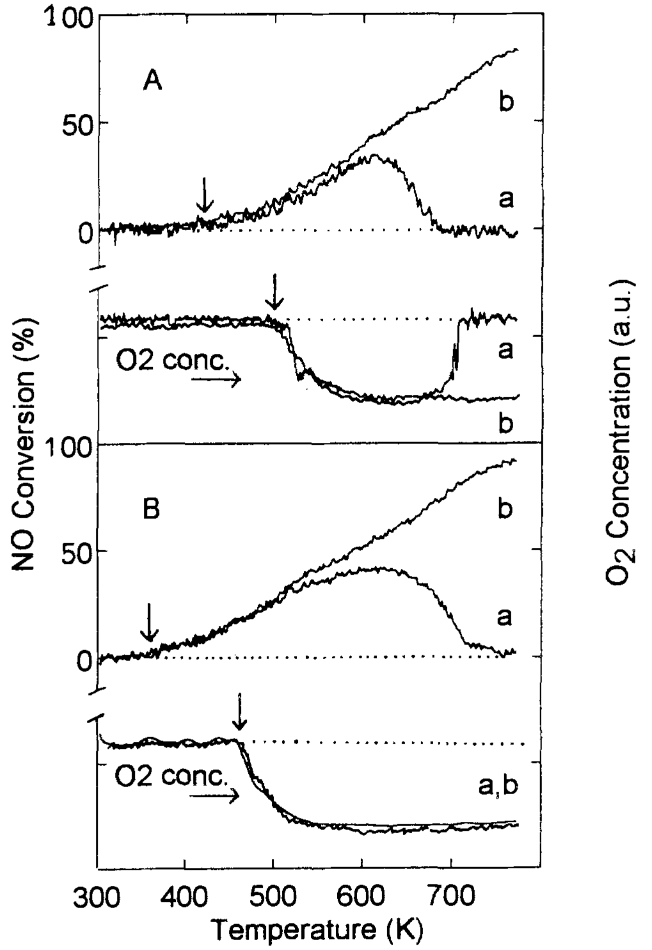

Fig. 1. NO conversion profiles obtained in He + 800 ppm NO (TPSR, traces a) and in He + 800 ppm NO + 800 ppm NH_3 (TPR, traces b) following exposure of the V_2O_5/TiO_2 (A) and V_2O_5–WO_3/TiO_2 (B) samples to He + 0.5% of ammonia at 313 K for 30 min. The corresponding O_2 consumption traces are also reported. The arrows indicate the temperature thresholds for the occurrence of the SCR reaction and for oxygen consumption.

ginal oxygen concentration level is restored above 700 K during the TPSR run whereas is not restored in the case of the TPR run.

The observation that the impurity oxygen consumption occurs at temperatures well above those corresponding to the onset of the SCR reaction (500 vs. 420 K) is in line with a redox mechanism for the SCR reaction [9–11] that implies (for $T < 500$ K) the participation of the catalyst lattice oxygen (O_l) according to the stoichiometry:

$$2NH_3 + 2NO + O_l \rightarrow 2N_2 + 3H_2O + cat_{red} \qquad (1)$$

leading to catalyst reduction, followed by catalyst reoxidation by gas-phase O_2 at temperatures above 500 K. Indeed, as demonstrated by steady-state catalytic activity runs performed in the absence of oxygen [9], the catalyst cannot be reoxidized by NO at such low temperatures.

TPSR and TPR data clearly show that: (i) the consumption of NO at low temperatures, below the temperature threshold for oxygen consumption (500 K), is a transient phenomenon that involves the participation of the catalyst lattice oxygen. Accordingly, the temperature threshold for the occurrence of the SCR reaction is related to the lability of the catalyst lattice oxygen atoms, that is to the catalyst reducibility; (ii) once reduced, the catalyst is reoxidized by gas-phase oxygen. Since this process is observed at higher temperatures with respect to the reduction step, the catalyst reoxidation is more difficult than the catalyst reduction; (iii) in the low temperature region, the occurrence of the SCR process is not controlled by the NH_3 surface coverage: identical NO conversions have been measured both in the absence and in the presence of gas-phase ammonia, as pointed out by a comparison of the TPSR and TPR data (traces a and b, respectively). Only at high temperatures, above 550 K, significant differences are evident between the NO conversion measured in the case of the TPSR and of the TPR runs. This suggests that the activity in the low temperature region is not controlled by the NH_3 surface coverage, since the catalyst acidity is strong enough to guarantee high ammonia surface coverages even in the absence of gas-phase NH_3.

Similar results have been obtained in the case of the ternary V_2O_5–WO_3/TiO_2 catalyst (fig. 1B). However, in this case the onset of the SCR reaction is observed at lower temperatures since NO is converted starting from 360 K. This has been related to the greater reducibility of the ternary sample with respect to the V_2O_5/TiO_2 catalyst. Also, the temperature threshold for oxygen consumption is lowered (450 vs. 500 K). It is observed that during the TPSR experiments (traces a) the initial oxygen concentration level is restored over the V_2O_5/TiO_2 sample (fig. 1A) after the reaction between adsorbed NH_3 and NO has been completed, whereas it is not yet restored at the end of the run in the case of the ternary catalyst (fig. 1B). This eventually indicates an higher extent of reduction of the ternary catalyst.

The reactivity of a vanadium-free WO_3/TiO_2 sample ($WO_3 = 9\%$ w/w) was also investigated. The results (not reported for the sake of brevity) clearly pointed out the lower reactivity of this sample: indeed the SCR reaction was monitored at $T > 500$ K, and consumption of impurity oxygen was observed in the same temperature region where NO is converted ($T > 500$ K) [15].

Both TPSR and TPR data thus suggest that the addition of WO_3 to the vanadia/titania sample increases the redox properties of the catalyst, since the SCR reaction is monitored at lower temperatures (faster catalyst reduction) and oxygen is consumed at lower temperatures (faster catalyst reoxidation). This is in line with the results of the chemico-physical characterisation study performed over the same catalyst samples [7,8]. Indeed it has been shown that the structural and electronic interactions existing between the W and V surface species over the TiO_2 support favour the catalyst reducibility and accordingly modify the redox properties that govern the reactivity of the catalysts in the SCR reaction at low temperatures.

In line with our previous studies and with other literature reports [7–10], the V–O bridging oxygen atoms of vanadylic and/or polyvanadate species are likely involved in the SCR reaction via reaction (1), with the latter species being more reactive. The addition of WO_3 reduces the temperature onset of the SCR reaction by favouring the reducibility of the V surface species [8]; in this case the participation of W–O–V oxygen atoms is also likely.

The TPSR data present additional interesting features. From traces a of fig. 1 it is noted that the SCR reaction is monitored up to 680 K for the V_2O_5/TiO_2 sample, and up to 720 K in the case of the V_2O_5–WO_3/TiO_2 sample. Since in the course of TPSR experiments the NO conversion decreases at high-temperature due to the consumption of preadsorbed NH_3, it is apparent that ammonia is adsorbed over the ternary catalysts up to higher temperatures. This clearly indicates that WO_3 increases the catalyst acid properties and favours the adsorption and activation of ammonia at high temperatures. It is concluded that the surface acid properties likely influence the occurrence of the SCR reaction in the high temperature region by favouring the adsorption and activation of ammonia. This effect could be appreciated during the TPSR runs but not during the TPR and the steady-state experiments (see below) due to the presence of NH_3 in the feed that ensures high ammonia surface coverages also at high temperature.

TPSR and TPR experiments were also performed in the presence of 1% v/v oxygen in the gas-phase. Figs. 2A and 2B show the TPSR (traces a) and TPR (traces b) NO conversion traces measured over the V_2O_5/TiO_2 and the V_2O_5–WO_3/TiO_2 sample, respectively. The corresponding TPSR NO conversion traces obtained in the absence of oxygen and already reported in fig. 1 are also shown for the purpose of comparison (traces c). In the case of

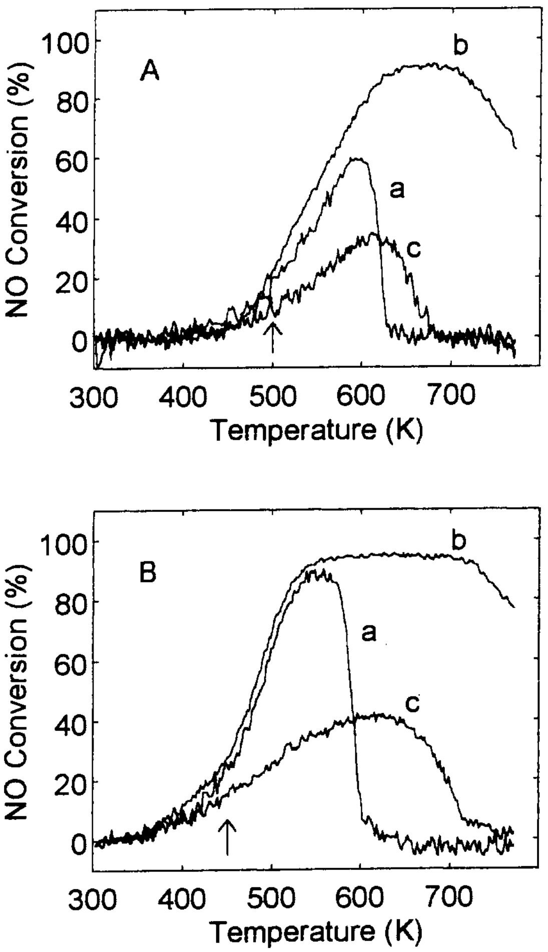

Fig. 2. NO conversion profiles obtained in He + 800 ppm NO + 1% v/v O_2 (TPSR, traces a) and in He + 800 ppm NO + 800 ppm NH_3 + 1% v/v O_2 (TPR, traces b) following exposure of the V_2O_5/TiO_2 (A) and V_2O_5–WO_3/TiO_2 (B) samples to He + 0.5% of ammonia at 313 K for 30 min. The corresponding TPSR NO-conversion profiles obtained in the absence of oxygen are also reported for comparison (traces c). The arrows indicate the temperature threshold for oxygen consumption during the corresponding TPSR and TPR runs in the absence of oxygen (fig. 1)

the V_2O_5/TiO_2 catalyst, both in the presence and in the absence of O_2 the SCR reaction is monitored starting from the same temperature, but above a temperature roughly corresponding to the consumption of the impurity oxygen in the TPSR and TPR run in NO + He (arrow in fig. 2A) the rate of NO consumption is greatly increased. A similar effect is apparent in the case of the V_2O_5–WO_3/TiO_2 catalyst (fig. 2B).

The results of the TPSR and TPR experiments performed in the presence of O_2 confirm that the SCR reaction occurs via a redox mechanism [9–11] that implies at first the participation of the catalyst lattice oxygen, leading to catalyst reduction, followed by catalyst reoxidation by gas-phase oxygen. The temperature threshold for the occurrence of the SCR reaction is not significantly affected by the presence of oxygen, as expected. Gaseous oxygen does accelerate the reaction only above a temperature roughly corresponding to the O_2 consumption during the TPSR experiments in He + NO, that is associated with the catalyst reoxidation. Accordingly, the rate determining step at low temperatures in the SCR reaction is associated with catalyst reoxidation. It is concluded that the higher reactivity of the ternary catalyst at low temperatures is associated with its easier reoxidation by gas-phase oxygen, that is with their superior redox properties. In line with previous characterisation studies, the higher redox properties of the ternary catalyst has been associated to the existence of structural and electronic interactions between the V and W oxide surface species and the TiO_2 support.

It is noted that also in the presence of oxygen the ammonia surface coverage does not affect the occurrence of the SCR reaction in the low-temperature region: indeed identical NO conversion have been measured both in the presence (TPR) and in the absence (TPSR) of gas-phase ammonia. Hence it is confirmed, as previously suggested, that the activity in the low-temperature region is not controlled by the NH_3 surface coverage.

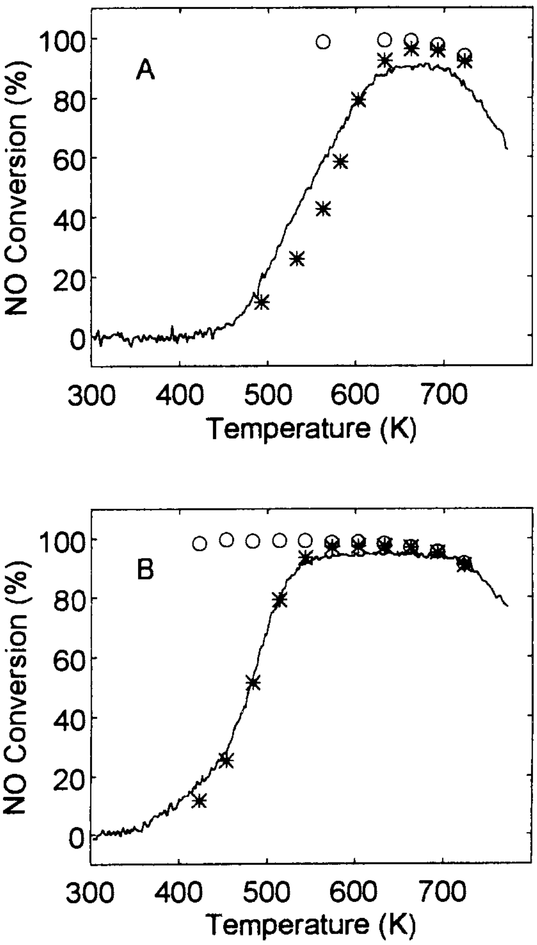

Fig. 3. NO conversion (∗) and N_2 selectivity (○) vs. temperature obtained under steady-state conditions over the V_2O_5/TiO_2 (A) and V_2O_5–WO_3/TiO_2 (B) samples. [NO] = 800 ppm, [NH_3] = 800 ppm, [O_2] = 1% v/v, GHSV = 22500 h^{-1}. The corresponding TPR NO conversion profiles have also been reported for comparison.

The NO conversion over the vanadia/titania and the V_2O_5–WO_3/TiO_2 catalysts were also measured under steady-state conditions. The results are reported in fig. 3, where they are compared with the results of the corresponding TPR experiments. For both samples, the N_2 selectivity is almost complete for temperatures below 650–700 K. The steady-state catalytic activity runs confirm the results of the TPSR and TPR experiments: indeed the higher reactivity of the V_2O_5–WO_3/TiO_2 catalyst is well evident in the low-temperature region, where a decrease in the temperature threshold for the occurrence of the SCR reaction is observed. Furthermore, high NO conversions are also preserved in the high-temperature region. It is noted that the NO conversion measured at low temperatures during the TPR experiments is slightly higher than that observed under steady-state conditions. This may be related to the different oxidation levels of the catalysts: indeed it is expected that the sample at the beginning of the TPR run is in a higher oxidation state due to the oxidative pretreatment in air. This effect is in line with the role of the catalyst reoxidation step in the SCR reaction at low temperatures.

4. Conclusions

The following main conclusions can be derived from the present steady-state and transient reactivity study of V_2O_5/TiO_2 and V_2O_5–WO_3/TiO_2 SCR-DeNO$_x$ catalysts:

(i) The SCR reaction occurs via a redox mechanism that involves at first the catalyst lattice oxygen and then the reoxidation of the reduced catalyst by gas-phase oxygen.

(ii) The onset of the SCR reaction is not significantly affected by an increase in the gas-phase oxygen concentration, whereas O_2 does accelerate the reaction above a temperature roughly corresponding to the temperature threshold for the catalyst reoxidation. Accordingly, the rate determining step at low temperatures in the SCR reaction is the catalyst reoxidation process.

(iii) The reactivity of V_2O_5/TiO_2 in the SCR reaction is increased by addition of WO_3. The higher reactivity of the ternary catalysts in the low temperature region is apparently related to their superior redox properties.

(iv) Both the catalyst redox and acid properties are likely playing a role in the SCR reaction over TiO_2-supported V_2O_5–WO_3-based catalysts. The redox catalyst functions seem to govern the catalyst reactivity in the low temperature region, whereas the occurrence of the SCR reaction in the high temperature region is likely controlled (in addition to the catalyst redox properties) also by the surface acid properties.

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References

[1] H. Bosch and F. Janssen, Catal. Today 2 (1988) 369.
[2] P. Forzatti and L. Lietti, Heterog. Chem. Rev. 4 (1996).
[3] V.I. Marshneva, E.M. Slavinskaya, O.V. Kalinkina, G.V. Odegova, E.M. Moroz, G.V. Lavrova and A.N. Salanov, J. Catal. 155 (1995) 171.
[4] V.M. Mastikhin, V.V. Terskikh, O.B. Lapina, S.V. Filimonova, M. Seidl and H. Knözinger, J. Catal. 156 (1995) 1.
[5] J.P. Chen and R.T. Yang, Appl. Catal. A 80 (1992) 135.
[6] M.A. Vuurman, I.E. Wachs and A.M. Hirt, J. Phys. Chem. 95 (1991) 9982.
[7] L.J. Alemany, L. Lietti, N. Ferlazzo, P. Forzatti, G. Busca, E. Giamello and F. Bregani, J. Catal. 155 (1995) 117.
[8] M.C. Paganini, L. Dall'Acqua, E. Giamello, L. Lietti, P. Forzatti and G. Busca, J. Catal., submitted.
[9] L. Lietti and P. Forzatti, J. Catal. 147 (1994) 241.
[10] G.T. Went, L.-J. Leu, R.R. Rosin and A.T. Bell, J. Catal. 134 (1994) 492.
[11] N.-Y. Topsøe, H. Topsøe and J.A. Dumesic, J. Catal. 151 (1995) 226.
[12] G. Ramis, Li Yi, G. Busca, M. Turco, E. Kotur and R.J. Willey, J. Catal. 157 (1995) 523.
[13] J.P. Chen and R.T. Yang, J. Catal. 139 (1993) 277.
[14] N.-Y. Topsøe, J.A. Dumesic and H. Topsøe, J. Catal. 151 (1995) 241.
[15] L. Lietti, Appl. Catal., in press.