ELSEVIER

Catalysis Today 42 (1998) 137–143

CATALYSIS TODAY

Selective catalytic reduction of nitric oxide from stationary diesel sources by methanol over promoted alumina catalysts

S.G. Masters, D. Chadwick*

Department of Chemical Engineering and Chemical Technology, Imperial College of Science, Technology and Medicine, Prince Consort Road, London SW7 2BY, UK

Abstract

Vanadia/alumina and molybdenum/alumina catalysts are active for nitric oxide reduction with methanol and dimethyl ether in the presence of excess oxygen in the temperature range 250–500°C. The distinctive feature of vanadia/alumina catalysts is the ability to promote oxidation of NO to NO_2, hence these catalysts are active even at low temperature. Both methanol and dimethyl ether were effective as reducing agents for selective reduction of NO. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Nitric oxide; Alumina; Vanadia/alumina; Molybdenum/alumina; Methanol

1. Introduction

The emission from stationary diesel sources typically consists of $\sim$1500 ppm NO_x, $\sim$500 ppm SO_2, $\sim$4% H_2O in excess oxygen leading to problems in NO_x control related to the high oxygen content and catalyst deactivation by SO_2 and H_2O. The present investigation is part of a research programme on NO_x emission control from stationary diesel sources by application of oxygenated hydrocarbons.

The catalytic reduction of NO_x can be achieved either by direct NO decomposition or selective reduction by the application of a reductant. It was previously widely believed that ammonia was the only applicable reducing agent in excess oxygen conditions [1]. However, many researchers have reported the successful application of hydrocarbons in selective reduction of NO in excess oxygen over ion-exchanged zeolites or mixed oxides [2–7]. It has been suggested [3] that the NO reduction by hydrocarbons proceeds via a two-step sequence, i.e.

$$NO + O_2 \rightarrow NO_2 \quad (1)$$

$$NO_2 + \text{hydrocarbon} \rightarrow N_2 + CO_x + H_2O \quad (2)$$

Nitric oxide is oxidized to nitrogen dioxide followed by reduction of nitrogen oxide to nitrogen by the hydrocarbon.

Oxygenated hydrocarbons, especially alcohols [8] and ethers [9] have recently been reported to achieve higher NO conversion and selectivity in NO reduction as compared to hydrocarbons in excess oxygen conditions. It is expected that NO_x reduction by oxygenated hydrocarbons can be described by the same reaction scheme as (1) and (2).

In this study we investigated the performance of γ-alumina, vanadia/γ-alumina and molybdenum/alumina catalysts in nitric oxide reduction by methanol in

---

*Corresponding author. Tel.: +44 171 594 5579; fax: +44 171 594 5604; e-mail: d.chadwick@ic.ac.uk

PII S0920-5861(98)00084-4

compositions which simulated dry diesel exhaust gas except that SO_2 was omitted. The redox ability of vanadia is well established and the vanadia/γ-alumina catalyst was investigated on the expectation that NO oxidation to NO_2, and therefore NO_x reduction by methanol could be promoted. The activity of molybdenum based catalysts for oxy-dehydrogenation of methanol suggested that Mo might enhance NO_x reduction by activation of the oxygenated hydrocarbon.

2. Experimental

2.1. Catalyst and catalyst characterization

Three commercially available γ-alumina catalysts were studied, γ-Al_2O_3 (A), γ-Al_2O_3 (B) and γ-Al_2O_3 (C), respectively. Promoted alumina, 6% wt V_2O_5/γ-Al_2O_3 (B) and 3% wt MoO_3/γ-Al_2O_3 (C) catalysts were also studied. The γ-alumina support was impregnated by a solution of ammonium vanadate and oxalic acid [10]. The catalyst morphological properties and acidity are presented in Table 1.

The specific surface area (S_{BET}) and the pore volume distribution of the catalysts were determined by the standard N_2 isotherm method (BET method) at −196°C using an ASAP 2000 Micromeritics instrument. Ammonia TPD measurements were conducted for the unpromoted aluminas using a conventional TPD apparatus with a TCD detector and a linear heating rate of 10°C/min. from room temperature and with helium as the carrier gas. The sample (0.07 g) was pre-treated in a helium flow at 150°C for 1 h. After cooling to room temperature, the sample was exposed to 10% NH_3/He, followed by purging with helium. The acidity was obtained by NH_3 desorbing in the temperature range 110–650°C.

In situ EPR spectroscopy was conducted on vanadia/alumina catalysts using a Bruker EMX-073 10 in. spectrometer equipped with a 4114HT high temperature cavity. The measurements were conducted in the X-band with a field modulation of 60 kHz and with a sweep of the magnetic field 2400–4000 Gauss ($g \approx 2$). The in situ quartz flow microreactor has previously been described in detail [11] and the in situ EPR measurements were conducted as recently described [12].

2.2. Experimental set-up

The feed gas mixture was obtained by blending four channels of flow, i.e. NO/He, O_2/He and He (diluent and carrier gas) each controlled independently by mass flow controllers. All gases, certified quality, were used without further purification. Gaseous methanol (Aldrich ACS>99%) was introduced into the system via an evaporator–condenser system. The methanol condenser was kept at a constant temperature, −5°C, and from vapour-liquid equilibrium data the methanol concentration was determined to be 5000 ppm. Methanol was diluted with helium to achieve the desired concentration. The downstream line from the condenser was trace heated at 70°C to preheat the methanol containing gas stream.

A small fraction of the reactor effluent was diverted via a capillary tube to the inlet system of a VG quadruple mass spectrometer. The mass spectrometer was used for temperature-programmed reaction experiments. The effluent stream was analysed online with a Shimadzu 14B Gas Chromatograph with a TCD detector. A Chromosorb 102 column (1/

Table 1
Catalyst morphology and solid acidity

Catalyst	BET surface area (m^2/g)	Solid density (g/cm^3)	Average pore size (nm)	Loading (wt%)[a]	NH_3 desorption (mmol NH_3/g cat.)
γ-Al_2O_3 (A)	226	3.19	11.2		0.29
γ-Al_2O_3 (B)	238	3.17	11.6		0.43
γ-Al_2O_3 (C)	256	3.17	9.8		0.21
V_2O_5/γ-Al_2O_3 (B)	206	3.09	10.4	6.0	
MoO_3/γ-Al_2O_3 (C)	235	4.26	13.6	3.0	

[a] The catalyst loading was determined by AA.

8 in.×30 ft.) was used isothermally at 40°C. Helium was used as the carrier gas. Both the gas chromatograph and mass spectrometer could be operated either simultaneously or independently.

The microreactor consisted of a quartz tube mounted vertically in an electrical heated furnace. The catalyst samples were crushed and sieved (106–250 μm). The catalyst bed (0.070 g) was placed between two plugs of quartz wool. A temperature programmer with a type-K thermocouple placed just above the catalyst bed was used to control the temperature. During TPR the linear temperature increase was 5°C/min. The experiments were conducted with constant catalyst mass and volumetric flow rate and the space velocity quoted was based on the bulk density of the γ-alumina support (0.49 g/cm^3).

The NO conversion was calculated based on the N_2 formation

$$x_{NO} = \left\{\frac{2[N_2]}{[NO]_{in}}\right\} \times 100\%,$$

where $[N_2]$ was the N_2 concentration in the reactor outlet and $[NO]_{in}$ was the inlet NO concentration.

For TPR analysis of the $CH_3OH/O_2/NO$ system the following masses were monitored; H_2 (m/e=2), CH_3 (m/e=15), H_2O (m/e=18), N_2 (m/e=28), CH_3OH (m/e=29, 30, 31, 32), NO (m/e=30), O_2 (m/e=32), CO_2, N_2O (m/e=44), NO_2 (m/e=46) and CH_3OCH_3 (m/e=45,46). Both methanol and dimethyl ether have a fragmentation ion at m/e=30.

3. Results and discussion

3.1. NO *oxidation*

The promoting effect of oxygen in NO reduction has been widely studied and it is well established that NO_2 is more readily reduced than NO to N_2 by hydrocarbons serving as reducing agents [13]. NO oxidation over the catalysts was studied by temperature-programmed reaction (TPR) with 3000 ppm NO and 4% O_2. No detectable degree of NO oxidation was observed over a blank reactor, the γ-alumina catalysts or MoO_3/alumina. Fig. 1 presents the MS-signal of NO and NO_2 in excess oxygen as a function of reactor temperature. Despite some initial fluctuation in the MS data there is a clear trend in the MS-signal above 250°C of an increase in NO_2 MS-signal and decrease in that of NO. Fig. 1 indicates the commencement of NO oxidation over the 6 wt% vanadia/alumina catalyst at low temperature and this is consistent with the well-known ability of vanadia promoted catalysts to catalyse oxidation reactions. In promoting the oxidation of NO, vanadium pentoxide becomes partially reduced from V(V) → V(IV) [12,14]. In situ EPR spectroscopy is one of the few direct methods available to study the content of V(IV) in operating catalysts, since only the paramagnetic [Ar]3d^1 V(IV) species are detectable. V(V) ([Ar]3d^0) is diamagnetic and V(III) resonates far from the field applied here due to the zero field splitting of the electron spin state. EPR is therefore very sensitive to changes in the V(IV) content. Double integration of the EPR spectra can qualitatively monitor the change in the V(IV) content. Fig. 2 displays the V(IV) content obtained by double integration. The EPR data were corrected for the changes in the Boltzmanns distribution and the Q-value of the EPR cavity. The V(IV) content increased slightly above 250°C and increased further as a function of the reactor temperature. The increase of the V(IV) content at low temperature corresponds with the increase in NO_2 MS-signal, Fig. 1. The results indicate that vanadia/alumina catalysts can promote NO oxidation at relatively low temperatures. Above 400°C it is possible that the V(IV) content was influenced by methanol oxidation.

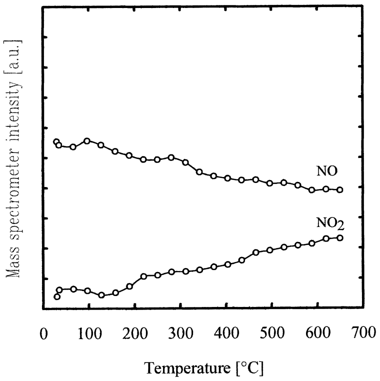

Fig. 1. NO oxidation to NO_2 over 6 wt% vanadia/γ-alumina in excess oxygen. Conditions: [NO]=3000 ppm, $[O_2]$=4%, GHSV= 21 000 h^{-1}.

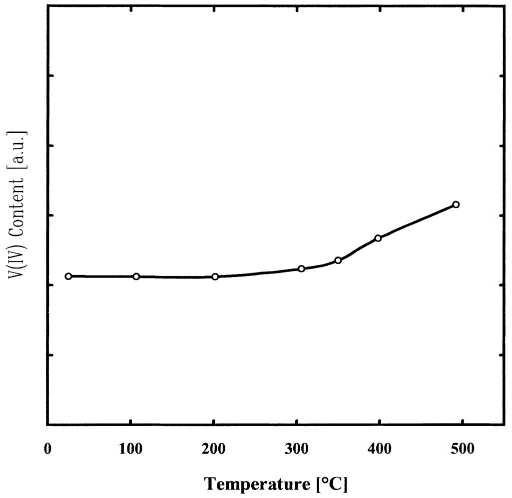

Fig. 2. Change in V(IV) content for 6 wt% vanadia/γ-alumina as function of reactor temperature. Conditions: [NO]=1500 ppm, [CH_3OH]=3000 ppm and [O_2]=2.5%. GHSV=24 000 h^{-1}.

3.2. *Selective reduction of* NO *by methanol*

Temperature-programmed reaction (TPR) experiments of NO reduction by methanol were conducted on all the studied catalysts. Fig. 3(a)–(c) shows the TPR spectra which are uncorrected for overlapping cracking fractions. Dimethyl ether formation was observed at low temperature in all cases. For pure alumina catalysts, the dimethyl ether formation commenced in the temperature range 190–230°C. It was observed that the efficiency to form dimethyl ether was correlated to the solid acidity for unpromoted γ-alumina defined as the ability to adsorb ammonia. The TPR experiments showed that promoted alumina catalysts, particularly molybdenum promoted, are able to dehydrate methanol to form dimethyl ether at even lower temperature. Dimethyl ether formation commenced over vanadia/alumina and MoO_3/alumina at 150°C and 125°C, respectively. For both the promoted

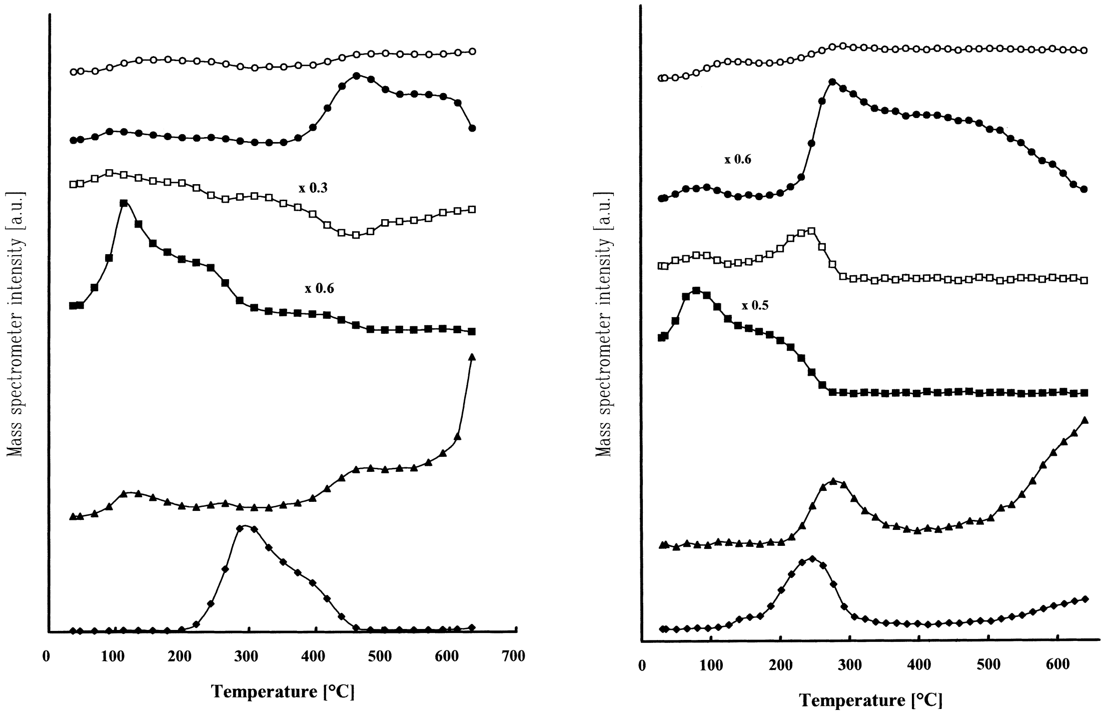

Fig. 3. (a) TPR spectra of NO reduction by methanol over γ-Al_2O_3 (B). (○) H_2O; (●) N_2,CO; (□) NO; (■) CH_3OH; (▲) N_2O, CO_2; (◆) CH_3OCH_3. Conditions: [NO]=1500 ppm, [CH_3OH]=3000 ppm and [O_2]=2.5%. GHSV=24 000 h^{-1}. (b) TPR spectra of NO reduction by methanol over 6 wt% vanadia/γ-alumina. (○) H_2O; (●) N_2,CO; (□) NO; (■) CH_3OH; (▲) N_2O, CO_2; (◆) CH_3OCH_3. Conditions: [NO]=1500 ppm, [CH_3OH]=3000 ppm and [O_2]=2.5%. GHSV=24 000 h^{-1}. (c) TPR spectra of NO reduction by methanol over 3 wt% MoO_3/γ- alumina. (○) H_2O; (●) N_2,CO; (□) NO; (■) CH_3OH; (▲) N_2O, CO_2; (◆) CH_3OCH_3. Conditions: [NO]=1500 ppm, [CH_3OH]=3000 ppm and [O_2]=2.5%. GHSV=24 000 h^{-1}.

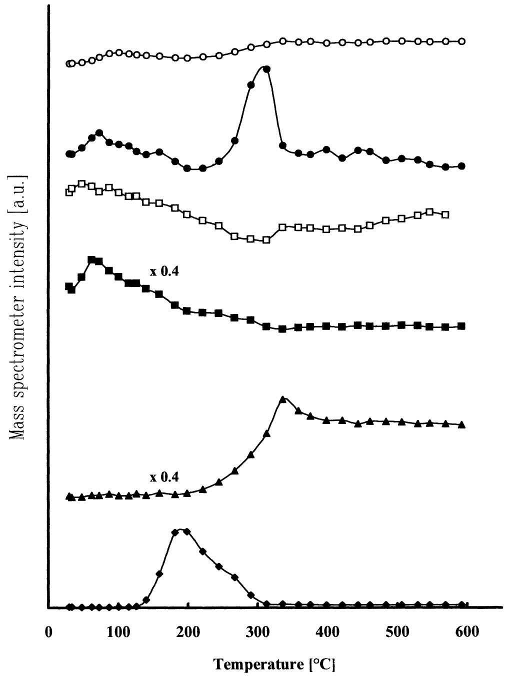

Fig. 3. (Continued)

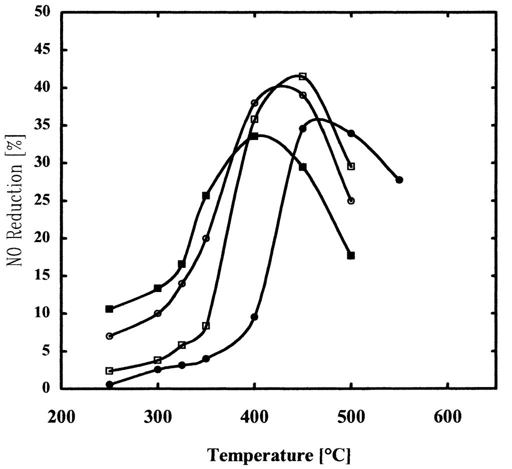

Fig. 4. Steady-state conversion of nitric oxide by methanol over (■) 6 wt% vanadia/γ-alumina, (●) γ-Al_2O_3 (B), (□) 3 wt% MoO_3/γ-alumina, (○) 50% (6 wt% vanadia/γ-alumina) +50% (3 wt% MoO_3/γ-alumina). Conditions: [NO]=1500 ppm, [CH_3OH] =3000 ppm and [O_2]=2.5%. GHSV=24 000 h^{-1}.

and pure γ-alumina catalysts the commencement of NO reduction and hence N_2 formation coincided with the decrease in the dimethyl ether mass spectrometer signal. This suggests that over the present catalysts, dimethyl ether formation and subsequent reaction is related to the NO reduction process. Previous results in this laboratory have shown that CO, H_2 and a $CO+H_2$ mixture does not reduce NO over γ-Al_2O_3 at low temperatures. The decomposition of methanol and dimethyl ether into CO and H_2 will not be responsible therefore for the observed NO reduction over the γ-alumina and promoted aluminas. We have observed dimethyl ether to be very stable in the absence of oxygen during TPR over these catalysts. It seems likely that either dimethyl ether in the presence of NO and excess oxygen is activated to form an intermediate specie probably by oxy-dehydrogenation, or the intermediate in dimethyl ether formation is intercepted by NO. The nature of the these active species is uncertain. However, the oxy-dehydrogenation of methanol to formaldehyde over vanadia and molybdenum based catalysts is well-known and it could be that the NO reduction (via NO_2) involves activation of methanol by either methoxy formation, methanol dehydration followed by dimethyl ether oxy-dehydrogenation, or direct methanol oxy-dehydrogenation, or a combination of these. Unfortunately, the main signal from formaldehyde as detected by mass spectroscopy analysis is *m*/*e*=29 and this mass coincides with mass fragmentation contributions from methanol and dimethyl ether, but work in progress is trying to resolve this problem.

The steady-state catalytic activity for NO reduction by methanol was studied on the series of γ-alumina and promoted γ-alumina catalysts. Fig. 4 presents the steady-state NO conversion at a fixed CH_3OH/NO molar ratio of 2 and with excess oxygen. Under the applied experimental conditions γ-alumina exhibited a maximum NO reduction of 36% at 469°C which agreed well with a performance previously reported [4,8]. Vanadia/alumina and MoO_3/alumina displayed activity maxima of 34% and 42% at 405°C and 445°C, respectively. The activity maxima for the vanadia/alumina and molybdena/alumina catalysts correspond to 0.090 mol NO converted/mol V/h and 0.16 mol NO converted/mol Mo/h. Nitrogen was the only product detected from NO reduction. The 6 wt% vanadia/alumina exhibited 10% NO conversion at 250°C. This shows that vanadia promoted alumina catalysts are active for NO reduction by methanol even at relative low temperature which is consistent with the observed promotion of NO oxidation (see above). The 3 wt% MoO_3/alumina catalyst displayed the highest activity for NO reduction. The high NO_x reduction activity is consistent with the well-known ability to promote oxy-dehydrogenation reactions as discussed above. A catalyst bed prepared by equal masses of 6 wt% vanadia/alumina and 3 wt% MoO_3/alumina displayed high catalytic activity in the temperature range 250–550°C. Below 350°C the efficiency of the vanadia/alumina catalyst for NO reduction was predominant and above 350°C the MoO_3/alumina catalyst was more active and hence an overall conversion of 40% was achieved under the applied experimental conditions. These preliminary results provide evidence for a slight synergy effect and suggest that improved catalytic activity in the temperature range 250–500°C would be achieved by a co-promoted vanadia–molybdenum catalyst for NO reduction. Work is in progress on this aspect.

3.3. *Effect of reducing agent*

Methanol was found to be effective for NO reduction in an oxidizing atmosphere over the all studied catalysts (Fig. 4). The decrease in NO conversion at higher temperatures was due to the increasing rate of direct methanol oxidation. H_2O and CO_2 were the only products detected from methanol oxidation. In view of the observation of dimethyl ether in TPR at low temperature and its possible role in NO reduction, dimethyl ether was likewise applied as a reductant over γ-alumina and vanadia/γ-alumina catalysts. Fig. 5 compares the steady-state NO conversion of methanol and dimethyl ether for NO reduction at a constant C/N molar ratio of 2. Both reducing agents display similar peak performances. Above 400°C the selectivity of dimethyl ether declined more sharply due to the direct oxidation into CO_2 and H_2O. Overall the results show that both methanol and dimethyl ether are effective as reducing agents in selective reduction of NO in the temperature range 250–500°C. Methanol was readily dehydrated to dimethyl ether over the γ-alumina and promoted γ-alumina catalysts. The higher degree of NO reduction achieved by dimethyl ether compared to methanol at low temperatures supports the view that dimethyl ether might be significant in methanol activation over these catalysts. This does not necessarily mean that the formation of dimethyl ether is a prerequisite for NO reduction by methanol. It may simply be that methanol dehydration is facile over the γ-alumina and promoted γ-alumina catalysts studied here, and as pointed out above it could be the intermediate in dimethyl ether formation which is intercepted by NO.

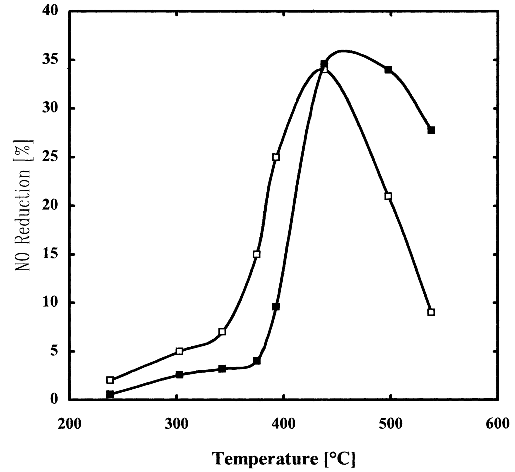

Fig. 5. Selective reduction of NO over γ-alumina (γ-Al_2O_3 (A)) by (■) methanol and (□) dimethyl ether. Conditions: [NO]=1500 ppm, [CH_3OH]=3000 ppm or [CH_3OCH_3]=1500 ppm and [O_2]=2.5%. GHSV=24 000 h^{-1}.

Acknowledgements

The authors are grateful to Dr K.M. Eriksen, Department of Chemistry, Technical University of Denmark for assistance during the EPR measurements. Mr. M. Sadler and Mr. Y. Liow are thanked for technical assistance. SGM is grateful for financial support from Kund Højgaards Foundation.

References

[1] H. Bosch, F.J.J.G. Janssen, Catal. Today 2 (1988) 369.
[2] G. Centi, S. Perathoner, Appl. Catal. A 132 (1995) 179.
[3] M.D. Amiridis, T. Zhang, R.J. Farrauto, Appl. Catal. B 10 (1996) 203.
[4] H. Hamada, Y. Kintaichi, M. Sasaki, T. Ito, M. Tabata, T. Yoshinari, Appl. Catal. 88 (1992) L1.
[5] M. Tabata, H. Tsuchida, K. Miyamoto, T. Yoshinari, H. Yamazaki, H. Hamada, Y. Kintaichi, M. Sasaki, T. Ito, Appl. Catal. B 6 (1996) 169.
[6] Y. Li, J.N. Armor, Appl. Catal. B 3 (1993) L1.

[7] M. Iwamoto, H. Yahiro, S. Shundo, Y. Yu, N. Mizuno, Appl. Catal. 69 (1991) L15.
[8] H. Hamada, Y. Kintaichi, M. Sasaki, T. Ito, M. Tabata, Appl. Catal. 70 (1992) L15.
[9] K. Masuda, K. Tsujimura, K. Shinoda, T. Kato, Appl. Catal. B 8 (1996) 33.
[10] G.C. Bond, J.P. Zurita, S. Flamerz, P.J. Gellings, H. Bosch, J.G. van Ommen, B.J. Kip, Appl. Catal. 22 (1986) 361.
[11] K.M. Eriksen, R. Fehrmann, N.J. Bjerrum, J. Catal. 132 (1991) 263.
[12] S.G. Masters, A. Chrissanthopoulos, K.M. Eriksen, S. Boghosian, R. Fehrmann, J. Catal. 166 (1997) 16.
[13] H. Hamada, Y. Kintaichi, M. Sasaki, T. Ito, M. Tabata, Appl. Catal. 70 (1992) L15.
[14] S.G. Masters, K.M. Eriksen, R. Fehrmann, J. Mol. Catal. A 120 (1997) 227.