

Hysteresis phenomena in sulfur dioxide oxidation over supported vanadium catalysts

S.G. Masters¹, K.M. Eriksen, R. Fehrmann^{*}

Department of Chemistry, Building 207, Technical University of Denmark, DK-2800 Lyngby, Denmark

Received 20 July 1996; accepted 17 September 1996

Abstract

Catalyst deactivation and hysteresis behavior in industrial SO₂-oxidation catalysts have been studied in the temperature region 350–480°C by combined in situ EPR spectroscopy and catalytic activity measurements. The feed gas compositions simulated sulfuric acid synthesis gas and wet/dry deNO_x'ed flue gas. The vanadium (IV) compound K₄(VO)₃(SO₄)₅ precipitated during all the investigated conditions hence causing catalyst deactivation. Hysteresis behavior of both the catalytic activity and the V(IV) content was observed during reheating.

Keywords: Vanadium based SLP catalysts; Hysteresis; Deactivation; SO₂ oxidation; Flue gas desulfurization

1. Introduction

Oxidation of SO₂ into SO₃ over vanadium based supported liquid phase (SLP) catalysts, is the key stage in the industrial production of sulfuric acid. The catalyst is usually made by calcination of diatomaceous earth, vanadates and alkali promoters usually in the form of oxides or sulfates. During the activation process, the catalyst takes up sulfur oxides, hence forming molten alkali pyrosulfates which dissolve the vanadium salts. At operating temperature, 400–600°C, the catalyst is well described by the molten–salt gas system M₂S₂O₇/V₂O₅–SO₂/O₂/SO₃/N₂,

where M usually is a mixture of K and Na. The alkali–vanadium molar ratio, is ranging between 2–5.

Below a specific temperature, designated the ‘break point temperature’, a sudden loss in the catalytic activity occurs. This is regarded as a major problem, since the break point temperature usually occurs in the range 420–450°C (depending on the partial pressure of SO₂, alkali composition and alkali–vanadium molar ratio). Therefore with the present technology available, costly interstage SO₃ absorption is necessary, in order to comply with governmental SO₂ emission regulations [1]. It is now well established, that deactivation of the catalyst, is attributed to precipitation of crystalline compounds of vanadium. As shown by Boghosian et al. [2] precipitation of V(III) and V(IV) compounds drains the melt of the catalytic active V(V)-complexes. Such a deactivation process is expected to be

^{*} Corresponding author.

¹ Present address: Department of Chemical Engineering and Chemical Technology, Imperial College of Science, Technology and Medicine, Prince Consort Road, London SW7 2BY, UK.

reversible, and the catalytic activity must be regained upon heating the catalyst bed up to 500°C. Hereby the precipitated V(III) and/or V(IV) compounds decompose and dissolve, hence allowing reoxidation into catalytic active V(V)-complexes [3,4].

Although the vanadium based SO₂ oxidation catalyst is designed for use in the manufacture of sulfuric acid it is also utilized in the flue gas desulfurization process in coal fired power plants, where an estimated 150 mill. metric tons of SO₂ annually is emitted into the atmosphere. In a coal fired power plant, the untreated flue gas from the boiler is first led to a selective catalytic reduction (SCR)-reactor for the reduction of nitrogen oxides, NO_x (NO and NO₂). The flue gas then typically consists of 0.2% SO₂, 4% O₂, 7% H₂O, 14% CO₂ and ~75% N₂ before entering the SO₂ converter upstream [5].

In the present work, we describe the hysteresis behavior in the temperature range 350–480°C, of two industrial SLP catalysts designed for sulfuric acid production and flue gas cleaning respectively, having the same chemical composition, but different average pore size of the support. The methods applied are combined in situ EPR (electron paramagnetic resonance) spectroscopy and catalytic activity measurements. Three types of feed gases were used in the investigation, i.e. unconverted sulfuric acid synthesis gas and wet/dry flue gas. In the wet flue gas, only catalytic activity measurements were performed since it has been shown recently [6] that the catalyst most likely deactivates due to precipitation of EPR-silent V(III)-compounds.

2. Experimental

The investigated catalysts were VK-WSA and VK-38, two widely used types of catalysts manufactured by Haldor Topsøe A/S, Denmark. They have a chemical composition of 6.5% w/w V₂O₅ on kieselguhr, with a molar ratio of

M/V = 3.8 (K/Na/V = 3/0.8/1). The VK-WSA catalyst has an average pore size < 500 Å whereas in the case of the VK-38 catalyst, the average pore size is 3000–4000 Å. The VK-WSA catalyst is designed for utilization in the desulfurization process under humid conditions. The sulfuric acid synthesis gas and dry flue gas were prepared by premixing gases of commercial quality to the desired gas composition in an evacuated special steel bottle and then electrically heated at the bottom over night to obtain a uniform gas mixture by convection. The wet flue gas with a 7% water vapor content was obtained by bubbling the dry gas until saturation through water which was contained in two flasks connected in series and immersed in a thermostat controlled at the appropriate temperature. With a thermostat temperature of 40°C a 7% water vapor content was achieved.

The catalyst pellets were gently crushed to a size of ~1 mm, and about 20 mg of the catalyst was placed in a quartz reactor flow cell, as described in detail earlier [7]. An external Mn(II)-standard was used for the field calibration. The reactor flow cell fits into a Bruker ER4114HT high temperature X-band cavity, mounted in a slightly modified JEOL-JES-ME 1X EPR spectrometer and connected to a PC-based acquisition system. EPR-spectroscopy is probably the only direct method available, to study V(IV) in these supported catalysts in situ, since V(IV) with the paramagnetic electron configuration [Ar]3d¹ selectively is detectable by EPR, without interference of the support. Similarly, NMR spectroscopy might be useful for in situ studies of V(V) in oxidized catalysts as judged from our previous investigations on catalysts model melts [8].

The SO₂ concentration was determined by UV-spectroscopy at 300.2 nm, on a Perkin Elmer Lambda 9 spectrophotometer using a 10 mm (for synthesis gas) and 100 mm (for flue gas) optical flow cuvette (Suprasil from Hellma, Germany). A linear p(SO₂) versus A_{300.2nm} calibration curve was constructed to correlate the SO₂ pressure to the measured absorbance. The

entire SO₂ monitoring procedure was conducted on the exit gas at room temperature. All 1/8" stainless steel tubes in the experimental set-up were heated to 80–90°C with wrapped electric heating tape in order to prevent possible condensation of SO₃ (and H₂O, in the wet flue gas experiments). Drying columns of P₂O₅ were placed before the massflowmeters and just before the reactor inlet (except in the wet flue gas experiments). Steady state conditions were reached within 15–20 min at temperatures above the deactivation temperature, evaluated both by EPR and the conversion. However, the time intervals between all measurements were 60 min. The flow rate was initially adjusted so the SO₂ conversion was always below 20% at all temperatures, indicating that the reactor works differentially.

3. Results and discussion

3.1. Catalytic activity

The industrial SO₂-oxidation catalysts VK-WSA and VK-38 were studied in simulated sulfuric acid synthesis gas and dry flue gas in the temperature range 350–480°C. Furthermore, catalytic activity measurements of VK-WSA in wet flue gas were conducted. The performance of both catalysts is displayed in the Arrhenius plot in Fig. 1. Remarkable are the differences in

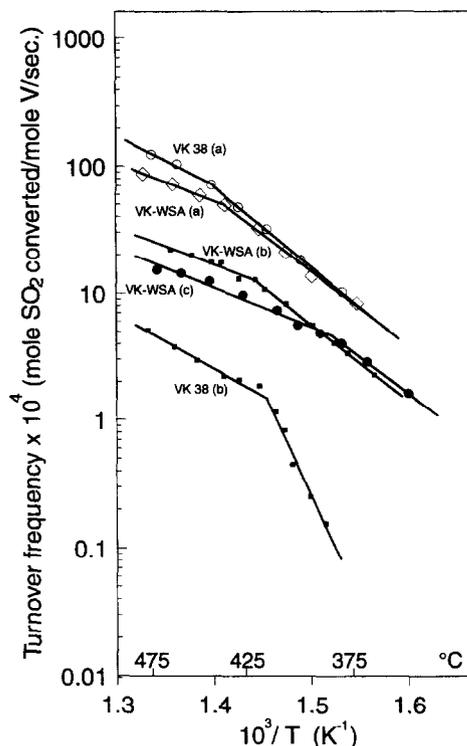


Fig. 1. Arrhenius plots of the industrial SO₂-oxidation catalysts VK-WSA and VK38 in (a) 10% SO₂, 11% O₂ and 79% N₂; (b) 0.2% SO₂, 4.5% O₂, 15% CO₂ and ~80% N₂; (c) 0.2% SO₂, 4% O₂, 7% H₂O, 14% CO₂ and ~75% N₂.

catalytic activity (at the same temperature and gas composition), calculated as the turnover frequency (mol SO₂ converted/mol V/s). In simulated sulfuric acid synthesis gas both catalysts show relatively high activity, whereas in simulated dry flue gas the catalytic performance has

Table 1
Deactivation temperature and precipitated compound

Type of catalyst	T_b (°C) ^a	T_p (°C) ^b	Precipitated compound	g_{iso} -value ^f
VK38 ^c	440	430–443	K ₄ (VO) ₃ (SO ₄) ₅	1.970(5)
VK38 ^d	418	409–425	K ₄ (VO) ₃ (SO ₄) ₅	1.967(5)
VK-WSA ^c	435	435–445	K ₄ (VO) ₃ (SO ₄) ₅	1.968(5)
VK-WSA ^d	419	401–419	K ₄ (VO) ₃ (SO ₄) ₅	1.972(5)
VK-WSA ^e	385	340–350 ^g	K ₄ (VO) ₃ (SO ₄) ₅ ^g + V(III)-salt	1.972(5) ^g

^a T_b is the temperature for the break point in the Arrhenius plot.

^b T_p is the temperature at which precipitation of crystalline V(IV)-compounds occur as detected by EPR.

^c Sulfuric acid synthesis gas: 10% SO₂, 11% O₂ and 79% N₂.

^d Dry flue gas: 0.2% SO₂, 4.5% O₂, 15% CO₂ and ~80% N₂.

^e Wet flue gas: 0.2% SO₂, 4% O₂, 7% H₂O, 14% CO₂ and ~75% N₂.

^f g_{iso} was obtained at 350°C after field calibration with an external MnO reference at 18°C.

^g Ref. [6].

decreased. This is attributed to the small content of SO_2 which is the limiting factor for obtaining a higher activity. The activity measurements displayed in Fig. 1 have the same feature for both catalysts, i.e. in the high temperature region, an apparent activation energy of around ~ 70 kJ/mol was found. At the break point temperature a sharp decrease in the catalytic activity was observed, and the apparent activation energy increased to ~ 115 kJ/mol. The apparent activation energies coincide well with

earlier investigations [2,9–13] except for the VK-38 catalyst in dry flue gas. In Table 1 the break point temperatures are listed. As seen, for both catalysts the deactivation commence 20°C lower in the dry flue gas as compared to sulfuric acid synthesis gas conditions. This is most likely due to the presence of only 0.2% SO_2 in the dry flue gas, and subsequently the relative amount of V(IV) species in the melt becomes considerable lower than in the sulfuric acid synthesis with 10% SO_2 . In the wet flue gas, pyrosulfates

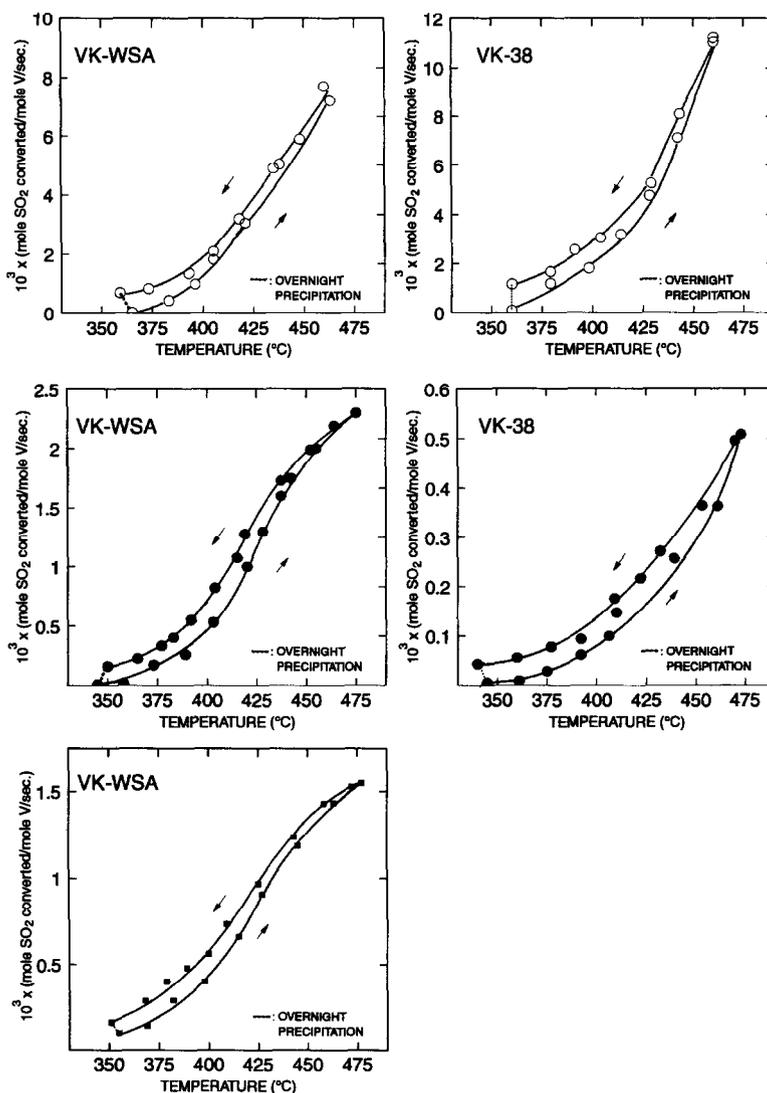


Fig. 2. Catalytic activity versus temperature for VK-WSA and VK-38 in (○) 10% SO_2 , 11% O_2 , 79% N_2 ; (●) 0.2% SO_2 , 4.5% O_2 , 15% CO_2 , $\sim 80\%$ N_2 ; (■) 0.2% SO_2 , 4% O_2 , 7% H_2O , 14% CO_2 , $\sim 75\%$ N_2 .

take up water, hence forming hydrogen sulfate, which changes the molten medium and thus is most likely to affect the complex formation. However, the catalytic activity of VK-WSA is almost unaffected by the presence of water vapor in the flue gas, but the breakpoint temperature is significantly reduced to around 385°C. A recent study, [6] has shown that EPR silent vanadium(III) compounds precipitate and thus cause deactivation. The vanadium(IV) compound, $K_4(VO)_3(SO_4)_5$, precipitates at 350°C when the solubility curve for V(IV) is exceeded.

As mentioned above, the VK-WSA and the VK-38 catalysts have identical chemical compositions but different average pore size. In catalysts with wide pores (above 1000 Å) crystals are able to grow into large sizes without any physical limitations of the pore walls and equilibrium is rapidly obtained. Thus, when the support has small pores (< 500 Å), the crystal size is limited by the pore size, and the solubility of V(IV) increases accordingly [14]. A considerable part of V(IV) will therefore stay in the liquid state at low temperature leading to a higher catalytic activity below the deactivation temperature of the large pore catalyst. A detailed study concerning the relationship between pore size and activity has shown that support characteristics are very important for obtaining a high catalytic activity and low break point temperature [15].

By plotting the catalytic activity versus temperature as shown in Fig. 2 the hysteresis loop becomes clear. As expected the activity is higher for a non-deactivated catalyst (during progressive cooling) than a previously deactivated catalyst (during progressive reheating). The activity is fully regained after reheating to above 450°C. The hysteresis behavior is related to phase transitions in the melt. More specifically it is attributed the slow dissolution of the vanadium compounds precipitated in the pores of the catalyst carrier, probably in poor contact with the residual melt [16,17]. The necessity of heat treatment well above the deactivation temperature, T_b , might be due to the oxidative decom-

position of the precipitated inactive V(III) and/or V(IV) compounds into catalytic active V(V) complexes dissolved in the melt [4]. Temperature stability measurements of the pure isolated V(IV) deactivation compounds [17] has shown that most compounds are stable up to around 460°C. Previous EPR investigations by Eriksen et al. [7] has indeed shown, that heat treatment of a deactivated catalyst led to the disappearance of the spectra from the precipitated compounds, and to reappearance of the EPR spectra from dissolved V(IV)-complexes. The change in color of the studied catalyst sample, showed that prior to the experiments the catalyst samples had a orange–yellow color, and thus vanadium was completely oxidized. At 350°C the color was light greenish, as a sign of reduced vanadium. After reheating to 480°C orange–yellow tints on a light greenish background was observed.

3.2. *In situ* EPR spectroscopy

The investigated catalysts were studied by *in situ* EPR spectroscopy in the magnetic field range 2400–4400 G, with modulation frequency of 100 kHz, modulation width of 12 G and a sweep time of 50 s. For convenience, only the selected EPR spectra of VK-WSA in synthesis gas are shown in Fig. 3. As seen, in Fig. 3 both during cooling and reheating, the line features of the spectra remained isotropic. In the high temperature region (above 435°C) a broad isotropic line was observed ($g \approx 1.98$, $\Delta B_{pp} \approx 330$ G), which was attributed to dissolved polymeric and/or dimeric V(IV) complexes. The spin coupling among neighboring vanadium nuclei resulted in complicated unresolved superimposed multiline spectra [17,18] hence giving rise to the very large line width. At a specific temperature, T_p , an almost isotropic narrow line appeared, which became increasingly dominant upon decreasing temperature. This narrow feature was due to precipitation of crystalline V(IV) compounds. From the EPR parameters, $g_{iso} = 1.968(5)$ and $\Delta B_{pp} = 120$ G the precipitated

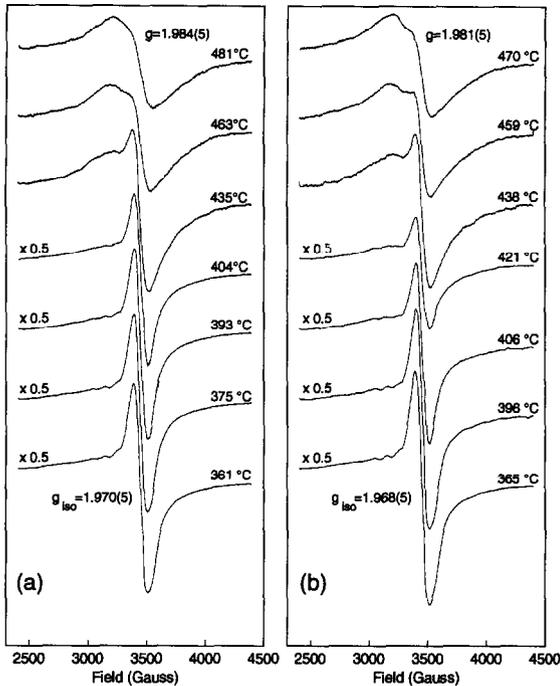


Fig. 3. EPR spectra of the VK-WSA catalyst at selected temperatures in 10% SO₂, 11% O₂ and 79% N₂ during cooling (a) and reheating (b).

compound was identified as K₄(VO)₃(SO₄)₅ [7]. During stepwise reheating of the catalyst bed, the sharp central isotropic line feature of the EPR spectra, gradually decreased in intensity. A broad line with no sign of a central line is observed above 460°C hence indicating the non-existence of V(IV) in the crystalline phase. The EPR investigations of the VK-38 catalyst in synthesis gas and in dry flue gas show an almost identical behavior to that observed for the VK-WSA catalyst, with K₄(VO)₃(SO₄)₅ precipitating and hence causing deactivation. The g -values obtained at 350°C in sulfuric acid synthesis gas and dry flue gas were $g_{iso} = 1.970(5)$ and $g_{iso} = 1.967(5)$, respectively.

As seen from Table 1 T_b and T_p coincide well which is a direct indication that the loss in catalytic activity is due to the depletion of the active vanadium species from the system caused by the precipitation of V(IV) compounds. Where comparable, the data fits well with previous measurements [6,17]

Double integration of the EPR spectra has been performed, followed by temperature correction measures, with reference to the change in Boltzmann distribution and the Q -value of the EPR cavity. This allows qualitatively to follow the relative V(IV) content in the melt, as shown in Fig. 4. The data obtained from the double integration is normalized with the value acquired after overnight precipitation at 340°C, assuming that this value represents the complete reduction of V(V) into V(IV). The error of such double integration is 10–20% absolute (with respect to the number of moles of vanadium present), highest at elevated temperatures. However, the relative error of the integrated spectra is much less making the hysteresis effects on Fig. 4 significant. As expected, the V(IV) content increases upon decreasing temperature, hence shifting the equilibrium V(V) \rightleftharpoons V(IV) to

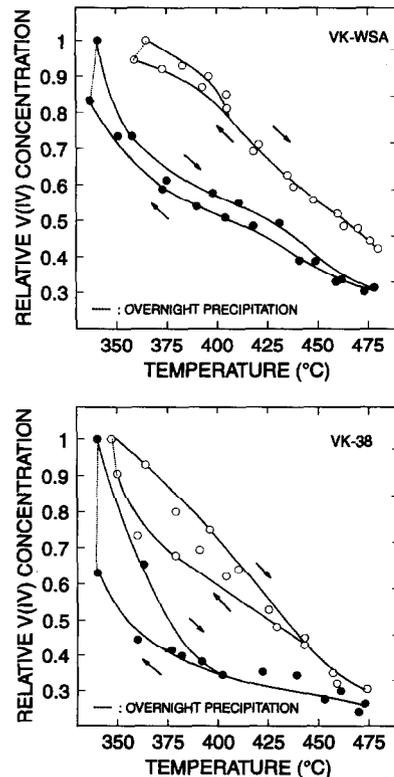


Fig. 4. Relative V(IV) concentration versus temperature for VK-WSA and VK-38 in (○) 10% SO₂, 11% O₂, 79% N₂ and (●) 0.2% SO₂, 4.5% O₂, 15% CO₂, ~80% N₂.

the right. The overnight temperature of 340°C subsequently secured complete precipitation of $K_4(VO)_3(SO_4)_5$ hence further increasing the V(IV) content. During the duration of the re-heating process, the data obtained closely followed, in a parallel manner, the data observed during stepwise cooling, and the initial V(IV) content is fully regained at 480°C, where the catalytic activity also is fully regained.

Acknowledgements

This investigation has been supported by the Danish Natural Science Research Council and EU program BRITE-EURAM II (contr. No. BRE2.CT93.0447). Haldor Topsøe A/S, Denmark, is acknowledged for providing the VK-WSA and VK-38 catalyst samples.

References

- [1] D.J. Smith, *Power Eng. Int.* April (1994) 21.
- [2] S. Boghosian, R. Fehrmann, N.J. Bjerrum and G.N. Papatheodorou, *J. Catal.* 119 (1989) 121.
- [3] J. Villadsen and H. Livbjerg, *Catal. Rev. Sci. Eng.* 17 (1978) 203.
- [4] G.K. Borekov, R.A. Buyanov and A.A. Ivanov, *Kinet. Catal.* 8 (1967) 153.
- [5] H. Jensen-Holm and O. Rud-Bendixen, in: *Sulfur '90: Proc. of Int. Conf., Cancún, Mexico (1990)* p. 75–84.
- [6] S.G. Masters, A. Chrissanthopoulos, K.M. Eriksen, S. Boghosian and R. Fehrmann, *J. Catal.*, in press.
- [7] K.M. Eriksen, R. Fehrmann and N.J. Bjerrum, *J. Catal.* 132 (1991) 263.
- [8] O.B. Lapina, V.M. Mastikhin, A.A. Shubin, K.M. Eriksen and R. Fehrmann, *J. Mol. Catal.* 99 (1995) 123.
- [9] G.K. Borekov, L.P. Polyakova, A.A. Ivanov and V.M. Mastikhin, *Dokl. Akad. Nauk. SSSR.* 210 (1973) 626; *Dokl. Akad. Nauk. SSSR. (Engl. Transl.)* 210 (1973) 423.
- [10] F.J. Doering and D.J. Berkel, *J. Catal.* 103 (1987) 126.
- [11] P. Mars and J.G.H. Maessen, in: *Proc. 3rd Int. Congr. on Catalysis, Amsterdam, 1964, Vol. 1 (Wiley, New York, 1965)* p. 266; *J. Catal.* 10 (1968) 1.
- [12] K.C. Xie and A.J. Nobile, *J. Catal.* 94 (1968) 323.
- [13] H. Livbjerg and J. Villadsen, *Chem. Eng. Sci.* 27 (1972) 21.
- [14] B.S. Balzhinimaev, N.P. Belyaeva and A.A. Ivanov, *Rasplavy* 1(1) (1987) 92; (1988) 74 (Engl. transl.).
- [15] C. Oehlers, R. Fehrmann, S.G. Masters, K.M. Eriksen, D.E. Sheinin, B.S. Balzhinimaev and V.I. Elokhin, *Appl. Catal.*, in press.
- [16] S. Kovenklioglu and G.B. DeLancey, *Can. J. Chem. Eng.* 57 (1979) 165.
- [17] K.M. Eriksen, D.A. Karydis, S. Boghosian and R. Fehrmann, *J. Catal.* 155 (1995) 32.
- [18] D.A. Karydis, K.M. Eriksen, R. Fehrmann and S. Boghosian, *J. Chem. Soc. Dalton Trans.* (1994) 2151.