The effects of catalyst aging under industrial conditions: ethylene oxide conversion over Ag–Cs/α-Al_2O_3 catalysts

Norman Macleod, James M. Keel, and Richard M. Lambert *
Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK

Received 22 August 2002; accepted 13 November 2002

SEM, XRD and XPS have been used to characterize a series of fresh, conditioned and industrially aged Ag–Cs/α-Al_2O_3 catalysts. No significant loss or redistribution of the alkali promoter was observed, nor was there excessive pick-up of the chlorine promoter. These results are consistent with the aged supports *not* showing an increased activity toward the further conversion of ethylene oxide.

KEY WORDS: ethylene oxide; silver; SEM; XRD; XPS; cesium; isomerization; epoxidation.

1. Introduction

Continued interest in the heterogeneously catalyzed epoxidation of ethene derives both from the major technological importance of the industrial process and from the apparently unique behavior of silver as a catalyst. This has stimulated much fundamental and applied research [1] in which single-crystal studies have played an important role in uncovering the long-controversial molecular mechanism and in elucidating the role of chlorine [2] and alkali promoters [3]. However, in comparison, the phenomena associated with catalyst aging have received very little attention by way of systematic studies, despite the great technological importance of these effects. And nothing at all has been published that addresses the properties of ethylene epoxidation catalysts aged under industrial conditions in a commercial plant.

The lifetime of a commercial Ag epoxidation catalyst is typically 2–3 years. During this time a progressive loss in activity occurs, so that to maintain productivity it is necessary to steadily increase the operating temperature. In addition to the activity loss, a gradual decay in catalyst selectivity also takes place, and it is this loss in selectivity that ultimately determines when the catalyst is no longer economically viable and must therefore be replaced. The increase in temperature required to maintain productivity is at least partially responsible for this selectivity loss, as higher temperatures favor the total combustion of ethylene. However, it is not clear whether physical changes that may occur in the nature of the catalyst with aging (e.g. in the acidity of the support) also contribute. Here we report on (i) the characterization by XRD, SEM and XPS of fresh and industrially aged commercial Ag–Cs/α-Al_2O_3 samples and (ii) their activity for the further conversion of ethylene oxide—processes that play a significant role in determining overall reaction selectivity.

2. Experimental

The Ag–Cs/α-Al_2O_3 catalyst studied in this work was a commercial catalyst containing approximately 10 wt% Ag and dosed with a promoting quantity of Cs. The fresh catalyst was prepared by impregnation of cylindrical α-Al_2O_3 pellets with a solution containing a silver oxalate/ethylenediamine complex. Three separate samples of the catalyst were investigated: a fresh calcined and reduced sample (denoted F); a conditioned sample treated under full reaction conditions in a pilot plant until optimum activity was achieved ($\sim$100 h on line; denoted C); and an aged and deactivated sample removed from a commercial plant after 14 months under reaction conditions (denoted A). The aged sample discussed was taken from the center of the catalyst bed, although similar results were obtained from samples removed from both inlet and outlet positions. To investigate ethylene oxide conversion on the support material, and in particular the influence of Cs, samples of the bare α-Al_2O_3 support and a sample dosed with 350 ppm Cs/α-Al_2O_3 were also studied.

Ethylene oxide isomerization and combustion experiments were performed in a quartz microreactor system described previously [4] and operated under differential conditions. The ethylene oxide (BOC speciality gases, 1% EO/He) and O_2 (Messer UK) were delivered by independent mass flow controllers (MKS instruments) and further diluted in ultra-pure He to give the required gas-phase composition. Prior to testing the samples were heated to 200 °C in He. Organic products were analyzed

---

* To whom correspondence should be addressed.
E-mail: rml1@cam.ac.uk

1011-372X/03/0300-0051/0 © 2003 Plenum Publishing Corporation

using a GC/FID system (Shimadzu 14B), fitted with a Porapak N column. Carbon oxides were monitored using a NDIR CO/CO_2 detector (Siemens Ultramat 6). Temperature-programmed oxidation (TPO) experiments were also performed in this system, utilizing the NDIR analyser and a quadrupole mass spectrometer (Hiden RGA 301). The feed during TPO experiments contained 5% O_2 in He with a total flow of 60 ml min^{-1}. The sample, 200 mg, was ramped from room temperature to 800 °C with a linear heating rate of 10 K min^{-1}.

Powder XRD patterns were obtained using a Philips PW1710 instrument employing CuKα radiation. Scanning electron microscopy (SEM) was performed using a JEOL 6340 FEG microscope operating at 20 kV, employing back-scattered electrons for enhanced image contrast. XPS was performed using a VSW ARIES system equipped with a HA-100 hemispherical analyzer. Catalyst samples were mounted by pressing a small amount of the material between two discs of pure aluminum. Separating the discs produced two specimens consisting of a thin film of catalyst powder adhering to the aluminum. XP spectra were acquired with MgKα radiation and quoted binding energies (BEs) are referred to the C 1s emission at 284 eV.

3. Results and discussion

Representative SEM images obtained from the three samples investigated are shown in figure 1. Also included in this figure are the corresponding powder XRD patterns which focus on the region of the Ag(200) reflection used for line-broadening analysis. The average particle sizes determined via these two techniques are summarized in table 1. The SEM values were obtained by determining the volume-weighted average diameter for 200 particles imaged at various locations within each sample.

The fresh catalyst contained discrete silver particles with an average particle size of 97 nm as determined by

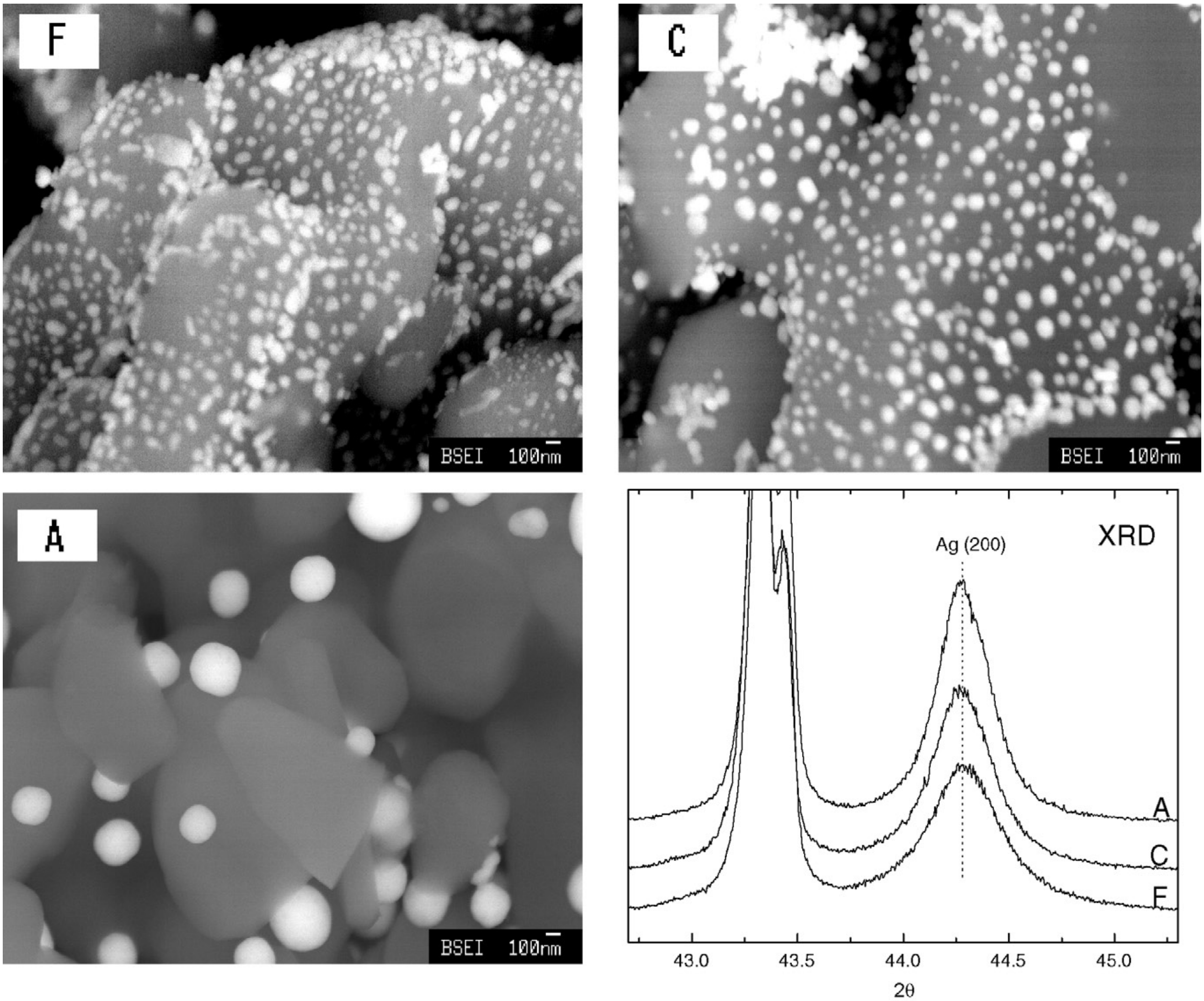

Figure 1. Representative SEM images and corresponding powder XRD profiles obtained from fresh (F), conditioned (C) and aged (A) catalyst.

Table 1
Comparison of average particle size values determined by XRD and SEM

Sample	Average particle size (nm)	
	XRD	SEM
Ag–Cs/Al_2O_3 (fresh)	47	97
Ag–Cs/Al_2O_3 (conditioned)	75	117
Ag–Cs/Al_2O_3 (aged)	116	341

SEM. Hoflund *et al.* [5–7] also employed SEM to characterize a series of fresh and aged Ag/α-Al_2O_3 catalysts. In their fresh catalyst a thin film of silver was observed covering the alumina support [5]. No such film was observed in this case, which may reflect the different preparation techniques employed. Hoflund *et al.* utilized a method involving dissolution of Ag_2O into a lactic acid solution which was subsequently used for impregnation [8]. The catalysts studied in this work were prepared via a method involving complexation of Ag with an amine species prior to impregnation. Hoflund *et al.* also concluded that one of the major influences of Cs was to act as a "binder" between the support and silver, resulting in the formation of a more uniform Ag film covering the support surface. This enhanced coating of alumina by silver was thought to account for the Cs-induced decrease in ethylene oxide secondary conversion processes attributable to the support [7,9]. Clearly, however, this "coating" of the alumina surface by Ag does not occur in catalysts prepared by the method employed here, and the influence of Cs is therefore also different, as discussed below.

After a short period of time on line (100 h), during which the fresh catalyst was conditioned to reach optimum activity, a small increase in average Ag particle size occurred, from 97 to 117 nm as determined by SEM. In contrast, Hoflund and Minahan [6] observed gross changes in the morphology of the silver phase during this initial period. They attributed the requirement for a conditioning period to this change in the Ag morphology. However, it is clear from the images in figure 1 that no such gross changes in the nature of the silver component occurred with our catalyst. It is more likely that the requirement for a conditioning period is related to the accumulation of the Cl promoter during the initial period, gradually converging on its equilibrium coverage. Removal of carbonaceous material deposited during the catalyst preparation step may also contribute. TPO profiles obtained from all three Ag/α-Al_2O_3 catalysts are shown in figure 2. The fresh catalyst displays a very large CO_2 feature at 230 °C. This feature is significantly reduced on the conditioned catalyst, indicating that gradual oxidative removal of carbonaceous deposits occurs during this initial period.

Whilst both XRD and SEM reveal significant sintering of the silver phase with further use, it is clear that there is some discrepancy between the particle size values obtained by these techniques, particularly for the aged sample. This discrepancy between XRD and SEM particle size determination has been noted in earlier investigations of Ag supported on α-Al_2O_3 [10,11] and was attributed to the inaccuracy of the line-broadening technique, particularly for relatively large particles. However, the fact that the XRD method consistently underestimates average particle size values, in comparison to the corresponding SEM data, may indicate that there is significant disorder within individual Ag particles, with the majority of particles containing

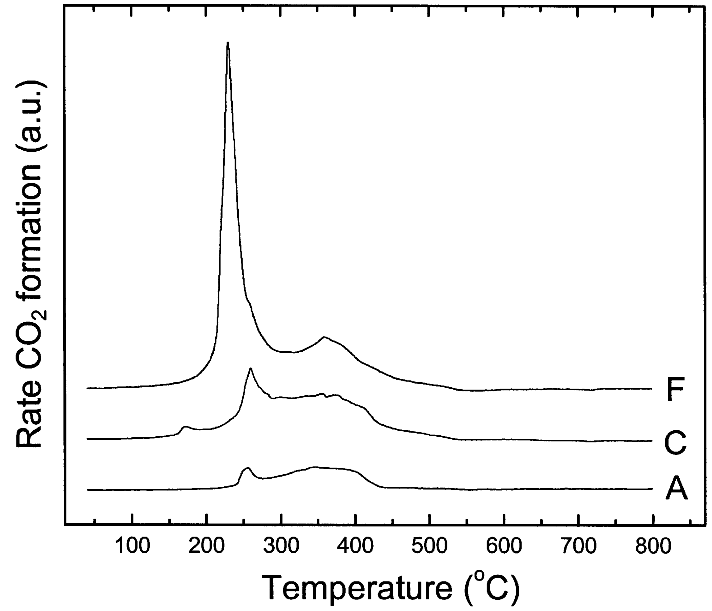

Figure 2. Temperature-programmed oxidation (TPO) profiles obtained from fresh (F), conditioned (C) and aged (A) catalysts (0.2 g, 5% O_2/He, 150 ml min^{-1}, $\beta = 10$ K min^{-1}).

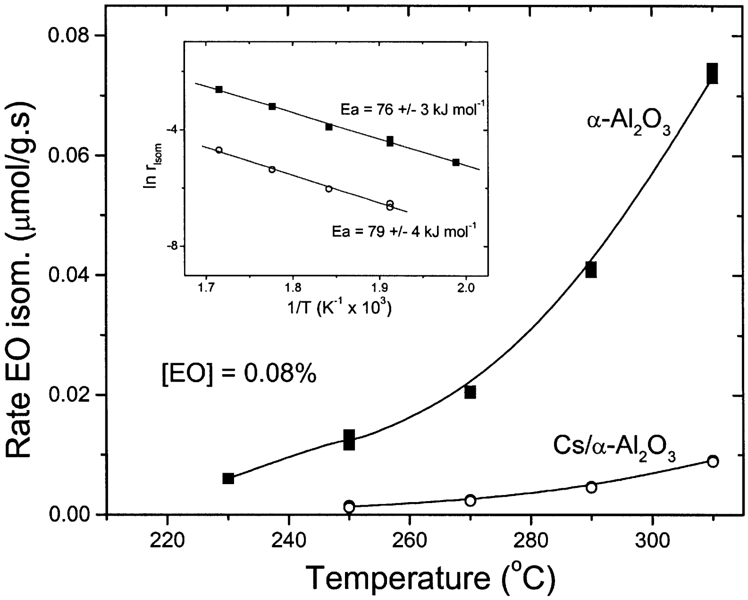

Figure 3. Rate of ethylene oxide isomerization to acetaldehyde versus temperature over α-Al_2O_3 and 350 ppm Cs/α-Al_2O_3 samples (0.08% ethylene oxide, 0.24 g s ml^{-1} (STP)). Inset shows the corresponding Arrhenius plots.

multiple domains and therefore a high concentration of grain boundaries [12].

As discussed previously, it is apparent that the major influence of Cs in the catalysts studied here does not involve it acting as a binder between Ag and alumina [5–7,9]. An alternative explanation offered for the beneficial effect of Cs is that it moderates the acidity of the support [13,14]. Accordingly, figure 3 shows rate versus temperature data for the isomerization of ethylene oxide to acetaldehyde over the blank alumina support and a sample dosed with 350 ppm Cs. The isomerization of ethylene oxide over α-Al_2O_3 was found to be first order in ethylene oxide (data not shown) with an apparent activation energy of 76 ± 3 kJ mol^{-1}. This value is in good agreement with that determined by Vannice and Mao for a high-surface-area α-Al_2O_3 [14] and that by Kanoh *et al.* for a series of aluminas treated at various temperatures [15]. For the low-surface-area α-Al_2O_3 support employed in this study ($\sim$1 m^2 g^{-1}), no detectable combustion of ethylene oxide to CO_2 was observed either in the presence or absence of O_2 (table 2), in agreement with the results of Bulushev *et al.* [16]. This indicates that direct combustion of ethylene oxide over the support is not a significant source of CO_2 with these catalysts. However, isomerization of ethylene oxide to acetaldehyde on the support followed by combustion of the acetaldehyde produced on silver particles may be a significant mechanism contributing to the loss in selectivity [13–15,17].

Loading 350 ppm Cs onto the support surface has a dramatic influence on the rate of isomerization. Although the apparent activation energy was similar to that of α-Al_2O_3, 79 ± 4 kJ mol^{-1} (figure 3), the rate decreased by nearly an order of magnitude. This is attributable to poisoning of the strong acid sites on the support surface responsible for ethylene oxide isomerization by Cs [13–15,17]. The rate of isomerization over the conditioned Ag–Cs/α-Al_2O_3 catalyst was found to be slightly, but reproducibly, lower than over the Cs/α-Al_2O_3 sample (table 2). This indicates that Ag, in the

Table 2
Secondary conversion of ethylene oxide in the presence and absence of O_2

Sample	Ethylene oxide feed [a]	Ethylene oxide + O_2 feed [b]	
	Rate isom. (µmol/g cat. s)	Rate isom. (µmol/g cat. s)	Rate comb. (µmol/g cat. s)
α-Al_2O_3	0.0314	0.0314	–
Cs/α-Al_2O_3	0.0038	0.0039	–
Ag–Cs/α-Al_2O_3 (C)	0.0029	0.0046	0.0089
Ag–Cs/α-Al_2O_3 (A)	0.0032	0.0041	0.0097

[a] 0.08% ethylene oxide, 280 °C.
[b] 0.08% ethylene oxide + 2.00% O_2, 280 °C.

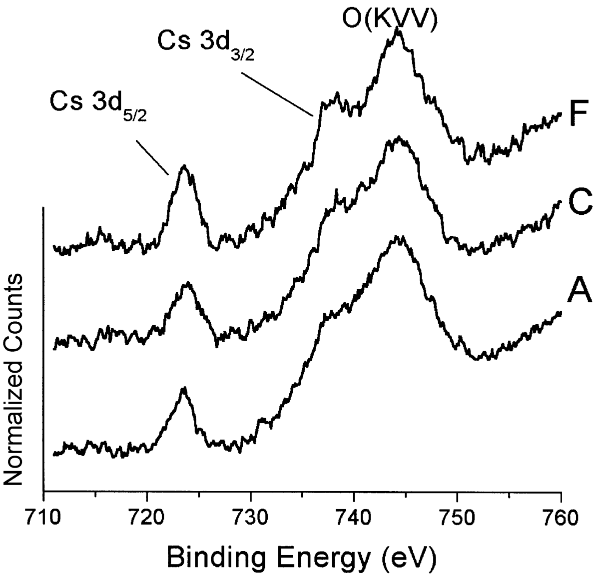

Figure 4. XPS Cs 3d spectra obtained from fresh (F), conditioned (C) and aged (A) samples.

absence of O_2, has a very low activity for ethylene oxide isomerization relative to the support. However, this changes significantly in the presence of oxygen as discussed in more detail below. Over the aged catalyst, again in the absence of O_2, only a very slight increase in isomerization activity was observed relative to that of the conditioned catalysts. This indicates that gradual acidification of the support, via loss of Cs and/or chlorine pick-up, is not a significant process contributing to the loss of selectivity in these catalysts. Indeed XPS analysis of the aged catalyst could not detect any Cl. The corresponding Cs 3d region (Cs $3d_{5/2}$ 723.5 eV) of the XPS spectra are shown in figure 4. Only a very slight decrease in the cesium peak intensity is observed on going from the fresh (F) to the aged (A) catalyst. XPS also showed the presence of sodium, silicon and calcium, which are assigned to an aluminosilicate binder material that is known to be present. No significant redistribution of these components was observed with aging.

As mentioned above, the presence or absence of O_2 had no influence on the rate of isomerization over α-Al_2O_3 or Cs/α-Al_2O_3, and no combustion was observed over the samples that do not contain silver. However, over both the conditioned and aged catalysts, the presence of oxygen had a significant influence on the rate of both combustion *and* isomerization. As shown in table 2, the rate of isomerization over the conditioned catalyst was significantly higher in the presence of 2% O_2 (0.0046 versus 0.0029 μmol g^{-1} s^{-1}) than in its absence. There was also significant CO_2 production. Indeed the rate of CO_2 formation was approximately twice that of acetaldehyde. The fact that oxygen appears to promote isomerization of ethylene oxide on silver may be due to poisoning of the silver surface in its absence, due to the build-up of a stable acetate species on the silver surface [16]. Another possible explanation for this observation comes from studies in which the conversion of ethylene oxide on Ag(111) [3,18] was investigated. It was found that pre-adsorbed oxygen considerably increased the rate of ethylene oxide isomerization relative to that observed over the clean Ag surface. This was attributed to a "soft" acid/base interaction between the oxygen atom of the epoxide molecule and an oxygen-induced $Ag^{\delta+}$ site [3].

Comparing the isomerization and combustion rates over the conditioned and aged samples in the presence of oxygen, it is again apparent that the aging process does not appear to alter significantly the activity of the catalyst toward the secondary conversion of ethylene oxide, despite appreciable sintering of the metal. The only change observed is a tendency for the aged sample to produce more CO_2 (at the expense of acetaldehyde) relative to the conditioned catalyst. Taken together, these results suggest that the aging process does not induce significant changes in the activity of Cs/α-Al_2O_3-based catalysts toward the further conversion of ethylene oxide. Therefore the loss in selectivity observed under industrial conditions is mainly due to the increase in temperature that is required to maintain productivity, through its effect on the silver-catalyzed chemistry.

4. Conclusions

1. SEM and XRD show that aging under industrial conditions results in very significant sintering of the silver component of Ag–Cs/α-Al_2O_3 catalysts. The discrepancy between the average particle size values determined by SEM and XRD techniques is greater after aging, suggesting that the aged metal particles are substantially multiply twinned.
2. The conditioning process that converts the freshly prepared catalyst into a material with optimum activity is not due to changes in the silver morphology. Rather, it is due primarily to Cl pick-up accompanied by oxidative removal of carbonaceous deposits remaining after catalyst synthesis.
3. XPS shows that Cs promoter redistribution and excessive chlorine pick-up are not implicated in the loss of performance that accompanies aging. This is consistent with the aged supports *not* showing an increased activity toward the conversion of ethylene oxide.

Acknowledgments

Financial support from the European Union under the "Competitive and Sustainable Growth" program is gratefully acknowledged (Contract no. G5RD-CT-1999-00154). We also thank Dr. J.W. Couves (BP Chemicals) for many helpful discussions.

References

[1] J.G. Serafin, A.C. Liu and S.R. Seyedmonir, J. Mol. Catal. A 131 (1998) 157.

[2] R.B. Grant and R.M. Lambert, J. Catal. 92 (1985) 364.

[3] R.B. Grant and R.M. Lambert, J. Catal. 93 (1985) 92.

[4] N. Macleod and R.M. Lambert, Appl. Catal. B 35 (2002) 269.

[5] D.M. Minahan and G.B. Hoflund, J. Catal. 158 (1996) 109.

[6] G.B. Hoflund and D.M. Minahan, J. Catal. 162 (1996) 48.

[7] D.M. Minahan, G.B. Hoflund, W.S. Epling and D.W. Schoenfeld, J. Catal. 168 (1997) 393.

[8] M.M. Bhasin, P.C. Ellgen and C.D. Hendrix, US Patent 4,916,243.

[9] W.S. Epling, G.B. Hoflund and D.M. Minahan, J. Catal. 171 (1997) 490.

[10] D.E. Strohmayer, G.L. Geoffroy and M.A. Vannice, Appl. Catal. 7 (1983) 189.

[11] A. Gavriilidis, B. Sinno, and A. Varma, J. Catal. 139 (1993) 41.

[12] L.D. Marks and A. Howie, Nature 282 (1979) 196.

[13] J.K. Lee, X.E. Verykios and R. Pitchai, Appl. Catal. 44 (1998) 223.

[14] C. Mao and M.A. Vannice, Appl. Catal. A 122 (1995) 61.

[15] H. Kanoh, T. Nishimura and A. Ayame, J. Catal. 57 (1979) 372.

[16] D.A. Bulushev, E.A. Paukshtis, Y.N. Nogin and B.S. Bal'zhinimaev, Appl. Catal. A 123 (1995) 301.

[17] Y. Yong, E.M. Kennedy and N.W. Cant, Appl. Catal. 76 (1991) 31.

[18] S.A. Tan, R.B. Grant and R.M. Lambert, J. Catal. 106 (1987) 54.