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# Synergistic effects in the oxidation of methane on strontium and lead hydroxyapatites

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The oxidation of methane has been investigated on lead hydroxyapatite (PbHAp), strontium hydroxyapatite (SrHAp) and their binary mixtures at 873 K. PbHAp showed no activity for the oxidation of methane, while SrHAp produced carbon monoxide selectively at 2–4% conversion. On binary mixtures of the hydroxyapatites the conversion of methane and the selectivity to $C_2$ compounds reached values higher than those of the separate constituents of the mixture. With tetrachloromethane in the feed stream a similar synergistic effect was observed with conversions of methane and selectivities to $CH_3Cl$ higher on the binary mixtures than those on either SrHAp or PbHAp. The strontium-containing hydroxyapatite appears to play a crucial role in the activation of methane, while the presence of the lead-containing analogue is apparently required for the minimization of undesirable processes involving methyl radicals.

**Keywords:** methane, oxidation, strontium hydroxyapatite, lead hydroxyapatite, tetrachloromethane

## 1. Introduction

The addition of small quantities of lead to calcium and/or strontium hydroxyapatites (CaHAp and SrHAp, respectively), either through ion exchange or in the preparative process, results in the enhancement of the selectivities to $C_2$ compounds and/or the conversion in the catalyzed oxidation of methane [1–8]. Although the beneficial effects of lead may be attributed to its role in the activation of methane and the stabilization of methyl radicals on the surface, ensemble effects were tentatively proposed [4]. Similar effects were observed in the oxidation of ethane [8–10]. With CaHAp [2–11] the ion-exchanged lead occupies calcium(II) sites and with both the former and SrHAp [5,7,9,12] the formation of lead hydroxyapatite (PbHAp) was observed.

In the present study, further information on the participation of PbHAp in the oxidative process is obtained from a study of the catalytic properties of the afore-mentioned catalyst in the methane conversion reaction and of solid state mixtures of PbHAp and SrHAp. In view of earlier work, in which the advantageous effects of the introduction of tetrachloromethane (TCM) into the methane oxidation feed stream [13–18] has been demonstrated with the hydroxyapatites, similar studies have been included in the present report.

Synergistic effects have been observed in a variety of catalyzed processes, in particular the selective oxidation of hydrocarbons [19–21]. However, such observations have apparently not been reported for methane oxidation processes. In the present work, evidence is presented for the existence of a synergistic effect in the oxidation of methane on mixtures of lead and strontium hydroxyapatites.

## 2. Experimental

Lead hydroxyapatite (PbHAp) was prepared from $H_3PO_4$ and $Pb(NO_3)_2\cdot 5PbO$, the latter of which was obtained through dehydration of basic lead nitrates according to the procedure described in [22,23], and calcined at 773 K for 3 h. As described in a previous report [23], XRD patterns of all PbHAp prepared in the present study corresponded to those for $Pb_{10}(PO_4)_6(OH)_2$ (JCPDS 8-0259). The atomic ratio of Pb/P in all PbHAp, which was determined in aqueous $HNO_3$ solutions of the hydroxyapatites by inductively coupled plasma (ICP) spectrometry (ICPS-5000, Shimadzu), was between 1.87 and 1.89. Strontium hydroxyapatite (SrHAp) was prepared from $Sr(NO_3)_2$ and $(NH_4)_2HPO_4$ according to the procedure described in [17] and calcined at 773 K for 3 h. The atomic ratio of SrHAp in the present SrHAp was found to be 1.52 by ICP analyses and the XRD patterns were matched with $Sr_{10}(PO_4)_6(OH)_2$ (JCPDS 33-1348). The binary hydroxyapatites, PbHAp/SrHAp, were prepared by kneading the component hydroxyapatites with small quantities of water. The resultant paste was spread over a glass plate, dried overnight at 373 K, crushed, sieved to the particle size of 1.70–0.85 mm and recalcined at 773 K for 3 h in air. Each pure hydroxyapatite, PbHAp and SrHAp, was also treated

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Table 1
Surface areas and apparent densities of fresh catalysts.

| | PbHAp/SrHAp | | | | | | |
|---|---|---|---|---|---|---|---|
| | 10/0 | 9/1 | 2/1 | 1/1 | 1/3 | 1/9 | 0/10 |
| Surface area ($m^2$/g) | 6.4 | 7.8 | 14.4 | 33.5 | 33.7 | 52.6 | 56.8 |
| Apparent density (g/$cm^3$) | 1.54 | 1.27 | 0.87 | 0.77 | 1.01 | 0.78 | 0.36 |

in the same manner. The re-calcined catalysts are referred to as the "fresh catalyst". The surface areas and apparent densities of all fresh catalysts are summarized in table 1. In the present manuscript, Pb/Sr indicates the weight ratio in the binary hydroxyapatites. The catalytic experiments were performed in a fixed-bed continuous-flow quartz reactor operated at atmospheric pressure. Details of the reactor design and catalyst packing procedure have been described elsewhere [14]. Prior to the reaction the catalyst was calcined *in situ* in an oxygen flow (25 ml/min) at 873 K for 1 h. The reaction conditions were as follows: $W = 0.5$ g, $F = 30$ ml/min, $T = 873$ K, $P(CH_4) = 28.7$ kPa, $P(O_2) = 4.1$ kPa and $P(\mathrm{TCM}) = 0$ or 0.17 kPa; balance to atmospheric pressure was provided by helium. The reactants and products were analyzed with an on-stream gas chromatograph (Shimadzu GC-8APT) equipped with a TC detector and integrator (Shimadzu C-R6A). Two columns, Porapak N (6 m × 3 mm) and Molecular Sieve 5A (0.2 m × 3 mm), were employed in the analyses. The methane conversion was calculated from the products and the methane introduced into the feed. The selectivities were calculated from the conversion of methane to each product on a carbon base. The carbon mass balances were $100 \pm 5\%$. Powder X-ray diffraction (XRD) patterns were recorded with a Rigaku RINT 2500X, using monochromatized Cu K$\alpha$ radiation. X-ray photoelectron spectroscopy (XPS, Shimadzu, ESCA-1000AX) used monochromatized Mg K$\alpha$ radiation. The binding energies were corrected using 285 eV for C 1s as an internal standard. Argon-ion etching of the catalyst was carried out at 2 kV for 1 min with a sputtering rate estimated as ca. 2 nm/min for $SiO_2$.

## 3. Results and discussion

### 3.1. Catalytic activities of PbHAp for methane oxidation

It has been reported that the conversion of methane increases with increase in the content of lead on CaHAp and SrHAp ion-exchanged with lead [1,2,5,7,8], and on the former catalysts the selectivity to $C_2$ compounds is also enhanced with the lead content [1,2], while the selectivity to $C_2$ compounds (at 873 K) or CO (at 773 K) is enhanced by the introduction of lead in SrHAp [5,7,8]. Since the XRD peak intensity due to PbHAp in the fresh catalysts increased with the content of lead, PbHAp may itself be an active catalyst for the conversion of methane. However, somewhat surprisingly, pure PbHAp is inactive in the methane conversion process at 873 K (figure 1), at which approximately 5 and 12% conversion of methane were observed under the corresponding conditions on both CaHAp and SrHAp ion-exchanged with lead [1,2,7]. Upon addition of TCM, a small activity was observed, but the product was predominantly $CO_2$ (figure 2).

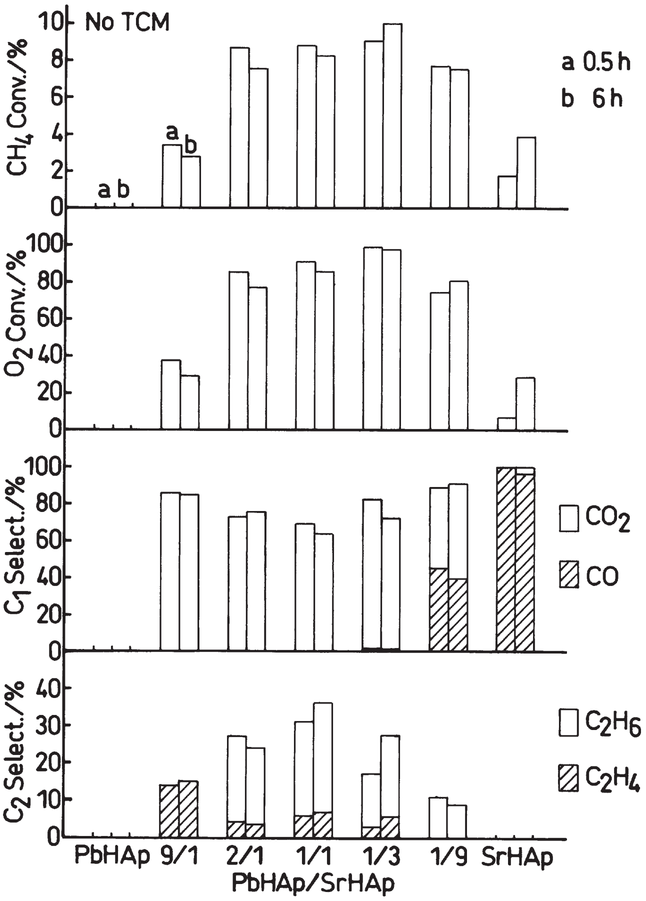

Figure 1. Oxidation of methane on binary hydroxyapatites consisting of PbHAp and SrHAp at 873 K in the absence of TCM. Reaction conditions: $W = 0.5$ g, $F = 30$ ml/min, $P(CH_4) = 28.7$ kPa and $P(O_2) = 4.1$ kPa; balance to atmospheric pressure was provided by helium.

### 3.2. Catalytic activities of PbHAp/SrHAp for methane oxidation

To assess the contribution of PbHAp in hydroxyapatites doped by lead, the oxidation of methane has been examined on binary hydroxyapatites consisting of PbHAp and SrHAp, on the latter of which the partial oxidation of methane to CO proceeded selectively (figure 1), as previously reported [5,7,17,18]. With increasing additions of PbHAp to SrHAp, the conversion of methane and the selectivity to $C_2$ compounds increased, as observed on SrHAp ion-exchanged with lead at the same reaction temperature [7], reaching a maximum on PbHAp/SrHAp = 1/3 and 1/1, respectively. Further increase in the proportion of PbHAp present in the binary system resulted in decreases of the conversion and the $C_2$ selectivity. With increasing PbHAp relative to SrHAp the selectivity to CO also decreased. Relatively small changes in the conversion and selectivities are observed on increase

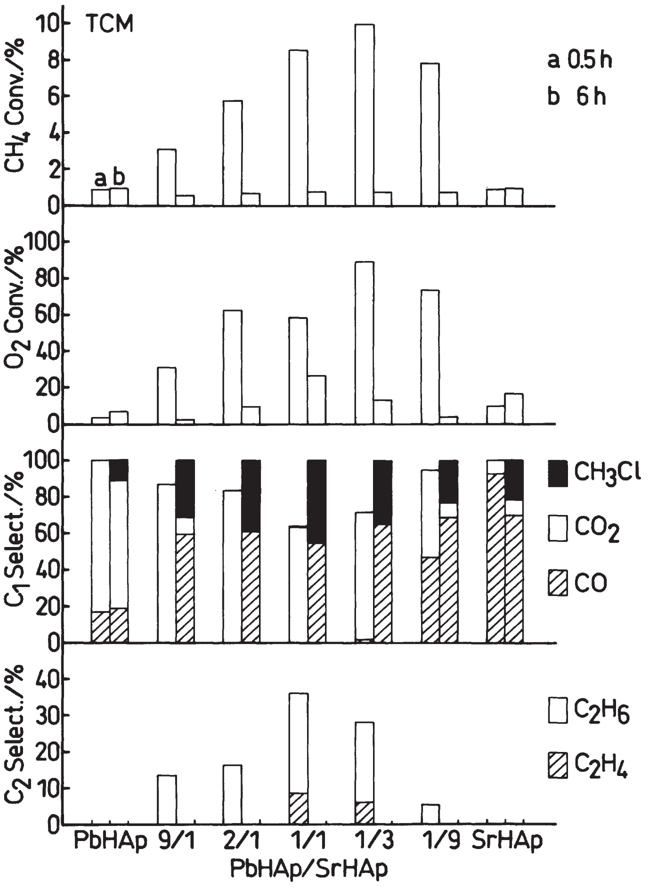

Figure 2. Oxidation of methane on binary hydroxyapatites consisting of PbHAp and SrHAp at 873 K in the presence of TCM. Reaction conditions: as in figure 1, except $P$(TCM) = 0.17 kPa.

of the time-on-stream from 0.5 to 6 h, apparently due to the conversion of SrHAp to $Sr_3(PO_4)_2$ [18]. It should be noted that no *in situ* method is currently available for the reversal of the apatite to phosphate transformation.

Upon addition of TCM to the feed stream the conversion and selectivities to all products at 0.5 h on-stream changed with composition in a manner similar to that observed in the absence of TCM (figure 2). At 0.5 h on-stream the selectivity to $CO_x$ decreases to a minimum at a Pb/Sr ratio of 1/1, while that to $C_2$ increases to a maximum. Concomitantly, the $CO_x$ product composition changes from predominantly CO to $CO_2$.

At 6 h on-stream and TCM present the conversion has decreased markedly to similar relatively small values on all catalysts. The product is almost entirely CO and $CH_3Cl$ with the former decreasing to a minimum at a Pb/Sr of 1/1, while the selectivity to the latter increases to a maximum.

XRD patterns of catalysts previously employed in obtaining the results shown in figure 2 showed that both PbHAp and SrHAp in the binary hydroxyapatites were completely converted to lead chlorapatite (PbClAp, JCPDS 19-0701 for $Pb_{10}(PO_4)_6Cl_2$) and strontium chlorapatite (SrClAp, JCPDS 16-0666 for $Sr_{10}(PO_4)_6Cl_2$), respectively, during the oxidation after 6 h on-stream (figure 3). In the XPS spectra of the previously employed catalysts, peaks attributed to Sr $2p_{3/2}$ (except PbHAp), O 1s, P 2s and Pb $4f_{7/2}$ (except SrHAp) were found at approximately 269.5, 531.5, 190.5 and 139 eV together with Cl 2p at 199 eV either before or after argon-ion etching. In catalysts of PbHAp/SrHAp = 1/1 and 9/1, a small peak due to the metallic state of lead ($Pb^0$) was also found after argon-ion etching, as previously reported in SrHAp ion-exchanged with lead [7]. The values of Cl/P in the near-surface region of the previously employed catalysts are in table 2. With increasing proportion of SrHAp in the binary catalysts, the Cl/P ratio appears to increase either with or without the argon-ion etching consistent with observations that SrClAp is easily deep-chlorinated to the corresponding chloride with TCM at temperatures as low as 773 K [9].

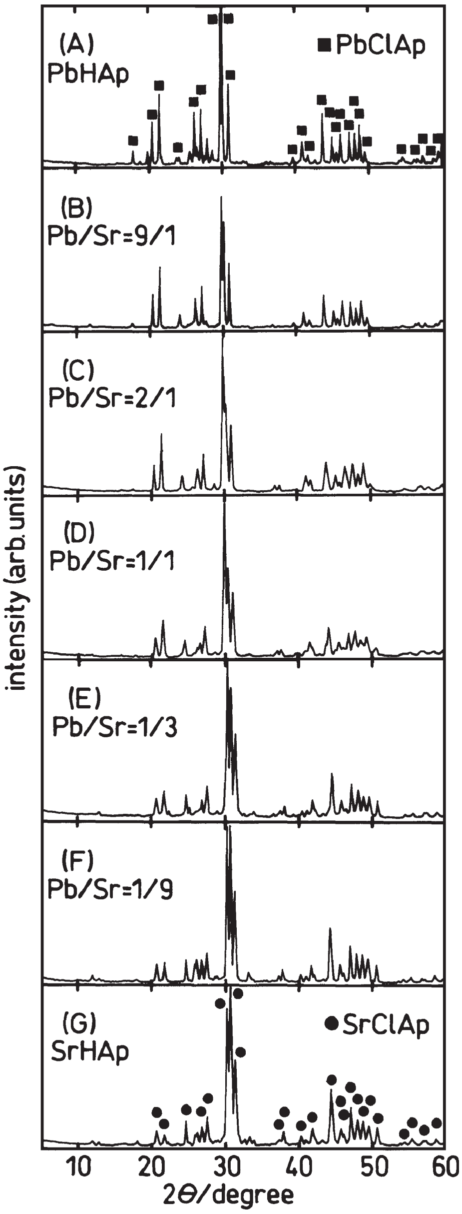

Figure 3. XRD patterns of the binary hydroxyapatites previously employed in obtaining the results shown in figure 2, but after 6 h on-stream. Pb/Sr refers to the weight ratio of PbHAp/SrHAp.

Table 2
Cl/P of used[a] catalysts.

| | PbHAp/SrHAp | | | | | | |
|---|---|---|---|---|---|---|---|
| | 10/0 | 9/1 | 2/1 | 1/1 | 1/3 | 1/9 | 0/10 |
| Cl/P[b] | 0.17<br>(0.19) | 0.27<br>(0.20) | 0.19<br>(0.16) | 0.46<br>(0.37) | 0.55<br>(0.53) | 0.64<br>(0.46) | 0.49<br>(0.42) |

[a] Previously employed in obtaining the results shown in figure 2, but after 6 h on-stream.

[b] Atomic ratio determined by XPS. Values in parentheses: after argon-ion etching for 1 min.

### *3.3. Role of PbHAp in hydroxyapatites doped by lead for methane oxidation*

Although the present work is intended to demonstrate the existence of a synergistic effect in the methane oxidation process on lead and strontium hydroxyapatite mixtures, it may be worthwhile to comment on the selectivities to CO obtained with other catalysts. It is well known that supported noble metal catalysts produce high selectivities to CO from $CH_4$ [24]. However, catalysts containing metallic cobalt in the cubic form are both stable and selective in the production of CO [25], and ternary oxides containing Co, Mg and Al have yielded CO selectivities of 97–99% [26].

The present study demonstrates that PbHAp is not active for the oxidation of methane in contrast to other lead-containing catalysts [27–30]. Since the introduction of SrHAp to PbHAp produces a catalyst which is active in the oxidative process, it must be assumed that the presence of the strontium-containing solid is necessary in the activation of methane to form methyl radicals [30]. As noted in an earlier report [4], this suggests that the presence of PbHAp provides sites for the stabilization of the methyl radicals while holding these radicals in sufficiently close proximity to encourage the combination of the radicals with each other. It should be noted that, unlike other lead-containing catalysts, PbHAp is stable at temperatures higher than 973 K [23].

Two theories for the existence of synergistic effects in catalysis have been proposed: that of coherent interfaces which are extant where the crystal structures of the two phases are closely related and the crystallographic misfit is low, and that usually referred to as a remote control mechanism. It has been argued that, regardless of the model, a low crystallographic misfit should be considered as a necessary, but not sufficient, condition for the observation of synergy [19]. In the present work, the existence of identical crystal structures for the two phases involved would satisfy this requirement.

In the remote control model, which has been invoked to explain the synergistic effects observed in the selective oxidation of isobutene to methacrolein on catalysts prepared by mechanically mixing $MoO_3$ and $BiPO_4$ [20] and in the dehydration–dehydrogenation of 2-butanol to butene and methyl ethyl ketone on a mixture of $SnO_2$ and $MoO_3$ [21], it is considered that one of the phases activates molecular oxygen into a highly active species which spills over onto the surface of the acceptor phase with which it reacts. Thus, it could be conceptualized in the present work that methyl radicals are playing the role of the spillover species, resulting from the activation of methane on SrHAp and spilling over onto the surface of the acceptor phase, PbHAp, on which they are (temporarily) stabilized prior to the formation of the appropriate ensembles which facilitate their pairwise combination to form $C_2$ hydrocarbons [4]. Although this model is obviously speculative, nevertheless the necessary prerequisites are present to justify its proposition at the present time. Further work is in progress.

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## References

[1] Y. Matsumura and J.B. Moffat, Catal. Lett. 17 (1993) 197.
[2] Y. Matsumura, J.B. Moffat, S. Sugiyama, H. Hayashi, N. Shigemoto and K. Saitoh, J. Chem. Soc. Faraday Trans. 90 (1994) 2133.
[3] Y. Matsumura, S. Sugiyama, H. Hayashi and J.B. Moffat, J. Solid State Chem. 114 (1995) 138.
[4] Y. Matsumura, S. Sugiyama, H. Hayashi and J.B. Moffat, Catal. Lett. 30 (1995) 235.
[5] S. Sugiyama, Y. Iguchi, T. Minami, H. Hayashi and J.B. Moffat, Catal. Lett. 46 (1997) 279.
[6] S. Sugiyama, T. Minami, T. Moriga, H. Hayashi and J.B. Moffat, J. Solid State Chem. 135 (1998) 86.
[7] S. Sugiyama, Y. Iguchi, H. Nishioka, T. Minami, T. Moriga, H. Hayashi and J.B. Moffat, J. Catal. 176 (1998) 25.
[8] S. Sugiyama, K. Abe, T. Minami, H. Hayashi and J.B. Moffat, Appl. Catal. A 169 (1998) 77.
[9] S. Sigiyama, Y. Iguchi, H. Nishioka, T. Miyamoto, H. Hayashi and J.B. Moffat, J. Mater. Chem. 7 (1997) 2483.
[10] S. Sugiyama, K. Abe, T. Miyamoto, H. Hayashi and J.B. Moffat, J. Mol. Catal. A 130 (1998) 297.
[11] M. Miyake, K. Watanabe, Y. Nagayama, H. Nagasawa and T. Suzuki, J. Chem. Soc. Faraday Trans. 86 (1990) 2303.
[12] S. Sugiyama, T. Moriga, M. Gada, T. Minami, H. Hayashi and J.B. Moffat, J. Chem. Soc. Faraday Trans. 92 (1996) 4306.
[13] J.B. Moffat, S. Sugiyama and H. Hayashi, Catal. Today 37 (1997) 15.
[14] S. Sugiyama, T. Minami, H. Hayashi, M. Tanaka, N. Shigemoto and J.B. Moffat, J. Chem. Soc. Faraday Trans. 92 (1996) 293.
[15] S. Sugiyama, T. Minami, T. Moriga, H. Hayashi, K. Koto, M. Tanaka and J.B. Moffat, J. Mater. Chem. 6 (1996) 459.
[16] S. Sugiyama, T. Minami, H. Hayashi, M. Tanaka, N. Shigemoto and J.B. Moffat, Energy Fuels 10 (1996) 828.
[17] S. Sugiyama, T. Minami, H. Hayashi, M. Tanaka and J.B. Moffat, J. Solid State Chem. 126 (1996) 242.
[18] S. Sugiyama, T. Minami, T. Higaki, H. Hayashi and J.B. Moffat, Ind. Eng. Chem. Res. 36 (1997) 382.
[19] P. Courtine and E. Bordes, Stud. Surf. Sci. Catal. 110 (1997) 177.
[20] E.M. Gaigneaux, J. Naud, P. Ruiz and B. Delmon, Stud. Surf. Sci. Catal. 110 (1997) 185.
[21] E.M. Gaigneaux, S.R.G. Carrazan, L. Ghenne, A. Moulard, U. Roland, P. Ruiz and B. Delmon, Stud. Surf. Sci. Catal. 110 (1997) 197.
[22] A. Bigi, M. Gandolfi, M. Gazzano, A. Ripamonti, N. Roveri and S.A. Thomas, J. Chem. Soc. Dalton Trans. (1991) 2883.

[23] S. Sugiyama, T. Nakanishi, T. Ishimura, T. Moriga, H. Hayashi, N. Shigemoto and J.B. Moffat, J. Solid State Chem., submitted.

[24] P.M. Torniainen, X. Chu and L.D. Schmidt, J. Catal. 146 (1994) 1.

[25] V.D. Sokolovskii, J.C. Jeannot, N.J. Coville, D. Glasser, D. Hildebrandt and M. Makoa, in: *Natural Gas Conversion III*, eds. M. de Pontes, R.L. Espinoza, C.P. Nicolaides, J.H. Scholtz and M.S. Scurrell (Elsevier, Amsterdam, 1997) p. 416.

[26] V.D. Sokolovskii, N.J. Coville, A. Parmaliana, I. Eskendirov and M. Makoa, Catal. Today 42 (1998) 191.

[27] K. Otsuka, K. Jinno and A. Morikawa, Chem. Lett. (1995) 499.

[28] K. Aika and T. Nishiyama, in: *Proceedings 9th International Congress on Catalysis*, Vol. 2 (Chem. Inst. Canada, Ottawa, 1988) p. 907.

[29] K. Asami, S. Hashimoto, T. Shikada, K. Fujimoto and H. Tominaga, Ind. Eng. Chem. Res. 26 (1987) 1485.

[30] Y. Amenomiya, V.I. Birss, M. Goledzinowski, J. Galuszka and A.R. Sanger, Catal. Rev. Sci. Eng. 32 (1990) 163.