Alkene selectivity enhancement in the oxidation of propane on calcium-based catalysts

Shigeru Sugiyama [a,*], Etshushi Nitta [a], Hiromu Hayashi [a] and John B. Moffat [b]

[a] *Department of Chemical Science and Technology, Faculty of Engineering, The University of Tokushima, Minamijosanjima, Tokushima 770-8506, Japan*
E-mail: sugiyama@chem.tokushima-u.ac.jp

[b] *Department of Chemistry and The Guelph-Waterloo Centre for Graduate Work in Chemistry and Biochemistry, University of Waterloo, Waterloo, ON N2L 3G1, Canada*
E-mail: jbmoffat@uwaterloo.ca

Received 19 November 1998; accepted 16 March 1999

The oxidation of propane has been investigated in the presence and absence of tetrachloromethane (TCM) on calcium hydroxyapatite (CaHAp), $Ca_3(PO_4)_2$, $CaSO_4$ and CaO at 723 K. In the absence of TCM, the conversion of C_3H_8 on CaHAp was 7.7–9.2% during 6 h on-stream while that on $Ca_3(PO_4)_2$, $CaSO_4$ and CaO was 0.6, 0 and 0.2–0.4%, respectively. The principal products on all catalysts in the absence of TCM were CO and CO_2 with small selectivities to C_3H_6 and C_2H_4 (both 5–6%) observed on CaHAp. Upon addition of TCM, the selectivity to C_3H_6 on all catalysts and the conversion of C_3H_8 on $CaSO_4$ increased while, with increasing time-on-stream, the changes in the conversion and selectivity were dependent upon the nature of the catalysts. XPS and XRD analyses provide evidence for the presence of chlorine in the surface and/or bulk of three of the catalysts, suggesting that chlorinated species on the solids play a role in the selectivity enhancement, but the absence of chlorine from the sulphate demonstrates the dissimilarities of the catalysts in their abilities to sorb and decompose TCM.

Keywords: propane, oxidation, calcium-based catalysts, tetrachloromethane

1. Introduction

Catalytic oxidative conversion of light paraffins into olefins has advantages, in comparison with steam cracking, of lower reaction temperatures, reduction of coke deposition at the reactor walls and increase in the olefin productivity [1]. For the oxidative dehydrogenation of propane (ODP), typical oxidation catalysts are vanadium- or molybdenum-based compounds [2,3]. Although the introduction of oxygen reduces the operating temperatures, products additional to the desired alkene are also formed with a resulting lowering of the selectivity to the latter. Consequently, much of the research on the oxidative dehydrogenation of propane has been concerned with the development of catalysts capable of generating high selectivities to the alkene as well as the elucidation of the factors governing the formation of this product [4]. While investigations of the role played by the acidity and basicity of the catalysts in ODP continue, the selectivity appears to be more related to the coordination of the metallic species in these catalysts and the lability of the oxygen atoms [4–6].

In our laboratories, the effect of the introduction of small partial pressures of tetrachloromethane (TCM) on the oxidative dehydrogenation of methane and ethane has been investigated with a wide variety of catalysts [7] including heteropoly oxometalates [8,9], alkali and alkaline earth compounds [10,11] in particular, sulphates [12,13], and hydroxyapatites [14–18]. The conversion and/or the selectivity to the dehydrogenated products has been shown to be enhanced by the introduction of TCM into the feedstream for methane and ethane oxidation processes on the aforementioned catalysts.

A comparison of the effect of the introduction of TCM in the ODP process with that in the oxidative coupling of methane is of interest and the present work investigates the former on calcium-deficient hydroxyapatite (CaHAp: $Ca_{10-x}(HPO_4)_x(PO_4)_{6-x}(OH)_{2-x}$, $0 < x \leqslant 1$), β-$Ca_3(PO_4)_2$, $CaSO_4$ and CaO at 723 K.

2. Experimental

All catalysts except CaHAp, which are similar to those previously employed in the oxidation of methane [12], were pressed, crushed and sieved to the particle size of 0.85–1.70 mm. The preparation procedure of CaHAp was similar to that previously employed [14] but the atomic ratio of Ca/P was 1.59 ($x = 0.55$). The surface areas and apparent densities of the catalysts are listed in table 1. The catalytic experiments were performed in a fixed-bed continuous-flow quartz reactor operated at atmospheric pressure. Details of the reactor design have been described elsewhere [16]. In all experiments, the catalyst (0.5 g) was heated to 723 K while maintaining a continuous flow of helium and was then conditioned at this temperature under a 25 ml/min flow

---

[*] To whom correspondence should be addressed.

Table 1
Surface areas and apparent densities.

Catalyst	Surface area BET N_2 78 K (m^2/g)	Apparent density (g/cm^3)
CaHAp	63	0.54
β-$Ca_3(PO_4)_2$	4	1.01
$CaSO_4$	2	0.95
CaO	28	0.83

of oxygen for 1 h. The reaction conditions were as follows: $T = 723$ K, $F = 30$ ml/min, $P(C_3H_8) = 14.4$ kPa, $P(O_2) = 4.1$ kPa, and $P(\mathrm{TCM}) = 0$ or 0.17 kPa. No evidence for the conversion of propane in the absence of a catalyst was found under the present conditions. The balance to the atmospheric pressure was provided by helium. The reaction was monitored with an on-stream Shimadzu GC-8APT gas chromatograph with a TC detector and integrator (Shimadzu C-R6A). Two columns, Porapak Q (6 m$\times$3 mm) and Molecular Sieve 5A (0.2 m $\times$ 3 mm) were employed in the analyses. The conversion of propane was calculated from the products and propane introduced into the feed. The selectivities were calculated from the conversion of propane to each product on a carbon base. Blank experiments conducted with propane absent from the feed (O_2 + TCM + He) indicated that TCM undergoes oxidation to carbon oxides. Although the quantities of carbon oxides relative to those of propane were small, all of the data reported were corrected by performing duplicate experiments with propane absent under otherwise identical values of the process variables. The carbon mass balances were $100 \pm 5\%$. Powder X-ray diffraction (XRD) patterns were recorded with a Rigaku TINT 2500X, using monochromatized Cu Kα radiation. X-ray photoelectron spectroscopy (XPS, Shimadzu ESCA-1000AX) used Mg Kα 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

The conversion of propane and selectivities on the four calcium-containing solids in the presence and absence of TCM are summarized in figure 1. In the absence of TCM (figure 1(A)), propane was oxidized on CaHAp with a conversion of 8–9% with a small selectivity to propylene while the remaining three catalysts showed small activities and CO_x was obtained on the phosphate and oxide. It should be noted that in the oxidation of methane on these catalysts at 973 K the conversion of methane on CaHAp was similar to that on CaO but substantially higher than that observed on β-$Ca_3(PO_4)_2$ and $CaSO_4$, but in CaHAp the atomic ratio of Ca/P was 1.67 ($x = 0$) [14].

In the presence of TCM, the selectivity to propylene was dramatically improved (with the exception of that on CaHAp at 0.5 h on-stream) while the effects of the introduction of TCM on the conversion varied with the catalysts (figure 1(B)). On CaHAp, the conversion of propane decreased with increasing time-on-stream as observed in the oxidation of methane and ethane [14–18]. Furthermore, the selectivity to propylene and CO_2 increased and decreased, respectively, with time-on-stream, suggesting that the composition of the surface is strongly time-on-stream dependent. On β-$Ca_3(PO_4)_2$ and CaO, the conversion remained relatively unchanged on introduction of TCM while the selectivity to propylene increased and that to CO decreased. With all four catalysts, in the presence of TCM the product composition varied significantly with time-on-stream with CO_2 being reduced in favour of CO, suggesting that the surface chlorine tends to inhibit further oxidation of the monoxide.

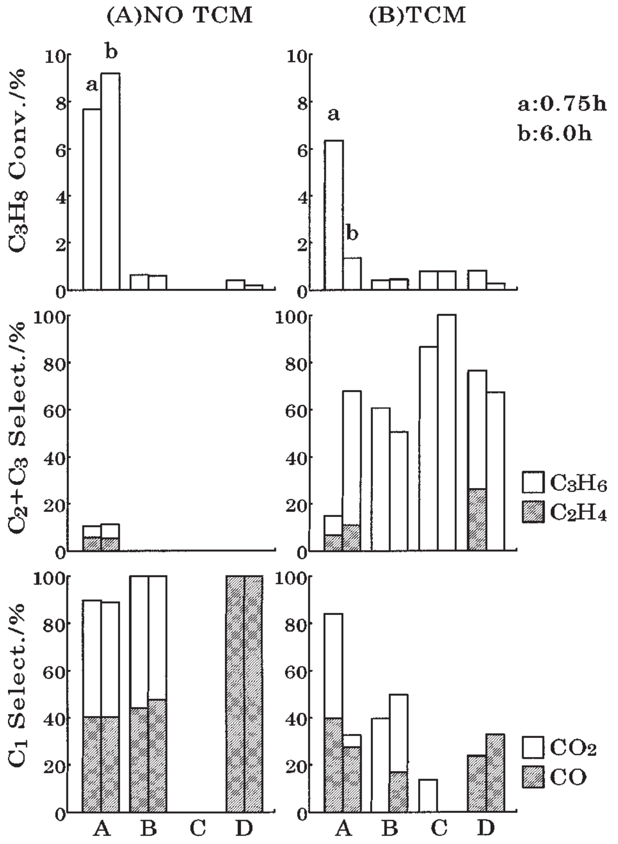

Figure 1. Propane oxidation on CaHAp (A), β-$Ca_3(PO_4)_2$ (B), $CaSO_4$ (C) and CaO (D) at 723 K in the absence and presence of TCM.

XRD and XPS analyses of the used catalysts have been carried out to investigate the nature of the interaction of TCM with the bulk phase and the catalyst surface, respectively. As observed in the oxidation of methane and ethane on hydroxyapatites [14–18], CaHAp was completely converted to calcium chlorapatite (CaClAp) ($Ca_{10}(PO_4)_6Cl_2$, JCPDS 33-0271) during the oxidation of propane in the presence of TCM (figure 2(A)). XRD patterns of β-$Ca_3(PO_4)_2$ and $CaSO_4$ previously used in the presence of TCM were matched with JCPDS 9-0169 and 37-1496, respectively, and chlorinated species were not detected (figure 2 (B) and (C), respectively), although a small amount of calcium chlorapatite was detected in the XRD of β-$Ca_3(PO_4)_2$ previously employed in the oxidation of methane with TCM at 973 K [14]. Although XRD of CaO used in the oxidation of methane in the presence of TCM showed no chlorinated species were formed during the oxidation [12], $Ca(ClO)_2{\cdot}4H_2O$ (JCPDS 1-1165) and unidentified species together with CaO were detected in XRD patterns of CaO used in the oxidation of propane with TCM (figure 2(D)).

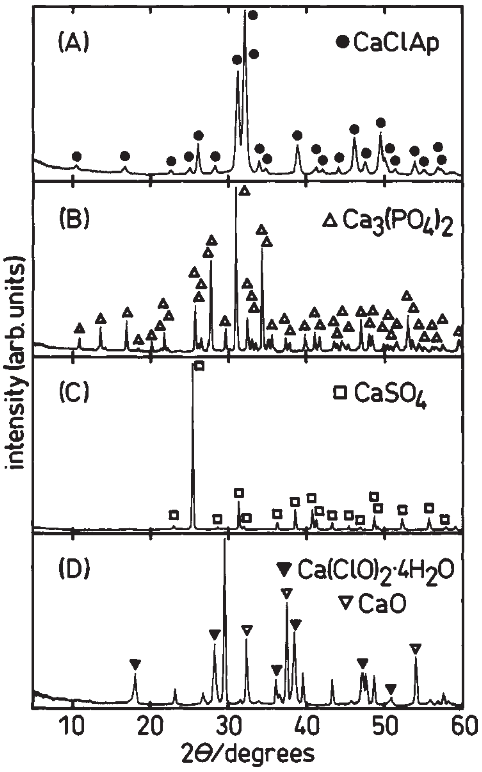

Figure 2. XRD patterns of catalysts previously employed in obtaining the results shown in figure 1 but in the presence of TCM after 6 h on-stream. (A) CaHAp, (B) β-$Ca_3(PO_4)_2$, (C) $CaSO_4$, and (D) CaO.

As described in table 2, the binding energies of each component element of all catalysts in the near-surface region were virtually identical before and after use in the oxidation of propane in the presence of TCM. It should be noted that a second peak with a lower intensity appeared at a lower binding energy after argon ion etching for the oxygen in CaO. Chlorinated species were detected on CaHAp, $Ca_3(PO_4)_2$ and CaO used in the presence of TCM and the atomic ratios of Cl/Ca in the near-surface region of these three catalysts were similar to those found on the same catalysts after use in the oxidation of methane in the presence of TCM [14]. No chlorinated species were detected on $CaSO_4$ used in the oxidation of propane with TCM (table 2), in contrast to the observations after use in the oxidation of methane with TCM [14], possibly due to the resistance of the sulfate to form an associated chlorinated compound and/or the relatively weak binding of any chlorine in the surface region of this solid. It is of interest to note that the P/Ca ratios in the near-surface region of CaHAp and $Ca_3(PO_4)_2$ used in the oxidation where TCM was present were similar to those of the corresponding fresh catalysts, while the O/Ca ratios of all used catalysts were similar to those of the fresh solids, with the exception of CaHAp. Formation of the fully chlorinated analogue of CaHAp would be expected to reduce the value of O/Ca by approximately 90% while that of P/Ca remains unchanged. Although the experimentally measured values of these quantities for the surface region are in semiquantitative agreement with the aforementioned expectations, indicating that the chlorinated analogue exists on the surface as well as in the bulk, nevertheless the measured Cl/Ca values are higher than expected by a factor of approximately two, indicating that nonstruc-

Table 2
Binding energies of each element in fresh and used[a] catalysts.

Catalyst	F or U[b]	Etching time (min)	Binding energy (eV)					
			Ca $2p_{3/2}$	Ca $2p_{1/2}$	O 1s	P 2p	S 2p	Cl 2p
CaHAp	F	0	347.1	350.7	531.1	133.0	–	–
		1	347.3	350.9	531.3	133.3	–	–
	U	0	347.6	351.0	531.5	133.4	–	198.8
		1	347.8	351.4	531.6	133.7	–	199.2
$Ca_3(PO_4)_2$	F	0	347.3	350.8	531.1	133.0	–	–
		1	347.7	350.2	531.7	133.5	–	–
	U	0	347.7	351.4	531.5	133.4	–	198.9
		1	347.1	351.6	532.0	133.8	–	199.4
$CaSO_4$	F	0	347.8	351.6	532.3	–	169.3	–
		1	347.8	351.6	532.5	–	169.5	–
	U	0	347.8	351.4	532.3	–	169.1	–
		1	347.5	351.0	531.8	–	168.7	–
CaO	F	0	346.9	350.4	531.3	–	–	–
		1	346.7	350.3	531.3	–	–	–
	U	0	347.2	350.9	531.7	–	–	198.7
		1	347.3	351.0	531.7	–	–	199.1

[a] Used in the presence of TCM.
[b] F, fresh; U, used in the presence of TCM.

Table 3
Atomic ratio estimated by XPS in the fresh and used[a] catalysts.

Catalyst	F or U[b]	Etching time (min)	O/Ca	P/Ca	S/Ca	Cl/Ca
CaHAp	F	0	2.26	0.77	–	–
		1	2.03	0.70	–	–
	U	0	2.01	0.70	–	0.39
		1	1.86	0.67	–	0.40
$Ca_3(PO_4)_2$	F	0	2.52	0.79	–	–
		1	2.32	0.74	–	–
	U	0	2.55	0.85	–	0.22
		1	2.25	0.72	–	0.11
$CaSO_4$	F	0	3.55	–	1.12	–
		1	2.76	–	0.84	–
	U	0	3.62	–	1.23	–
		1	2.85	–	0.87	–
CaO	F	0	2.26	–	–	–
		1	1.84	–	–	–
	U	0	2.12	–	–	0.38
		1	1.70	–	–	0.37

[a] Used in the presence of TCM.

[b] F, fresh; U, used in the presence of TCM.

tural chlorine is also present in the surface region. In contrast, with $Ca_3(PO_4)_2$ the experimentally measured values of O/Ca and P/Ca remain relatively unchanged after use in the oxidation process in which TCM is present. It is to be noted, however, that these values are similar to those expected for the fully chlorinated analogue of CaHAp and, in addition, the Cl/Ca ratio for used $Ca_3(PO_4)_2$ is similar to that expected for CaClAp. Although these results do not preclude the possibility of nonstructural chlorine in the surface region of chlorinated $Ca_3(PO_4)_2$, the formation of the chlorinated analogue of CaHAp appears possible. It should be noted, however, that the XRD pattern of used $Ca_3(PO_4)_2$ shows no evidence of such a compound in the bulk structure.

The conversions and selectivities in the oxidation of propane as obtained with the four catalysts and the effect of the addition of TCM are significantly dissimilar. In the absence of TCM CaHAp and $CaSO_4$ were the most and least active, respectively. With CaHAp and $Ca_3(PO_4)_2$ oxygenated species dominate in the product with selectivities to CO and CO_2 being approximately equal while with CaO only CO forms. While care must be exercised in comparing selectivities at dissimilar conversions the aforementioned results suggest that, at least under the conditions of the present work, C–H bond scission occurs more readily on CaHAp than on the remaining catalysts while the oxygen atoms in CaHAp and $Ca_3(PO_4)_2$ may be more labile than those in $CaSO_4$ and CaO, although it should be noted that oxygenated hydrocarbons are not formed with any of the present catalysts.

Earlier work on stoichiometric CaHAp ($Ca/P = 1.67$) has shown that methanol decomposes at 600 °C, in the absence of oxygen, to produce predominantly carbon monoxide [19]. As the Ca/P ratio decreases, the selectivities to formaldehyde and dimethyl ether increase to approximately 80% at a value of Ca/P equal to 1.51. Both IR and TPD experiments indicated that the concentration of acidic sites is increasing and basic sites decreasing as the Ca/P ratio decreases. Studies of the adsorption of O_2 [20], the oxidation of CO [20] and the application of EPR [21] found that O_2 is irreversibly adsorbed on stoichiometric CaHAp but reversibly on the nonstoichiometric analogue producing O_2^- species on the former but not on the latter. With $Ca_3(PO_4)_2$ the decomposition of methanol, as with CaHAp, produced predominantly H_2CO and $(CH_3)_2O$, although the selectivity to CO was as high as 25%. In contrast, CaO generated greater than 95% selectivity to CO under similar conditions.

The present results, where TCM is not present, appear to be consistent with the aforementioned data from methanol decomposition, in suggesting that the oxidative dehydrogenation of propane may, at least in part, be dependent on the relative numbers of acidic and basic sites.

On introduction of TCM the selectivity to $C_{2\text{–}3}$ hydrocarbons is significantly enhanced with all catalysts. However, with CaHAp the increase in selectivity is strongly time-on-stream dependent as is evident from figure 3. The most substantial changes in the conversion and selectivities to the various products occur within the first 2.5 h. Subsequent to this time these measurables achieve virtually constant values. XRD patterns (figure 4) show that significant quantities of the hydroxyapatite remain after 0.75 h on-stream, but after 2.5 h essentially complete conversion to the chlorinated analogue has occurred. XPS analyses demonstrate that the composition of the surface region changes in a manner similar to that in the bulk as the time-on-stream increases (table 4).

Similar comments can be made on the results with CaO although with this catalyst no CO_2 is observed either with or without TCM. Again, as with CaHAp, surface chlorine is found, but only partial transformation of the bulk to the hypochlorite is evident from the XRD pattern.

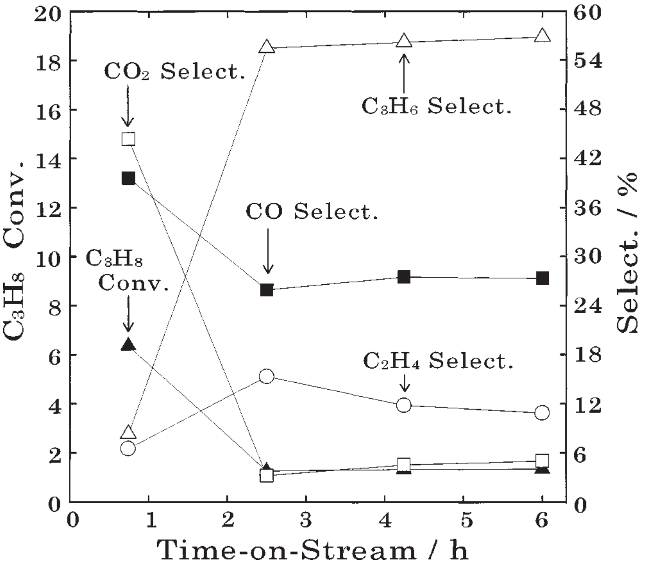

Figure 3. Propane oxidation on CaHAp at 723 K in the presence of TCM at various times-on-stream.

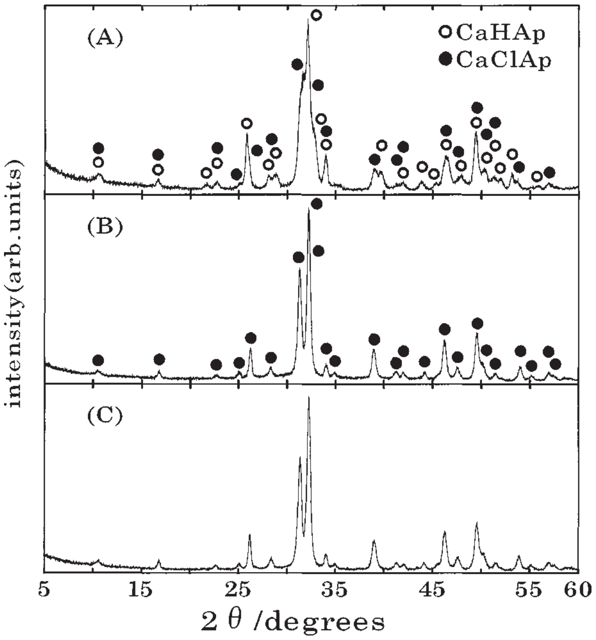

Figure 4. XRD patterns of CaHAp previously employed in obtaining the results shown in figure 3 but after 0.75 (A), 2.5 (B) and 4.25 h (C) on-stream.

With $Ca_3(PO_4)_2$ and $CaSO_4$ $C_{2–3}$ hydrocarbons are formed with TCM present but not in its absence and, with the latter catalyst, the $C_{2–3}$ selectivities approach 100% at 6 h on-stream although the conversion is low. However, neither of these two catalysts show XRD evidence for the formation of a chlorinated analogue although $Ca_3(PO_4)_2$ has significant quantities of chlorine in the surface region.

While it is clear that the introduction of TCM into the ODP feedstream suppresses the deep oxidation reaction and leads to increases in the selectivities to alkenes with all four catalysts studied in the present work, the dissimilarity of the XPS and XRD results between the various catalysts is indicative of disparities among the catalysts with respect to their abilities to sorb and retain chlorine, in whatever form, and to permit its diffusion into the bulk under the conditions of the present experiments. Although the absence of any evidence of chlorine in either the surface or bulk of $CaSO_4$ may suggest that the enhancement of the selectivity to $C_{2–3}$ hydrocarbons produced by TCM is a purely gas-phase phenomenon a more probable explanation, particularly in view of the earlier results with methane, takes account of the relative abilities of the four catalysts to sorb and decompose TCM together with their retentive and diffusive properties for chlorine and/or chloride. Last, but not least, the existence of structural and nonstructural chlorine and their relative importance in the activation process requires further investigation.

Table 4
Atomic ratio estimated by XPS in CaHAp used in the oxidation of methane in the presence of TCM at various times-on-stream.

Time-on-stream (h)	Etching time (min)	O/Ca	P/Ca	Cl/Ca
0.75	0	2.42	0.61	0.08
	1	2.15	0.55	0.05
2.50	0	2.24	0.72	0.30
	1	2.17	0.61	0.24
4.25	0	1.83	0.71	0.27
	1	1.78	0.64	0.23

Acknowledgement

This work was partially funded by the Natural Sciences and Engineering Research Council of Canada to JBM, to which our thanks are due.

References

[1] M.V. Landau, M.L. Kaliya, A. Gutman, L.O. Kogen, M. Herskowitz and P.F. van den Oosterkamp, Stud. Surf. Sci. Catal. 110 (1997) 315.
[2] V. Soenen, J.M. Herrmann and V.C. Volta, J. Catal. 159 (1996) 410.
[3] D.L. Stern and R.K. Grasselli, J. Catal. 167 (1997) 560.
[4] H.H. Kung, Adv. Catal. 40 (1994) 1.
[5] O.V. Buyevskaya, D. Müller, I. Pitsch and M. Baerns, Stud. Surf. Sci. Catal. 119 (1998) 671.
[6] F. Arena, F. Frusteri, A. Parmaliana, G. Martra and S. Coluccia, Stud. Surf. Sci. Catal. 119 (1998) 665.
[7] J.B. Moffat, S. Sugiyama and H. Hayashi, Catal. Today 37 (1997) 15.
[8] S. Ahmed and J.B. Moffat, Catal. Lett. 1 (1988) 141.
[9] S.S. Hong and J.B. Moffat, Catal. Lett. 40 (1996) 1.
[10] S. Sugiyama, K. Satomi, N. Shigemoto, H. Hayashi and J.B. Moffat, Catal. Lett. 25 (1994) 201.
[11] S. Sugiyama, K. Satomi, H. Hayashi and J.B. Moffat, J. Mol. Catal. 105 (1996) 39.
[12] S. Sugiyama, K. Satomi, H. Hayashi, N. Shigemoto, K. Miyaura and J.B. Moffat, Appl. Catal. A 103 (1993) 55.
[13] S. Sugiyama, K. Satomi, H. Hayashi, M. Tanaka and J.B. Moffat, J. Chem. Eng. Jpn. 28 (1995) 204.
[14] S. Sugiyama, T. Minami, H. Hayashi, M. Tanaka, N. Shigemoto and J.B. Moffat, Energy Fuels 10 (1996) 828.

[15] S. Sugiyama, T. Minami, T. Higaki, H. Hayashi and J.B. Moffat, Ind. Eng. Chem. Res. 36 (1997) 328.
[16] S. Sugiyama, Y. Iguchi, H. Nishioka, T. Minami, T. Moriga, H. Hayashi and J.B. Moffat, J. Catal. 176 (1998) 25.
[17] S. Sugiyama, Y. Iguchi, H. Nishioka, T. Miyamoto, H. Hayashi and J.B. Moffat, J. Mater. Chem. 7 (1997) 2483.
[18] S. Sugiyama, T. Miyamoto, H. Hayashi and J.B. Moffat, J. Mol. Catal. A 135 (1998) 199.
[19] Y. Matsumura and J.B. Moffat, J. Chem. Soc. Faraday Trans. 92 (1996) 1981.
[20] Y. Matsumura, H. Kanai and J.B. Moffat, J. Chem. Soc. Faraday Trans. 93 (1997) 4383.
[21] Y. Matsumura, H. Kanai and J.B. Moffat, J. Mol. Catal. A 115 (1997) L229.