Inorganica Chimica Acta, 132 (1987) 123–128

Role of Lattice Oxygen Atoms in Partial Oxidations of Methane, Ethane and Ethylene over Samarium Oxides

KIYOSHI OTSUKA

Department of Chemical Engineering, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan

and ABDEL-AZIZ AHMED SAID

Chemistry Department Faculty of Science, Assiut University, Assiut, Egypt

(Received January 30, 1987)

Abstract

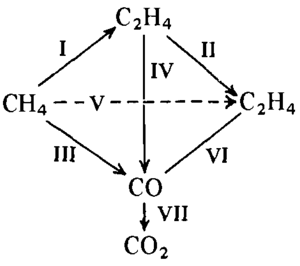
The contribution of lattice oxygen atoms of Sm_2O_3 catalysts in the oxidative coupling of methane has been examined by comparing the distributions of products and reactivities of the catalysts observed in the presence and absence of oxygen in the gas phase. The products of the reaction of CH_4 with lattice oxygen atoms (without oxygen in the gas phase) at 873–998 K were H_2, CO, C_2H_4 and H_2O without a trace of C_2H_6. The main products H_2 and CO were speculated to be produced from HCHO as the reaction intermediate. The amount of C_2H_4 did not depend on the reaction temperatures. Direct formation of C_2H_4 from CH_4 suggested the formation of $CH_2=$ groups on special active sites on the surface. In contrast, the reation of CH_4 with the adsorbed oxygens (in the presence of gaseous oxygen) gave C_2H_6, C_2H_4, CO_2, CO and H_2O. The selectivity to C_2-compounds ($C_2H_6 + C_2H_4$) was remarkably high compared to that observed for the lattice oxygen atoms. Thus the adsorbed oxygens are better oxidants for oxidative coupling of CH_4. The main products observed in the reactions of C_2H_6 and C_2H_4 with lattice oxygen atoms were CO, H_2 and CH_4. CO_2 was not produced at temperatures below 973 K. In contrast, the reactions with adsorbed oxygens in the presence of gaseous oxygen produced only CO_2, CO and H_2O without any H_2 or CH_4.

The reactivity of the adsorbed oxygen for converting CH_4 was more than three orders of magnitude greater than that of the lattice oxygen atoms. Thus, oxidative coupling of CH_4 in the presence of gaseous oxygen can be ascribed to the role of adsorbed oxygens.

Introduction

Rare earth metal oxides are active and selective catalysts for converting methane to C_2-hydrocarbons ($C_2H_6 + C_2H_4$) in oxidative dehydrogenation and coupling of methane [1, 2]. Among the oxides tested, Sm_2O_3 was the most active and selective catalyst for the reaction [1, 2]. Kinetic studies on the reaction over Sm_2O_3 suggested that the oxygen species responsible for activating methane is an adsorbed dioxygen such as O_2^{2-}, O_2^-, or O_2 on the surface [3].

There are many reports describing the reactivity and behavior of lattice oxygen atoms in metal oxides for the catalytic oxidation of olefins and the other oxidation reactions [4]. The main interest in the present work is to examine whether the lattice oxygen atoms of Sm_2O_3 have better catalytic properties, activity and selectivity than the oxygen adsorbed on the surface of Sm_2O_3 for the oxidative coupling of CH_4. The over-all reaction paths for the oxidation of CH_4 can generally be written as follows:



Reactivity and selectivity of the lattice oxygen atoms of Sm_2O_3 for each path (I–VII) will also be examined by using CH_4, C_2H_6, C_2H_4 and CO as the starting reactants.

Experimental

The samarium oxide (Sm_2O_3) used was a reagent grade powder (purity >99.9%) obtained from Asahi Chemical Industry. The BET surface area of the sample calculated from the adsorption of N_2 was 8.4 $m^2\ g^{-1}$. The kinetic curve for each oxidation reaction was measured using a conventional gas-circulation apparatus of *ca.* 340 cm^3 volume, capable of achieving a vacuum to 1.3×10^{-4} Pa. The samarium

0020-1693/87/$3.50

oxide samples were pretreated in an atmosphere of oxygen (13 kPa) at 873 K and degassed for 2 h under a vacuum of 1.3×10^{-3} Pa at the same temperature.

Kinetic measurements for the reactions of lattice oxygen atoms of Sm_2O_3 with CH_4, C_2H_6, C_2H_4 and CO were carried out using 5.00 g of the catalyst placed at the bottom of a quartz reactor (25 mm i.d. and 30 mm height). Oxidations of CH_4, C_2H_6, C_2H_4 and CO in the presence of O_2 in the gas phase were carried out using 10 mg Sm_2O_3. The reactions were initiated by circulating the reactants over the catalysts. Small amounts of gaseous products were removed to analyse the composition of the products by gas-chromatography at appropriate time intervals. The column packings were a series of MS13X (1 m) and active carbon (2 m) for the separation of CH_4, CO, O_2 and H_2; and Gaskuropack 54 (2 m) for the separation of CO_2, C_2H_6, C_2H_4 and H_2O. Typically a 95% carbon mass balance was achieved by quantitative analysis of the products.

Results

Oxidation of CH_4

(a) Reaction with lattice oxygen atoms

The measurement of oxygen adsorption on Sm_2O_3 at temperatures above 823 K showed that the adsorption of oxygen was reversible with increasing and decreasing the pressure of oxygen. The adsorption isotherm could be expressed by a Henry's equation. These observations indicate that there is no measurable oxygen adsorbed on Sm_2O_3 after pretreatment of the sample under a vacuum at 873 K. Thus, we consider that the oxidation of CH_4 by contacting CH_4 with Sm_2O_3 is caused by the lattice oxygen atoms of the oxides.

The reaction between CH_4 and the lattice oxygen atoms of Sm_2O_3 has been carried out at 873, 923, 973 and 998 K at an initial pressure of CH_4 12.0 kPa. The kinetic curves observed at 873, 923 and 973 K, for example, are shown in Figs. 1, 2 and 3, respectively. The products observed at 873 and 923 K were H_2, CO, C_2H_4 and H_2O. CO_2 was produced at >973 K, but the rate was very slow compared to the formation of CO. The results in Figs. 1–3 show that the main products are H_2 and CO at any temperature. The H_2 : CO ratio observed at 873 K was about 2 (except the initial points), but the ratio decreased as the temperature was raised. The formation of H_2O was not observed at 873 K, but it was clearly observed above 923 K. The quantity of H_2O formed, however, could not be measured accurately because of a large experimental error in the quantitative analysis of H_2O. It is to be noted that C_2H_4 is the only coupling product of CH_4 without a trace of C_2H_6. The formation of C_2H_4 was complete within 60 min at all temperatures. The final amounts of C_2H_4 formed did not change with temperature (0.38 ± 0.04 μmole/g-cat).

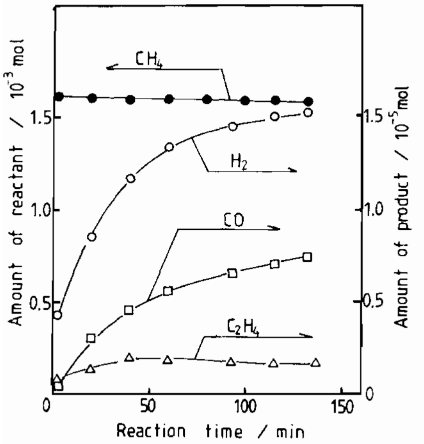


Fig. 1. Oxidation of methane by lattice oxygen atoms of Sm_2O_3 at 873 K.

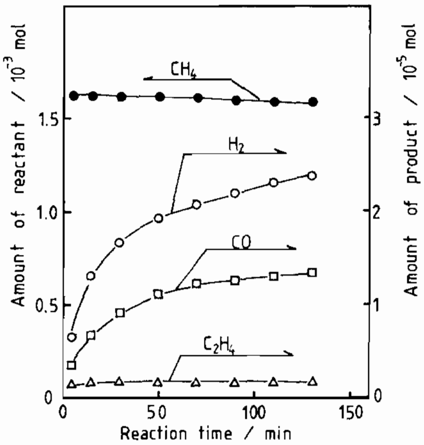


Fig. 2. Oxidation of methane by lattice oxygen atoms of Sm_2O_3 at 923 K.

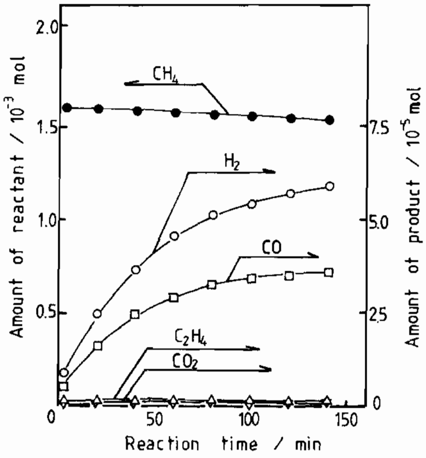


Fig. 3. Oxidation of methane by lattice oxygen atoms of Sm_2O_3 at 973 K.

(b) Reaction with adsorbed oxygens

When the weight of catalyst used was decreased to 10 mg, the products of the reaction between CH_4 (12.0 kPa) and the lattice oxygen atoms were too small to be measured at <1023 K. However, fast oxidation of CH_4 took place after adding oxygen (1.8 kPa) to the gas phase. The reaction for the CH_4 and O_2 mixture did not take place at all in the absence of the catalyst at <1023 K. Thus we can consider that the reaction observed for the mixture of CH_4 and O_2 in the presence of Sm_2O_3 is caused by the adsorbed oxygen on the catalyst.

The reaction between CH_4 and the adsorbed oxygen on Sm_2O_3 has been examined at 873, 923 and 973 K. The reaction was carried out at 12.0 (1.63×10^{-3} mol) and 1.8 kPa (0.24×10^{-3} mol) for CH_4 and O_2, respectively, using 10 mg of Sm_2O_3. Since the kinetic features of the reaction carried out using a gas-flow system have already been described elsewhere [2, 3], only the results at 923 K are shown in Fig. 4 for comparison with Fig. 2. The kinetic curves in Fig. 4 indicate that C_2H_6 is the initial coupling compound, in contrast to the results for the reaction of CH_4 with lattice oxygen atoms. Only a trace of hydrogen was observed, suggesting that the most of the hydrogen produced was oxidized quickly to H_2O by adsorbed oxygen. CO_2 was the main carbon oxide formed in the reaction with adsorbed oxygen (Fig. 4). In contrast to this observation, the lattice oxygen atoms oxidized CH_4 only to CO and further oxidation to CO_2 was very slow (Figs. 1–3).

The rates of conversion of CH_4 were also quite different between the reaction of CH_4 with the adsorbed oxygen and the reaction with lattice oxygen atoms. The initial rate per gram of the catalyst for the former reaction is more than three orders of magnitude greater than the rate for the latter (see Figs. 2 and 4). Thus, there are large differences between the reactivities of the adsorbed oxygens and the lattice oxygen atoms for the reaction with CH_4.

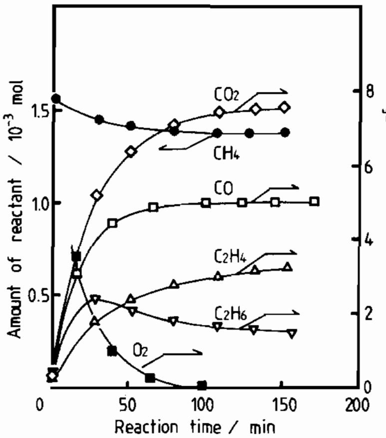


Fig. 4. Oxidation of methane by adsorbed oxygens on Sm_2O_3 at 923 K.

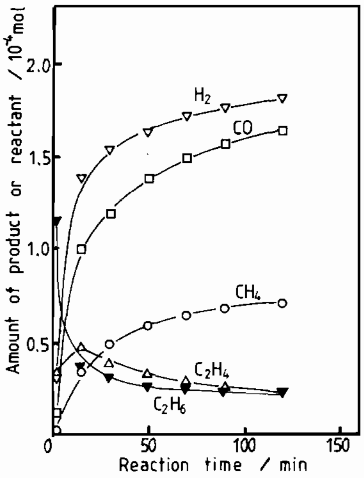


Fig. 5. Oxidation of ethane by lattice oxygen atoms of Sm_2O_3 at 873 K.

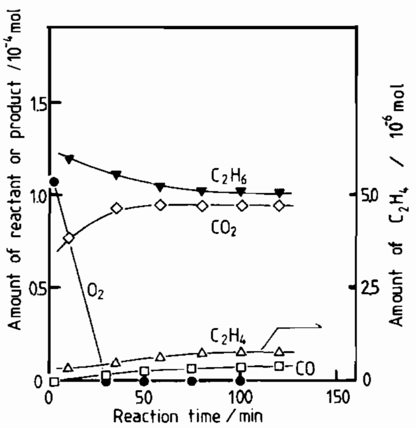


Fig. 6. Oxidation of ethane by adsorbed oxygens on Sm_2O_3 at 873 K.

Oxidation of C_2H_6

(a) Reaction with lattice oxygen atoms

The reaction of the lattice oxygen atoms with C_2H_6 has been examined at 823, 873 and 973 K at the initial pressure of C_2H_6 of 1.2 kPa. The products were H_2, CO, C_2H_4, CH_4 and H_2O. H_2O was only a trace at <873 K. The kinetic curves observed at 873 K, for example, are shown in Fig. 5. CO_2 was not observed at the experimental temperatures. This observation shows that further oxidation of CO is difficult for the lattice oxygen atoms, which is coincident with the observations in Figs. 1–3.

(b) Reaction with adsorbed oxygens

Oxidation of C_2H_6 in the presence of oxygen in the gas phase was observed at 873 and 973 K. The features of the kinetic curves are indicated in Fig. 6 for the reaction at 873 K. Very rapid oxidation of C_2H_6 to CO_2 was observed at the initial stage of the reaction. Oxygen in the gas phase was consumed within 30 min. The product distributions shown in Figs. 5 and 6 are quite different. CO_2 is the main product in Fig. 6 and the formation of CH_4 was not observed at all, in contrast to the results in Fig. 5. It is to be noted that only a trace of C_2H_4 was formed in Fig. 6. This observation suggests that the CO_2 is not produced from C_2H_4 but directly from C_2H_6. The kinetic curves in Fig. 6 show that the conversion of C_2H_6 and the formation of CO still continue after complete consumption of oxygen in the gas phase. These observations may be explained in terms of the reaction of C_2H_6 with H_2O. However, because of the difficulty in the quantitative analysis of H_2O, this reaction will not be discussed further.

Rough estimation for the initial rates of conversion of C_2H_6 per gram catalyst in the presence and absence of oxygen in the gas phase indicated that the reactivity of adsorbed oxygens is at least two orders of magnitude greater than that of lattice oxygen atoms on the surface.

Oxidation of C_2H_4

(a) Reaction with lattice oxygen atoms

Gas–solid reaction between C_2H_4 and Sm_2O_3 gave CO, H_2, CH_4, C_2H_6 and H_2O at the temperatures 773, 823, 873 and 973 K. H_2O was only a trace at <873 K. Kinetic curves for the reaction at 873 K at 1.2 kPa of the initial pressure of C_2H_4 are given in Fig. 7 as examples. The quantities of the carbon compounds produced were in the order of $CO > CH_4 > C_2H_6$ irrespective of the experimental temperatures. CO_2 was not observed here either.

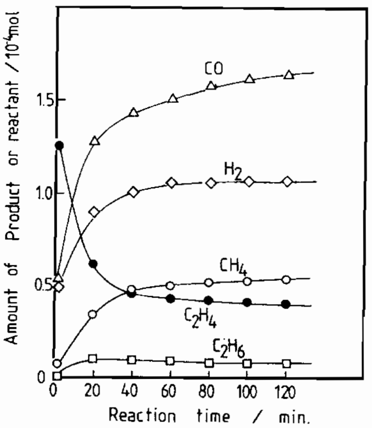


Fig. 7. Oxidation of ethylene by lattice oxygen atoms of Sm_2O_3 at 873 K.

(b) Reaction with adsorbed oxygens

The reaction of C_2H_4 with adsorbed oxygen atoms was examined at 773, 823, 873 and 973 K. In contrast to the results observed for the reaction with lattice oxygen atoms, there were neither CH_4, C_2H_6, nor H_2 produced. The products were only CO_2, CO and H_2O. The kinetic curves observed at 873 K are shown in Fig. 8 as examples.

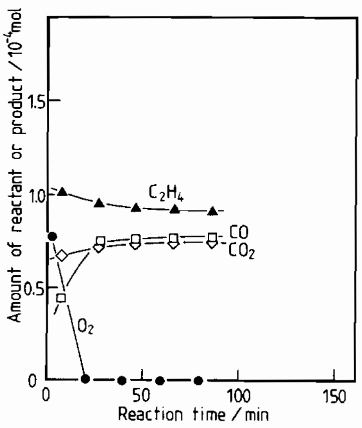


Fig. 8. Oxidation of ethylene by adsorbed oxygens on Sm_2O_3 at 873 K.

The rate of the initial conversion of C_2H_4 per gram catalyst estimated from Fig. 8 is at least three orders of magnitude greater than that estimated from Fig. 7. This shows that the oxidation power of adsorbed oxygens is much greater than that of lattice oxygen atoms.

Oxidation of CO

The kinetic curves of CO_2 formation in the oxidation of CO with lattice oxygen atoms and with adsorbed oxygens at 873 K are shown in Fig. 9. The initial pressure of CO was 12.0 kPa. The kinetic curve *a* in Fig. 9 shows that oxidation of CO with lattice oxygen atoms is very slow at 873 K, which is coincident with the observation that CO_2 was not produced in the reactions of CH_4, C_2H_6 and C_2H_4 with lattice oxygen atoms at <923 K. On the other hand, oxidation of CO with adsorbed oxygen was

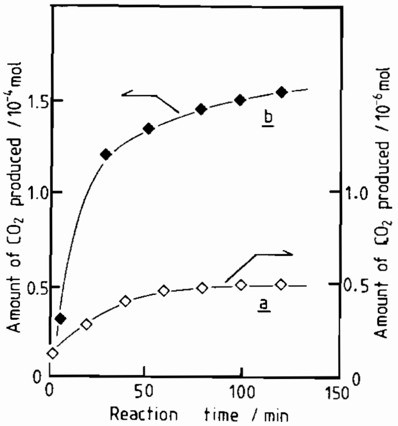


Fig. 9. Oxidations of CO by: (a) lattice oxygen atoms, and (b) adsorbed oxygens, at 873 K.

very fast (kinetic curve *b* in Fig. 9). Since the weight of catalyst used for this reaction was 1/500 of that used for the reaction with lattice oxygen atoms, the rates of oxidation per gram of catalyst are four to five orders of magnitude greater for the former than the latter. The fast conversion of CO to CO_2 in the presence of O_2 in the gas phase explains the observation that CO_2 was the main carbon oxide in the oxidations of CH_4 and C_2H_6 with adsorbed oxygens.

Discussion

The amount of lattice oxygen atoms on the surface per 5.00 g Sm_2O_3 are roughly 1.2×10^{-3} mol on the basis of the lattice parameters of the oxide and the surface area of the sample. The amounts of CO produced by the reactions of lattice oxygen atoms with CH_4, C_2H_6 and C_2H_4 were less (<20%) than that of surface lattice oxygen atoms. However, this cannot preclude the idea that the lattice oxygen atoms in the bulk would also contribute to the reaction because the diffusion of lattice oxygen atoms in the bulk at 873 K is very fast compared to the gas–solid reactions described above. The fast diffusion of the lattice oxygen atoms has been confirmed by measuring the rate of $^{18}O_2$(gas)–^{16}O(lattice) exchange reaction (to be published).

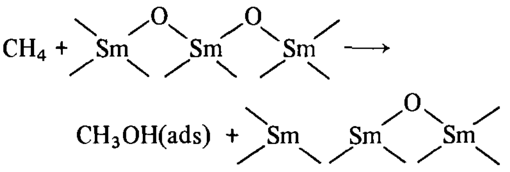
Reaction Schemes

As described earlier, the product distributions observed were quite different between the reaction with lattice oxygen atoms and the reaction with adsorbed oxygens for each hydrocarbon (CH_4, C_2H_6 and C_2H_4). The reactivity of the adsorbed oxygens was two to five orders of magnitude greater than that of the lattice oxygen atoms. These observations strongly suggest that the reaction mechanisms for the oxidations of the hydrocarbons caused by the two oxygen species are quite different. Furthermore, we can conclude that the contribution of lattice oxygen atoms to the oxidations of CH_4, C_2H_6, C_2H_4 and CO can be neglected when oxygen is present in the gas phase.

The following discussions on the reaction mechanisms will be limited to the reactions with lattice oxygen atoms because the details on the reaction mechanism for the partial oxidation of CH_4 by O_2 over Sm_2O_3 have already been described elsewhere [2, 3]. Moreover, the experimental results obtained in this work for the reactions of C_2H_6 and C_2H_4 with adsorbed oxygens are not adequate to discuss the reaction mechanism. The adsorbed oxygen species responsible for each reaction must also be clarified. Further work is needed on these subjects.

Oxidation of CH_4 with lattice oxygen atoms

The results shown in Figs. 1–3 indicate that the lattice oxygen atoms of Sm_2O_3 do not convert CH_4 into C_2-hydrocarbons in good selectivity but produce H_2 and CO as the main products. The observation that the ratio of H_2:CO was about 2 (Fig. 1) implies that CH_4 is oxidized through CH_3OH and HCHO as reaction intermediates, as follows:

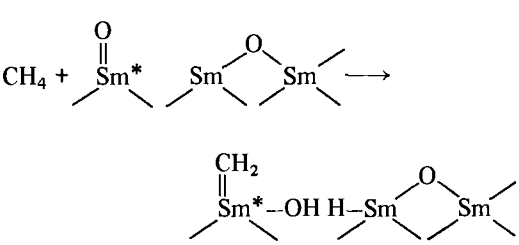


(1)

$$CH_3OH(ads) \longrightarrow HCHO(ads) + H_2 \quad (2)$$

$$HCHO(ads) \longrightarrow CO + H_2 \quad (3)$$

Where coordination numbers for the surface Sm and oxygen were tentatively written in eqn. (1). The conversion of CH_3OH(ads) and HCHO(ads) must be very fast since neither CH_3OH nor HCHO was observed in the gas phase during the reaction. The decrease in the ratio H_2:CO to below 2 at higher temperatures >923 K (Figs. 2 and 3) can be ascribed to the further oxidation of H_2 by lattice oxygen atoms. The formation of C_2H_4 without a trace of C_2H_6 observed in Figs. 1–3 strongly suggests that C_2H_4 is produced directly from CH_4 (path V in the general scheme for CH_4 oxidation described earlier). This is quite unusual because C_2H_6 is generally believed to be the precursor of C_2H_4 in oxidative coupling of CH_4 by O_2 over metal oxides [2, 5–8]. As pointed out earlier, the quantity of C_2H_4 formed was limited to 0.38 ± 0.04 µmol/g-Sm_2O_3 irrespective of the reaction temperatures. This quantity corresponds to 0.16% of the number of surface oxygen atoms. Thus, the number of active sites converting CH_4 directly into C_2H_4 is very low. Although the nature of the active sites is not known at the moment, we speculate that C_2H_4 may be formed through the dimerization of the CH_2= groups generated on the active sites (=Sm*=O) as follows:



(4)

$$2(CH_2=) \longrightarrow C_2H_4 \quad (5)$$

Oxidation of C_2H_6 and C_2H_4 with lattice oxygen atoms

Figure 5 indicates that the selectivity of formation of C_2H_4 is quite high at the early stage of the reaction between C_2H_6 and Sm_2O_3. This observation shows that the lattice oxygen atoms are efficient oxidants for oxidative dehydrogenation of C_2H_6. In contrast to this, the adsorbed oxygen oxidizes C_2H_6 quickly to CO_2 (Fig. 6).

The reactions of C_2H_6 and C_2H_4 with lattice oxygen atoms gave many products (Figs. 5 and 7) such as CO, H_2, CH_4, C_2H_4 (from C_2H_6) and C_2H_6 (from C_2H_4). These products complicated the situation for discussing the reaction mechanism because several intermediates on the surface could be hypothesized to explain the products. Moreover, we cannot neglect the subsequent reactions of the products. Therefore, further discussions on the reaction mechanism will not be made here. Spectroscopic and more detailed kinetic works are needed to clarify the reaction mechanism.

The adsorbed oxygen did not produce any CH_4, H_2 and C_2H_6, as can be seen in Fig. 8. This observation is explained by the idea that the reaction intermediates for the CH_4, H_2 and C_2H_6 must be oxidized rapidly to CO, CO_2 and H_2O because the reactivity of the adsorbed oxygen is so strong compared to that of lattice oxygen atoms, as described earlier.

Acknowledgement

The authors wish to express their gratitude to Professor A. Morikawa for helpful discussions.

References

1 K. Otsuka, K. Jinno and A. Morikawa, *Chem. Lett.*, 499 (1985).
2 K. Otsuka, K. Jinno and A. Morikawa, *J. Catal.*, *100*, 353 (1986).
3 K. Otsuka and K. Jinno, *Inorg. Chim. Acta*, *121*, 237 (1986).
4 G. W. Keulks, L. D. Krenzke and T. M. Notermann, *Adv. Catal.*, *27*, 183 (1978).
5 G. E. Keller and M. M. Bhasin, *J. Catal.*, *73*, 9 (1982).
6 W. Hinsen, W. Bytyn and M. Baerns, *Proc. 8th Int. Cong. Catal.*, *3*, 581 (1984).
7 T. Ito, Ji-Xiang Wang, Chiu-Hsun Lin and J. H. Lunsford, *J. Am. Chem. Soc.*, *107*, 5062 (1985).
8 Chiu-Hsun Lin, K. D. Campbell, Ji-Xiang Wang and J. H. Lunsford, *J. Phys. Chem.*, *90*, 534 (1986).