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On the reaction mechanism for methane partial oxidation over yttria/zirconia

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Abstract

Oxidation of methane over yttria/zirconia mixed oxide shows two parallel oxidation pathways, i.e. partial oxidation to $CO+H_2+H_2O$ and full oxidation to CO_2+2H_2O. Both reactions proceed via a Mars van Krevelen mechanism with first order kinetics for methane and oxygen and are retarded by water. A mechanism is suggested in which methane is homolitically dissociated over $O^-_{(s)}$ sites and via the formation and decomposition of a formaldehyde precursor reacted to CO, H_2 and H_2O. In parallel, CO_2 is obtained from decomposition of bicarbonate that is formed via further oxidation of dioxymethylene.

Keywords: Yttria/zirconia; Methane partial oxidation; Kinetics; Methane pulse

1. Introduction

Partial oxidation of methane $CH_4+1/2O_2\rightarrow CO+2H_2$ recently attracted significant interest. The reaction is mildly exothermic ($\Delta H^\circ_{298\ K}=-45$ kJ/mol) and yields a synthesis gas mixture with a H_2/CO ratio of 2, which compares favorably to the conventional steam reforming of methane for synthesis gas production ($\Delta H^\circ_{298\ K}=206$ kJ/mol, $H_2/CO=3$). Over the past years a large number of supported transition metal and noble metal catalysts along with a number of partially reduced mixed metal oxides were reported to be suitable for partial oxidation of methane [1–8]. In general, these catalysts are found to produce synthesis gas via the so called indirect partial oxidation mechanism that was first reported by Prettre [9] in 1946 for supported Ni catalysts. The oxygen is first consumed in the full oxidation of methane to carbon dioxide and water ($CH_4+2O_2\rightarrow CO_2+2H_2O$, $\Delta H^\circ_{298\ K}=-802$ kJ/mol). Subsequently, the remaining methane is converted to synthesis gas by reforming with produced water and carbon dioxide ($CH_4+CO_2\rightarrow 2CO+2H_2$, $\Delta H^\circ_{298\ K}=247$ kJ/mol, ($CH_4+H_2O\rightarrow CO+3H_2$, $\Delta H^\circ_{298\ K}=206$ kJ/mol). Though high conversions to synthesis gas can be obtained in this way the primary full oxidation is considered to be problematic. Scale-up from the laboratory experiments to an industrial scale reactor causes difficult temperature control and may easily result in runaways due to the heat production from the highly exothermic full combustion [10].

Direct partial oxidation in contrast has been claimed to occur over Rh and Pt coated monoliths in ultra short contact time reactors above 1000°C [11–14]. Direct partial oxidation was also reported over Ru/TiO_2 [15] and over $Ni/CaO\cdot 2Al_2O_3$ [16]. The oxidation state, or degree of oxidation of the metal is suggested to play a crucial role in the selectivity between direct partial oxidation and direct full oxidation. However, the

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mechanistic aspects of the partial oxidation over these catalysts are still unknown.

In this paper, we report on the oxidative conversion of methane over yttria/zirconia, which is a mixed oxide catalyst suitable for direct partial oxidation [17]. Steady state and transient kinetics measurements in combination with kinetic modeling are used to elucidate the possible mechanistic steps over this catalyst.

2. Experimental

The yttria/zirconia mixed oxide catalyst was prepared from powder (Zircar), obtained from Gimex, that consists of 12 wt.% yttria in zirconia. The powder was pressed, crushed and sieved to a 0.3–0.6 mm particles fraction. After calcination at 900°C for 15 h, a BET surface area of 20 m_2/g was measured.

Catalytic experiments were carried out in a quartz tubular flow reactor with a 5 mm internal diameter. A gas flow of 170 ml/min containing He, CH_4, O_2 and N_2 in the ratio of 13:2:1:1 with a total pressure of 1 bar was passed through the reactor. The catalyst bed was diluted with 50 wt.% quartz particles with the same diameter of 0.3–0.6 mm. The 76 vol.% He dilution and the addition of the quartz particles are used to avoid significant temperature deviations between the catalyst particles and the oven temperature arising from the exothermicity of the reactions.

The product gases were analysed with a Varian 3300 GC equipped with TCD and a 3 m·1/8 inch Carboxan 1000 column with He as a carrier gas. Conversions (X) and yields (Y) are calculated as:

$$X_{\mathrm{CH_4}} = \frac{\mathrm{CH_4^{in}} - \mathrm{CH_4^{out}}}{\mathrm{CH_4^{in}}}, \quad X_{\mathrm{O_2}} = \frac{\mathrm{O_2^{in}} - \mathrm{O_2^{out}}}{\mathrm{O_2^{in}}}, \quad Y_{\mathrm{CO_2}} = \frac{\mathrm{CO_2^{out}}}{\mathrm{CH_4^{in}}}$$

$$Y_{\mathrm{CO}} = \frac{\mathrm{CO^{out}}}{\mathrm{CH_4^{in}}}, \quad Y_{\mathrm{H_2}} = \frac{\mathrm{H_2^{out}}}{2\mathrm{CH_4^{in}}}, \quad Y_{\mathrm{H_2O}} = \frac{\mathrm{H_2O^{out}}}{2\mathrm{CH_4^{in}}}$$

Pulse experiments were conducted at atmospheric conditions in a quartz tubular reactor with a 4 mm internal diameter. Prior to the pulses the catalyst was heated in flowing oxygen up to 800°C. After 30 min at 800°C, oxygen was replaced by helium for 30 min. Subsequently, methane pulses were admitted. The products H_2, H_2O, CO and CO_2 were measured by mass spectrometer using masses 2, 18, 28 and 44.

3. Results

3.1. Steady-state performance

Fig. 1 presents conversions and yields from oxidative conversion of methane over 300 mg yttria/zirconia between 550°C and 900°C. Significant contribution of gas phase reactions is excluded based on the measurement of negligible conversions in absence of the catalyst. Under the current set of reaction conditions the catalyst was active above 550°C. The products were CO, CO_2, H_2O and H_2. At temperatures above 800°C some ethane and ethylene were detected as well. Between 850°C and 900°C the oxygen conversion was complete. The amount of C_2 products still increased with temperature causing an increase in methane conversion and water yield. Above 850°C the CO and CO_2 yields did not change markedly with temperature, while the hydrogen yield showed some decrease in favor of water.

To distinguish between primary and secondary reaction products the inter-dependencies of conversion and selectivity were measured by variation of the contact time. Fig. 2 shows the yields of CO and CO_2 at different methane conversions. The results were obtained from a series of experiments at 600°C with a constant gas flow and different catalyst loadings to avoid the possibility of mass transfer effects. The graph shows that CO and CO_2 yields depend linearly upon conversion.

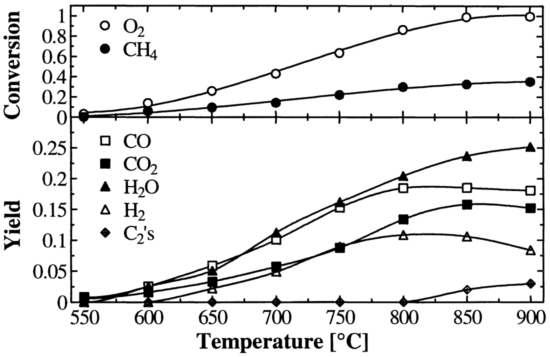

Fig. 1. Conversion and yield plot for partial oxidation of methane with 300 mg of 12 wt.% yttria/zirconia mixed oxide catalyst as a function of temperature (yields are normalised to CH_4 feed).

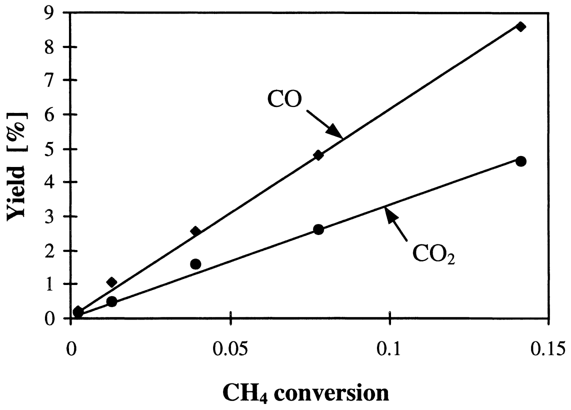

Fig. 2. CO and CO_2 yield as a function of methane conversion measured at 600°C, using catalyst loadings of 20, 100, 300, 600 and 1090 mg.

Fig. 3 shows the CO and the H_2 selectivity as a function of the methane conversion. The results were obtained at 700°C with different amounts of catalyst. The graph shows that the CO selectivity and the H_2 selectivity are constant at 61% and 36%, respectively.

3.2. Kinetics

The influence of temperature and partial pressure of reactants and products on CO and CO_2 formation was investigated. A summary of the results from the kinetic measurements is given in Table 1. The apparent activation energy for CO formation was 114 kJ/mol, while 105 kJ/mol was found for the CO_2 formation. The apparent reaction orders were measured at 600°C under differential conditions (conversion <5%).

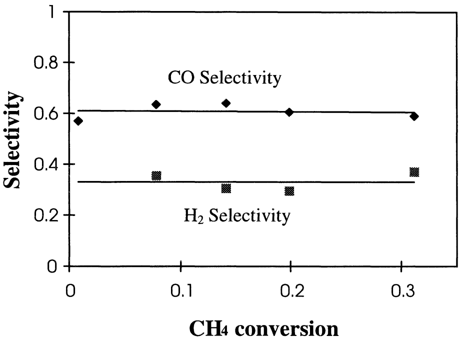

Fig. 3. The selectivity of CO and H_2 versus methane conversion at 700°C.

Table 1
Kinetic parameters for 12 wt.% yttria/zirconia

Primary reaction	Apparent activation energy	Reaction orders for		
		CH_4	O_2	H_2O
CO formation	114 kJ/mol	0.9	0.9	−0.5
CO_2 formation	105 kJ/mol	0.8	1.0	−0.4

From the formed products only water showed significant influence on the reaction rate and was therefore added to the reactant feed. With respect to the methane partial pressure (varied between 30 and 235 mbar), the order for CO and CO_2 formation were 0.9 and 0.8, respectively. With respect to the oxygen partial pressure (varied between 3 and 88 mbar) the reaction orders were 0.9 and 1.0 for CO and CO_2 formation, respectively. With respect to the water partial pressure (varied between 3 and 41 mbar) the reaction orders were −0.5 and −0.4 for the formation of CO and CO_2, respectively.

3.3. Methane pulse experiments

The role of lattice oxygen for methane conversion was tested by means of pulse experiments. The catalyst was pretreated with oxygen at 800°C for 30 min followed by flushing with helium at the same temperature for further 30 min to remove gas phase and adsorbed oxygen. Fig. 4 shows a representative result. The methane conversion was approximately 5% and

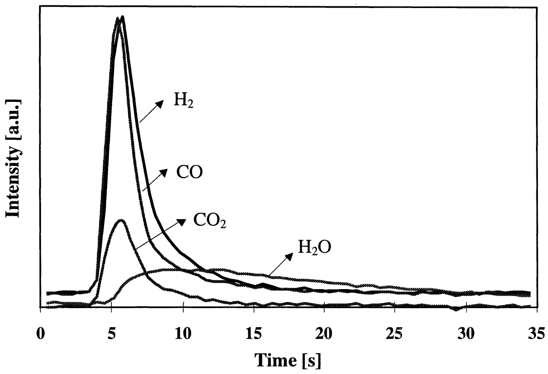

Fig. 4. Methane pulse over 300 mg yttria/zirconia after pretreatment of 30 min in oxygen followed by 30 min in helium, both at 800°C.

CO, CO_2, H_2 and H_2O were formed. The CO selectivity was close to 70% and the H_2:CO ratio was 1. Water showed a very broad peak indicating a strong interaction with the catalyst.

4. Discussion

As outlined above partial oxidation of methane may occur via two different mechanisms, i.e., direct partial oxidation or total oxidation followed by reforming reactions [9]. Characteristic for the indirect route is that all oxygen must be used up, before significant amounts of CO and H_2 are formed. Thus, the presence of CO in the products, before all oxygen is converted, indicates direct partial oxidation. Note that we have excluded the possibility of oxygen slip through the catalyst bed by varying the bed height. Direct evidence for the primary formation of CO is seen also from the conversion/yield plot (Fig. 2). The straight lines for CO and CO_2 indicate that CO and CO_2 are primary products and are not interconverted under our experimental conditions.

As to be expected from Fig. 2 the addition of CO_2 to the reactants did not significantly influence the product distribution. This excludes the possibility of CO formation from fast CO_2 reforming and simultaneously excludes the possibility that CO is formed via the reverse water gas shift ($CO_2+H_2 \rightarrow CO+H_2O$). Table 1 also shows that CO is not formed from steam reforming since steam decreases the CO formation rate.

Though the constant hydrogen selectivity up to 30% methane conversion shown in Fig. 3 indicates the absence of secondary reactions for hydrogen, we see a small decrease of the hydrogen yield above 850°C which is only partly the result of the increasing formation of C_2's and water by methane coupling (see Fig. 1). Zirconia is known to be active for hydrogenation e.g. butene hydrogenation [18] and isosynthesis [19]. The dissociative adsorption of hydrogen to form hydroxyl groups proceeds readily on zirconia. However, below full oxygen conversion hydrogen oxidation was not observed in partial oxidation of methane. This agrees with results of Ouyang et al. [20], who observed that the OH groups formed on the most active sites for H_2 dissociation disappeared under conditions where other hydrocarbons were present. These sites were preferentially covered with methoxy and formate groups. Thus, during our measurements no secondary reaction occurs until part of the catalyst is not in contact with gas phase oxygen anymore and the coverage of the competing adsorbates decreases.

We have so far concluded that the mixed yttria/zirconia oxide does catalyze direct partial oxidation of methane albeit not with 100% selectivity. But even taking into account the competing reaction to CO_2, the water yield is too high and the hydrogen yield is too low to account for a partial oxidation reaction according to the reaction $CH_4+1/2O_2 \rightarrow CO+2H_2$. This suggests that water is also a primary product in the direct partial oxidation and that the overall reaction proceeds according to Eq. (1).

$$CH_4 + O_2 \rightarrow CO + H_2 + H_2O \qquad (1)$$

Kinetic modeling (see Fig. 5) shows that the overall reaction can be described well with the contribution of partial oxidation according to Eq. (1) and full oxidation.

Then, the question arises in what elementary reaction steps CO, H_2 and H_2O are formed and how the parallel formation of CO_2 is linked to the overall reaction. First we analyze the evidence for the participation of adsorbed or lattice oxygen in the oxidation, i.e., whether the reaction follows a 'Langmuir-Hinshelwood' or a 'Mars van Krevelen' mechanism. The key experiment in that respect is shown in Fig. 4. The

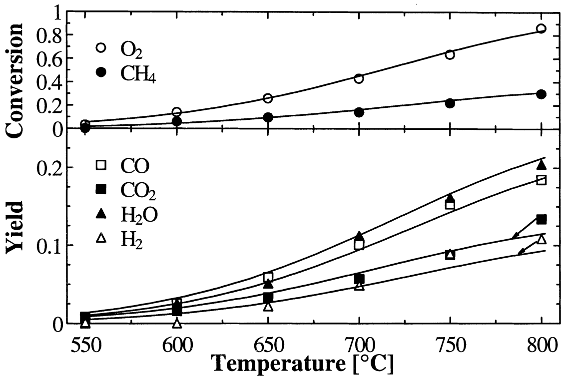

Fig. 5. Best fit for the partial oxidation experiment with 300 mg 12 wt.% yttria/zirconia mixed oxide using partial oxidation according to reaction 1 with $r = k_1 \exp(-114 \cdot 10^3/RT) \cdot CH_4 \cdot O_2 \cdot H_2O^{-1/2}$ and full oxidation with $r = k_2 \exp(-105 \cdot 10^3/RT) \cdot CH_4 \cdot O_2 \cdot H_2O^{-1/2}$. (Arrows point from measured data to fitted line.)

evolution of products seen here stems from exposing the oxidized catalyst to a pulse of methane. Approximately equal amounts of H_2 and CO were formed together with a smaller peak of CO_2 from the complete oxidation. Water was evolving in a rather broad peak with the maximum shifted towards longer residence times compared to the maximum of H_2 and CO evolution. This indicates that water is quite strongly adsorbed on yttria/zirconia even at such high reaction temperatures, and agrees with the negative reaction orders of -0.5 and -0.4 that were found for water with respect to CO and CO_2 formation. Since the total product composition also agrees well with the steady-state results a 'Mars van Krevelen'-type mechanism is concluded to be the foundation for the oxidation reactions that proceed under the methane oxidation conditions.

Having established that lattice oxygen is active for forming CO, CO_2 and H_2O, we turn to the question of how methane is activated. Following results for methane activation on metal surfaces the interaction of methane with the oxidic surface will start with the dissociative adsorption of methane to form a hydroxyl group with lattice oxygen and a methyl group. The active site for this reaction can be a coordinatively unsaturated cation where methane dissociates heterolytically. CH_3^- forms a methyl group on the Lewis site and H^+ is accepted on the adjacent lattice oxygen [21]. A second possibility is the homolytic dissociation of methane. In this case the active sites would be coordinatively unsaturated O^- oxygen sites that form a methoxy and a hydroxyl species [22]. In case of heterolytic dissociation the methyl is likely to undergo oxygen insertion or migration to a coordinatively unsaturated lattice oxygen to form a methoxy group [23,24]. In that context it is important to note that yttria/zirconia mixed oxides are known to have a defect structure that is dominated by oxygen vacancies, which allows a relatively high mobility of the oxygen anions [25–28]. Thus, the interaction of methane with the oxide surface in both cases leads to the formation of a methoxy and a hydroxyl group.

As is mentioned in the work of Finocchio et al. [29], in case of a stable molecule like methane the dissociation of the first C–H bond requires considerably more energy then the dissociation of a C–H bond in the formed surface species. Consequently, a C–H bond in the methoxy is dissociated to form a second OH group and the remaining OCH_2 forms a dioxymethylene.

The dioxymethylene can be considered the precursor of formaldehyde that easily decomposes to CO and H_2 at the temperatures applied for methane oxidation. This is supported by measurements of Busca et al. [30], who showed that the primary adsorbate from formaldehyde over zirconia, thoria and titania [31] is dioxymethylene. Furthermore, the formation of CO and H_2 from sorbed formaldehyde was proposed by Wada et al. on the basis of a kinetic study over lanthanum–boron oxides [32,33].

The two OH groups formed in the process of methane decomposition can eliminate water, leaving an oxygen vacancy and a free lattice oxygen site. The oxygen vacancies from decomposition of the dioxymethylene and water elimination are replenished by gas phase oxygen, closing the catalytic cycle. The negative reaction order in water (-0.5) suggests the interaction with water to be reversible and the coverage of hydroxyl groups to be relatively high. This also suggests that the sites for water formation are involved in the rate determining step for the formation of CO and CO_2.

Finally, we are left to explain the parallel formation of CO_2. The studies of Busca et al. also showed that upon heating above 300 K the dioxymethylene species react to form methoxy and formate. This means that under the reaction conditions used in our experiments parallel to the decomposition of dioxymethylene disproportionation to formate and methoxy species may occur ($2OCH_2O_2^{2-}(s) \rightarrow CH_3O^-(s) + OCHO(s) + O^{2-}(s) + e^-$). With surface oxygen readily available the formate can transform to a bicarbonate which subsequently decomposes to form CO_2 and a hydroxyl group. Infrared studies on CO_2 interaction with zirconia by He et al. [34] support that bicarbonate is a precursor for CO_2 formation. Note that in the process of CO_2 formation all methane hydrogen ends up as hydroxyl groups that will be eliminated to form water molecules. As with the other reaction the catalytic cycle is thought to be closed by chemisorption of oxygen.

Comparing the routes to CO and CO_2 formation one can conclude that to increase the CO selectivity the concentration of free $O^{2-}(s)$ sites should be lowered. In total the formation of CO_2 from dioxymethelene

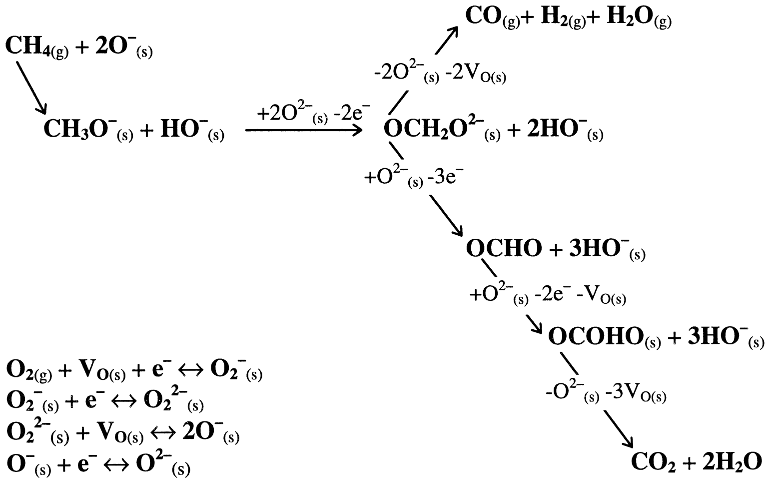

Fig. 6. Proposed mechanism for CO and CO_2 formation over yttria/zirconia mixed oxide.

$(OCH_2O^{2-}(s) + 2O^{2-}(s) \rightarrow CO_2(g) + 2OH^-(s) + 2VO(s) + 4e^-)$ requires more free O^{2-} sites than CO formation. The kinetic measurements showed that both CO and CO_2 formation have a reaction order for oxygen close to 1. This leads to conclude that the variation of the oxygen partial pressure in the range applied during the kinetic measurements did not significantly vary the concentration of free $O^{2-}(s)$ sites. Since variation of the oxygen partial pressure does influence the reaction rates, the rate determining step must involve a gas phase oxygen related species other than normal $O^{2-}(s)$ sites. This brings us back to the possible active site for methane activation. If we accept the homolytic dissociation of methane as the rate determining step, the concentration of $O^-(s)$ species changes the reaction rate. The O^- species may be formed from reaction of gas phase oxygen with oxygen vacancies according to $O_2(g) + VO(s) + e^- \leftrightarrow O_2^-(s), O_2^-(s) + e^- \leftrightarrow O_2^{2-}(s)$, followed by $O_2^{2-}(s) + VO(s) \leftrightarrow 2O^-(s)$. Eventually, the majority of these $O^-(s)$ sites form $O^{2-}(s)$ sites; $O^-(s) + e^- \leftrightarrow O^{2-}(s)$. If the reaction of gas phase oxygen with vacancies is considered to proceed relatively fast the concentration of $O^{2-}(s)$ sites can be high and almost unaffected by the oxygen gas phase concentration while only a low concentration of $O^-(s)$ as the stable intermediate is present to activate methane. Finally a summary of the proposed mechanism is presented in Fig. 6.

5. Conclusions

Yttria/zirconia is able to catalyse the direct partial oxidation of methane via $CH_4 + O_2 \rightarrow CO + H_2 + H_2O$. Next to this selective oxidation reaction the full oxidation of methane to CO_2 and H_2O occurs as a primary reaction. Both reactions involve a Mars van Krevelen oxidation reduction route with lattice oxygen sites. Contribution of secondary reactions over yttria/zirconia is small. The mechanism of the selective oxidation is proposed to proceed via the decomposition of a formaldehyde intermediate, while carbon dioxide is formed via the decomposition of a bicarbonate. With the activation of methane over $O^-(s)$ sites as the rate determining step the mechanism supports the first order reaction kinetics in both oxygen and methane for the partial and the full oxidation.

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References

[1] D. Dissanayake, M.P. Rosynek, K.C.C. Kharas, J.H. Lunsford, J. Catal. 132, 1991.

[2] K. Kunimori, S. Umeda, J. Nakamura, T. Uchijima, Bull. Chem. Soc. Jpn. 65, 1992.

[3] W.J.M. Vermeiren, E. Blomsma, P.A. Jacobs, Catal. Today 1992, 13.

[4] D.F. Vernon, M.L.H. Green, A.K. Cheetham, A.T. Ashcroft, Catal. Lett. 1990, 6.

[5] P.D.F., Vernon, M.L.H. Green, A.K. Cheetham, A.T. Ashcroft, Catal. Today, 13, 1992.

[6] P.E. Marti, M. Maceijewski, A. Baiker, J. Catal., 1993.

[7] A.T. Ashcroft, A.K. Cheetham, J.S. Foord, M.L.H. Green, C.P. Grey, A.J. Murrell, D.F. Vernon, Nature 1990, 344.

[8] R.H. Jones, A.T. Ashcroft, D. Waller, A.K. Cheetham, J.M. Thomas, Catal. Lett. 8, 1991.

[9] M. Prettre, Ch. Eichner, M. Perrin, Trans. Faraday Soc. 43, 1946.

[10] Y.-F. Chang, H. Heinemann, Catal. Lett. 21, 1993.

[11] D.A. Hickman, L.D. Schmidt, J. Catal. 138 (1992) 267.

[12] D.A. Hickman, L.D. Schmidt, Science 259 (1993) 343.

[13] S.S. Bharadwaj, L.D. Schmidt, J. Catal. 146 (1994) 11.

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

[15] Y. Boucouvalas, Z. Zhang, X.E. Verykios, Catal. Lett. 40 (1996) 189.

[16] A.A. Lemonidou, A.E. Stambouli, G.J. Tjatjopoulos, I.A. Vasalos, Catal. Lett. 43 (1997) 235.

[17] A.G. Steghuis, J.G. van Ommen, K. Seshan, J.A. Lercher, Stud. Surf. Sci. Catal. 107 (1997) 403.

[18] G.M. Pajonk, A. El Tanany, React. Kinet. Catal. Lett. 47(2) (1992) 167.

[19] H. Pichler, K-H. Ziesecke, Bur. Mines Bull. 448, 1950.

[20] F. Ouyang, J.N. Kondo, K. Maruya, K. Domen, J. Chem. Soc., Faraday Trans. 92(22) (1996) 4491.

[21] V.D. Sokolovskii, S.m. Aliev, O.V. Buyevskaya, A.A. Davydov, Catal. Today 4 (1989) 293.

[22] A. Bielanski, J. Haber, Oxygen in Catalysis, Marcel Dekker, New York, 1991.

[23] T. Ito, T. Tashiro, M. Kawasaki, T. Watanabe, K. Toi, H. Kobayashi, J. Phys. Chem. 95(11) (1991) 4476.

[24] T. Ito, T. Watanabe, T. Tashiro, M. Kawasaki, K. Toi, H. Kobayashi, Acid-Base Catalysis, Abstracts, Saporro, 1988, p. 483.

[25] Kh.E. Kurumchin, M.V. Perfilév, S.V. Karpachev, V.S. Muzykantov, Kinet. Katal. 17(2) (1976) 1305.

[26] E.Kh. Kurumchin, V.P. Ishchuk, Kinet. Katal. 23(2) (1982) 855.

[27] V.P. Ishchuk, E.Kh. Kuruchin, M.V. Perfilév, S.V. Karpachev, Kinet. Katal. 21(1) (1980) 528.

[28] P. Kofstad, Nonstoichiometry, Diffusion and Electrical Conductivity in Binary Metal Oxides, Wiley-Interscience/Wiley, New York, 1972.

[29] E. Finocchio, G. Busca, V. Lorenzelli, R.J. Willey, J. Catal. 151 (1995) 204.

[30] G. Busca, J. Lamotte, J.C. Lavalley, V. Lorenzelli, J. Am. Chem. Soc. 109 (1987) 5197.

[31] F.S. Feil, J.G. van Ommen, J.R.H. Ross, Langmuir 3 (1987) 668.

[32] S. Wada, T. Tagawa, H. Imai, Appl. Catal. 47, 1989.

[33] S. Wada, H. Imai, Catal. Lett. 8, 1991.

[34] M.Y. He, J.G. Ekerdt, J. Catal. 87 (1984) 381.