Thermodynamic Control of Product Formation During the Reaction Between CH₄ and Pt Promoted Ceria-zirconia Solid Solutions

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Abstract The reaction between CH₄ and framework oxygen of Pt promoted Ce_xZr_{1-x}O₂ ($x = 0.25, 0.5, 0.75, 1$) solid solutions was studied at 873 K for syngas (CO + H₂) production. The homogeneity and cubic/tetragonal structure of the solid solutions were confirmed by powder X-ray diffraction. The thermodynamic properties of the solid solutions, connected with Ce⁴⁺/Ce³⁺ redox reactions, were measured by titrating the oxygen content of the oxides after equilibration in flowing mixtures of H₂ and CO₂ with $10^{-31} < p_{O_2} < 10^{-22}$ atm. The transient reactions between the oxides and discrete pulses of CH₄, as well as of isotopically labeled ¹³CH₄ + ¹²CO mixtures (limited to the material with $x = 0.25$) were investigated and reactivity, conversion and selectivity were measured. A strong correlation between the thermodynamic properties of the oxides and the syngas selectivity was found. The ¹³C scrambling in CO and CO₂ during co-feed experiments

confirmed equilibration of these molecules with the oxides surfaces.

Keywords Cerium oxide · Methane partial oxidation · Degree of reduction

1 Introduction

Ceria based oxides have a great potential for catalytic applications, and have during the last years been investigated for processes like water gas shift, supports for reforming catalysts, VOCs catalytic combustion, CO preferential oxidation and conversion of emission gases [1–10]. The behavior of ceria based oxides in catalysis is typically connected with the redox couple Ce⁴⁺/Ce³⁺ and the consequent reversible oxygen storage capacity. One reaction where the reducibility of cerium oxide plays a central role is the conversion of CH₄ to syngas (CO and H₂) by framework oxygen (Eq. 1 below), and subsequent regeneration of the CeO₂ with air (Eq. 2). This approach to methane conversion might become particularly relevant in gas to liquids (GTL) offshore units, where the direct high-temperature reaction of CH₄ with O₂ (or air) has technological and risk challenges.

The use of cerium oxide in this partial oxidation reaction was first reported by Otsuka et al. [11]. Later, the same authors published a report where Pt/CeO₂ reactivity was investigated with the aim of obtaining insights in the reaction mechanism [12]. The following set of reactions were proposed:

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The recombination and desorption of hydrogen atoms was suggested as possible rate-determining steps but no details were given on the CO_2/CO selectivity. Subsequently, the use of $\text{CeO}_2\text{--ZrO}_2$ solid solutions was introduced for the same reaction by the same authors. In this case, CH_4 decomposition was suggested as the rate-determining step in the early stage of the reaction, and Zr^{4+} was pointed out as the catalytic center for methane activation [13]. At a later reaction stage, coke formation was observed and this was ascribed to the decrease in concentration or activity of the surface oxygen.

The relationship between selectivity towards syngas and degree of oxide reduction was first reported by Pantu et al. for $\text{Pt/CeO}_2\text{--ZrO}_2$ as catalyst and oxygen source. The selectivity was reported to vary with the composition of the $\text{CeO}_2\text{--ZrO}_2$ solid solution [14]. Generally, introduction of zirconia in the $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ solid solution reduced the selectivity toward syngas (i.e., more CO_2 and H_2O being formed). No difference in activity was reported as a function of Pt loading. In that work, methane activation and solid state oxygen diffusion were presented as two possible rate determining steps. However, none of these hypotheses could fit with the experimental results. Nevertheless, the authors speculated that the CO selectivity might be controlled by the relative rate of the CO oxidation and desorption reactions, and that the rate of CO oxidation is sensitive to the degree of oxide reduction. Fathi et al. investigated CeO_2 supported on $\gamma\text{-Al}_2\text{O}_3$ promoted with Pt or Rh for partial oxidation of methane [15, 16]. A relationship between selectivity to syngas and degree of reduction of the oxide was observed.

In spite of the rich literature on ceria based materials and their applications, the key factors governing syngas selectivity, and CH_4 conversion, and their relationship to the redox properties of the reducible oxide are still not clear. It was recently recognized that $\text{CeO}_2\text{--ZrO}_2$ solid solutions, compared to pure CeO_2 , have dramatically different thermodynamic properties, in addition to the well known effect on their kinetic properties [17–19]. The oxidation enthalpy reported for $\text{CeO}_2\text{--ZrO}_2$ solid solutions was approximately 240 kJ/mol lower than for pure CeO_2 [19]. However, no difference in the enthalpy of reduction was observed upon increasing Zr content in the solid solutions and the clear enhancement in reducibility was in this case explained by entropy effects [18, 19].

The aim of the present contribution is to identify and elucidate parameters controlling CH_4 conversion and CO selectivity during cyclic catalytic partial oxidation of

methane to syngas over $\text{Pt/Ce}_x\text{Zr}_{1-x}\text{O}_2$ catalysts. Four compositions of $\text{Pt/Ce}_x\text{Zr}_{1-x}\text{O}_2$ solid solutions were selected and studied during transient reactions with CH_4 pulses or $^{13}\text{CH}_4 + ^{12}\text{CO}$ pulses. Furthermore, the thermodynamic redox properties were measured for the same materials under flowing gas mixtures. The data obtained clearly indicate that the redox properties of the oxides are directly controlling the syngas selectivity. Our results provide new knowledge and highly valuable input for future design of improved materials for the current and similar cyclic oxidative catalytic processes.

2 Experimental

2.1 Material Synthesis

The materials were prepared by dissolving measured amounts of $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$ (Fluka p.a., $\geq 99\%$) and $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (Merck p.a., $\geq 99\%$) in water and then mixing the solutions. Subsequently a solution of NH_4OH was added during 15–20 min to precipitate CeZrO_2 while stirring at room temperature. The yellowish powders were washed 5–6 times until neutral solution and dried overnight at 373 K. The temperature was then raised to 1073 K and the samples were calcined for 10 h.

The calcined samples were impregnated with Pt by the incipient wetness method. Measured amounts of $(\text{NH}_3)\text{Pt}(\text{NO}_3)_2$ powder (AlfaAesar) were dissolved in water and deposited onto the CeZrO_2 materials by incipient wetness impregnation. The samples were then dried overnight at 383 K. The temperature was then raised to 1073 K (5 °C/min) and the samples were calcined at 1073 K for 10 h.

Samples with 100, 75, 50 and 25% CeO_2 impregnated with Pt were named Pt/CeO_2 , Pt/75CeZrO_2 , Pt/50CeZrO_2 , Pt/25CeZrO_2 respectively.

2.2 Material Characterization

Powder X-ray diffraction patterns were recorded with a position sensitive detector using a Siemens Bruker D5000 diffractometer and monochromatic $\text{Cu K}\alpha_1$ radiation. The average crystallite sizes of the oxidized samples were calculated using the Scherrer equation based on the width of the (101) diffraction peak.

2.3 Equilibrium Measurement

The oxygen non-stoichiometry was measured as a function of $p\text{O}_2$ at 873 K using a method similar to that reported by Kim and coworkers [17]. Data obtained in the present study were compared to those of Kim et al. for similar materials,

confirming that equilibrium was reached for the given material/conditions pairs [17]. The sample (Pt/CeO₂, Pt/75CeZrO₂, Pt/50CeZrO₂ and Pt/25CeZrO₂: 0.30, 0.80, 0.87 and 0.78 g, respectively) was loaded into a tubular quartz reactor (i.d. 8 mm) and heated under air flow (5 mL/min) to 873 K. The gas feed was then switched to a mixture of CO₂ and H₂ (eventually diluted in He to keep a constant flow rate) where a given pO₂ was realized through the equilibrium reactions 4 and 5.

In each experiment the sample was subjected to the specific CO₂–H₂–He gas mixture in a continuous flow mode (detailed gas flows and experimental conditions are reported in Table 1), thus at a predetermined pO₂, for 180 min and subsequently flushed with He (90 mL/min) for 30 min. To determine the non-stoichiometry, dry air was thereafter fed (5 mL/min) while using N₂ as internal standard to calculate the amount of adsorbed O₂. The effluent gases were monitored by an online mass spectrometer (Pfeiffer Omnistar), recording the mass numbers (m/z) 4, 14, 18, 28, 32 and 44. The initial oxygen content of the oxides before reacting with CH₄ in the transient tests (after exposure to He, AGA 99.9995%, for 10 min) was measured in a separate experiment. Samples were exposed to a stream of the carrier gas for 10 min and thereafter to air (5 mL/min), N₂ was used as internal standard to calculate the amount of absorbed O₂.

2.4 Transient Catalytic Test (CH₄/O₂)

Catalytic testing was performed in a tubular quartz reactor (i.d. 8 mm) at 873 K and 1 atm pressure. The catalyst (0.1 g, 0.2–0.5 mm diameter) was diluted by quartz (0.4 g, 0.2–0.5 mm). An automated setup equipped with 4-way and 6-way VICI VALCO valves was used. Feed gases (AGA, 99.996%) were used without further purification. The 4-way valve was used to switch between 10% CH₄/He

Table 2 Structural details

Sample	Unit cell volume (Å ³)	Space group	Particle size (Å) (XRD)
CeO ₂	158.4	Fm3 m	586
75CeZrO ₂	76.6	P42/nmcs	87
50CeZrO ₂	73.7	P42/nmcs	78
25CeZrO ₂	70.2	P42/nmcs	80

and 10% O₂/He mixtures. The 6-way valve was equipped with a loop (0.25 mL) and used to send discrete pulses of gas under a continuous stream of Ar (30 mL/min), to the reactor. O₂ pulses were sent to the reactor every second minute while the catalyst was heated to 873 K. The sample was equilibrated in He flow for 30 min at 873 K and thereafter subjected to a series of 50 CH₄ pulses (10% CH₄/He, 1.04 μmol CH₄/pulse) followed by a series of 100 O₂ pulses (10% O₂/He, 1.04 μmol O₂/pulse). Effluent gases were monitored by an online mass spectrometer (Pfeiffer Omnistar). Calibration values for quantification of CH₄, CO₂, CO and H₂ were found by sending known pulses of these gases to an empty reactor preheated to 873 K and integrating the area under the peaks of m/z 15, 44, 28 and 2, respectively. The contribution of CO₂ to m/z 28 was accounted for before quantification of CO. Carbon balance was calculated for each pulse as the sum of CO₂, CO and unconverted CH₄. H₂O was quantified as the difference between converted CH₄ and produced H₂(×0.5). The oxygen nonstoichiometry after each CH₄ pulse was calculated from the amount of oxygen released in terms of CO₂, H₂O and CO (Table 2).

2.5 Transient Catalytic Test (¹³CH₄–CO/Air)

Transient tests between Pt/Ce_{0.75}Zr_{0.25}O₂ and ¹³CH₄ + ¹²CO were performed in the same setup as described in Sect. 2.4. Experiments were performed using two different carrier gas flows, 15 and 30 mL/min. The sample was heated to 873 K while air pulses (dry air, 1.04 μmol air/pulse) were sent to the reactor every 2 min. The sample was equilibrated in He flow for 30 min at 873 K and thereafter subjected to a series of 60 ¹³CH₄ + ¹²CO pulses (1.4 μmol ¹³CH₄, 1.1 μmol ¹²CO, in each pulse) followed by a series of 50 air pulses (1.04 μmol air/pulse). The m/z = 2, 4, 12, 13, 14, 15, 16, 17, 18, 28, 29, 44, 45 were monitored by the online mass spectrometer.

In all catalytic tests, irrespective of possible co-feeding of CO, CO selectivity was calculated as: 100% × [p(CO)/(p(CO) + p(CO₂))], while CH₄ conversion was calculated as: 100% × [(p(CH₄)in–p(CH₄)out)/p(CH₄)in]. H₂ selectivity was calculated as 100% × p(H₂)/[2 × (p(CH₄)in–p(CH₄)out)].

Table 1 Experimental details for the equilibrium measurements

CO ₂ (mL/min)	H ₂ (mL/min)	He (mL/min)	–log p(O ₂) (atm)
20	0.5	10	21.5
5	5	20	24.2
1	5	24	25.4
0.1	10	20	28.3
0.03	10	20	28.9
0.01	10	20	30.5

Carbon balance was calculated for each pulse as the sum of unconverted CH_4 , CO_2 and CO . H_2O was quantified as the difference of the converted CH_4 and the produced H_2 .

The statistical $^{13}\text{C}/^{12}\text{C}$ distribution among the products in $^{13}\text{CH}_4/^{12}\text{CO}$ co-feed tests was calculated as: $[(p(^{13}\text{CH}_4)_{\text{in}} \times \text{CH}_4 \text{ conversion} \times 0.01)/((p(^{12}\text{CO})_{\text{in}} - p(^{12}\text{CH}_4)_{\text{out}})/p(^{12}\text{CO})_{\text{in}})]$. At full CH_4 conversion, the ratio was 1.27.

3 Results

3.1 Material Characterization

3.1.1 Structure

CeO_2 and ZrO_2 form solid solutions for a wide range of compositions and the phase diagram has been extensively studied since the 1950s [20–25]. A monoclinic ($P2_1/c$), a cubic ($Fm\bar{3}m$) and three tetragonal phases termed t , t' and t'' (all space group $P4_2/nmc$) are reported for temperatures below 1273 K [26–28]. Their existence regions are indicated in the upper abscissa in Fig. 1. The three tetragonal phases are characterized by the degree of tetragonal distortion (c/a) and by their nature (t is stable, while t' and t'' are metastable). The distinction between these phases, especially between the t and t' , and between t'' and cubic is quite subtle and can hardly be settled by laboratory scale powder X-ray diffraction. By using synchrotron radiation powder XRD, Lamas et al. studied the crystal structure of the CeO_2 – ZrO_2 solid solutions and distinguished between tetragonal and cubic phase [29]. In Fig. 1 the pseudo-cubic lattice parameter, defined for the tetragonal phases as

Fig. 1 Measured pseudo cubic lattice parameter for $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ (circle) and as reported in Ref [29] (square). Existence regions for the different CeZrO_2 crystalline phases are reported in the upper part of the figure [26–28]

Fig. 2 O/Ce ratio as a function of $p\text{O}_2$ for Pt/ CeO_2 (diamond), Pt/75CeZrO₂ (square), Pt/50CeZrO₂ (circle) and Pt/25CeZrO₂ (triangle) at 873 K

$a_{\text{average}} = (2(\sqrt{2}a) + c)/3$, is plotted for the solid solutions $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$, $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ and $\text{Ce}_{0.25}\text{Zr}_{0.75}\text{O}_2$ obtained in this work, together with values reported by Lamas et al. [29]. The unit cell volume variation obeys the Vegard's law which indicates incorporation of ZrO_2 into the CeO_2 phase without major additional interactions. A more thorough structural investigation is beyond the scope of this work.

3.1.2 $p\text{O}_2$ Dependency of Oxygen Non-Stoichiometry

Figure 2 shows the oxygen to cerium ratio as a function of $p\text{O}_2$. Since the Zr atoms do not take part in the reduction process, the degree of reduction of the oxide is reported as O/Ce in Fig. 2. When increasing the Zr content of the solid solutions the $\text{Ce}^{3+}/\text{Ce}^{4+}$ ratio increases at a given $p\text{O}_2$ value. This finding is in agreement with literature data on similar $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ solid solutions [17–19]. The enhanced reducibility of Ce^{4+} atoms when present in the solid solutions has been explained in terms of a combination of enthalpy and entropy effects [18, 19].

3.2 Reactivity

3.2.1 CH_4/O_2 Pulses

Results from studies of the reaction between the Pt/ $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ oxides and CH_4 pulses are reported as a function of the O/Ce-ratio of the oxide catalyst in Fig. 3. For the fully oxidized samples (O/Ce close to 2), the conversion is close to 100%. However, after repeated CH_4 pulses reacted with the oxide, the CH_4 conversion started to decrease. The specific O/Ce-ratio at which the CH_4

Fig. 3 CH₄ conversion (empty markers) and CO selectivity (full markers) for Pt/CeO₂ (diamond), Pt/75CeZrO₂ (square), Pt/50CeZrO₂ (circle) and Pt/25CeZrO₂ (triangle) as a function of O/Ce as measured by CH₄ pulses (873 K, 1.04 μmol/pulse)

conversion starts to decay was found to increase with increasing Zr content. Similarly, the CO (H₂) selectivity varies with the O/Ce ratio, starting at values close to 0% and rapidly increasing to close to 100% after passing a critical O/Ce ratio (Fig. 3). The critical value of O/Ce at which the CO selectivity started to rise, increased with increasing Zr content, just as found with respect to the CH₄ conversion. A peculiar feature of Fig. 3 is that the relationship between CH₄ conversion and CO selectivity is quite similar for all Zr containing samples. A CO selectivity versus CH₄ conversion plot for all samples is included in the additional informations, Fig. 1S.

As reported in Fig. 2 the oxygen potential over the Ce_xZr_{1-x}O₂ oxides vary with composition and degree of reduction. In order to compare how this change correlates with the observed variation in CO selectivity, the pO₂ versus O/Ce ratio data in Fig. 2 have been converted to values for equilibrium CO selectivity versus O/Ce ratio according to reaction (6). The transformed data are plotted together with the observed CO selectivity in Fig. 4.

Indeed, a good agreement was observed between the theoretically calculated CO selectivity (Eq. 3) and the CO selectivity measured during the reaction of CH₄ with the oxide. This suggests that CO selectivity is determined by the thermodynamic redox properties of the oxide.

Through investigation of the data in Fig. 4 showed that the experimental data were slightly shifted to the left of the predicted data, implying slightly higher CO selectivities than predicted from thermodynamics, especially for the Pt/50CeZrO₂ material. If our hypothesis of a thermodynamically determined CO selectivity holds, this result

Fig. 4 CO selectivity as a function of O/Ce as measured by flowing titration (full markers, 873 K) and CH₄ pulses (empty markers, 873 K, 1.04 μmol CH₄/pulse) for Pt/CeO₂ (diamond), Pt/75CeZrO₂ (square), Pt/50CeZrO₂ (circle) and Pt/25CeZrO₂ (triangle) as a function of O/Ce

indicates that oxygen diffusion from the bulk to the surface is too slow to maintain the same oxygen stoichiometry throughout the nCeZrO_{2-x} materials under the applied test conditions, i.e., that the surface was depleted in oxygen compared to the amount of bulk oxygen.

Accumulated data for C deposition, O consumption, CO, H₂ and CO₂ production, as well as average CH₄ conversions and CO selectivities over a sequence of 50 CH₄ pulses for each material are summarized in Table 3. The amount of CO₂ produced during the pulse series increased significantly when introducing Zr into ceria. As a consequence, the average CO yield over the pulse series decreased with increasing Zr content. Only the sample with highest Zr content gave detectable amounts of C deposition during a sequence of 50 pulses.

Overall, undoped ceria appears to possess the best potential as a support material for the cyclic catalytic partial oxidation reaction under the conditions studied here.

3.2.2 (¹³CH₄+¹²CO)/Air Pulses

Conversion, selectivity and isotope distribution for the reaction between pulses containing a mixture of ¹³CH₄ and ¹²CO over Pt/25CeZrO₂ are reported in Fig. 5. Experiments were performed with two different residence times in order to confirm or exclude kinetic effects. He flows of 15 and 30 mL/min (as in the standard pulse experiments reported in Sect. 3.2.1) were used; the results are reported in Fig. 5a and b, respectively. An expanded view of the second part of the same tests is shown in Fig. 4S. For some pulses the amount of one or more of the species was too small for accurate quantification of the ¹³C distribution

Table 3 Pulse test results. Accumulated carbon deposition and oxygen consumption during 50 methane pulses

Sample	CH ₄ Conversion (%)	CO Selectivity (%)	C Deposited (μmol/g ⁻¹)	O Used (μmol/g ⁻¹)	CO ₂ (μmol/g ⁻¹)	CO (μmol/g ⁻¹)	H ₂ (μmol/g ⁻¹)
BulkCeO ₂	78	96	<1	44	2	37	76
75CeZrO ₂	98	69	<1	90	14	33	68
50CeZrO ₂	97	63	<1	99	17	30	62
25CeZrO ₂	80	69	3	83	16	19	45

Fig. 5 CH₄ conversion (circle), CO selectivity (square) and statistical ¹³C/¹²C ratio (solid line), together with ¹³CH₄/¹²CH₄ (square), ¹³CO/¹²CO (circle) and ¹³CO₂/¹²CO₂ (star) as a function of O/Ce over Pt/25CeZrO₂

(i.e., pulses where CH₄ conversion was close to 100% or CO selectivity close to 0%). Hence, the ¹³C distribution is reported discontinuously. Statistical ¹³C/¹²C ratio (see experimental section) is reported, as a continuous red line in the same figures.

A comparison between the conversion and selectivity curves at the longer and shorter residence times (Fig. 5a and b, respectively) shows that the two curves cross each other at very similar O/Ce ratios at both residence times. It is interesting to note that at both residence times the ¹³C/¹²C ratio in CO and CO₂ corresponds to the statistical ¹³C/¹²C ratio in the whole range studied with only a small deviation during a O/Ce ratio of ~1.57–1.55. This implies that equilibration between the two products takes place in the whole O/Ce range. This observation supports the conclusion drawn above, i.e., that the syngas selectivity in the title reaction is determined by thermodynamics and not by kinetics. On the other hand, the ¹³C/¹²C ratio in CH₄ changed significantly during the pulse sequence. For both residence times, at high O/Ce, the ¹³CH₄ conversion was nearly complete, and the ¹³C/¹²C ratio in CH₄ could not be determined. When ¹³CH₄ conversion started to drop, at the longer residence time (Fig. 5a) ¹³C/¹²C ratio in CH₄ went through a minimum of 1.25 at an O/Ce ratio of 1.57. At the shorter residence time (Fig. 5b and 4S) the ¹³C/¹²C ratio

went through a similar change, however with a minimum at a higher ¹³C/¹²C value; approximately 1.5. The decrease in ¹³C/¹²C ratio in methane with oxygen depletion might suggest a change in the rate-determining step of reaction, from reaction (3) at high O contents to a later reaction step at lower O contents. The subsequent increase in ¹³C content in methane at even lower O contents, observed at both residence times, would suggest that even the back formation of methane was deactivated at lower O contents.

It has previously been suggested that the relative rates between CO desorption and further oxidation might control the CO selectivity in the title reaction over ceria-based catalysts [14]. Our observation of complete equilibration of C-containing products contradicts this view. We clearly propose to shift focus from kinetic to thermodynamic effects when searching for optimum cyclic partial oxidation catalysts. The present work thus represents an important step forward towards a better understanding of the connection between thermodynamic bulk properties of reducible oxides and their catalytic activity. The results now available suggest that design of improved oxidants for the conversion of CH₄ to syngas should undergo reduction in a suitable pO₂ range, i.e., below 10⁻²⁵ atm at 873 K.

4 Conclusions

The relationship between methane oxidation to products and the degree of oxide reduction was studied for a series of Pt promoted Ce_xZr_{1-x}O₂ materials by combining conversion-selectivity data and thermodynamic measurements in a lab scale tubular reactor.

The product distribution over the Pt promoted Ce_xZr_{1-x}O₂ solid solution was found to strongly correlate with the thermodynamic bulk properties of the reducible oxide. The present findings provide important input for the further development of selective reducible oxides for divided catalytic processes.

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References

- Bunluesin T, Gorte RJ, Graham GW (1998) *Appl Catal B-Environ* 15:107
- Craciun R, Shereck B, Gorte RJ (1998) *Catal Lett* 51:149
- Heck RM, Farrauto RJ (2001) *Appl Catal A-Gen* 221:443
- Ozawa M, Kimura M, Isogai A (1993) *J Alloy Compd* 193:73
- Shelef M, Graham WG, McCabe WR (2002) In: Trovarelli A (ed) *Catalysis by Ceria and Related Materials*. Imperial College Press, London, p 343
- Kaspar J, Fornasiero P, Graziani M (1999) *Catal Today* 50:285
- Trovarelli A, de Leitenburg C, Boaro M, Dolcetti G (1999) *Catal Today* 50:353
- Scire S, Minico S, Crisafulli C, Satriano C, Pistone A (2003) *Appl Catal B-Environ* 40:43
- Sedmak G, Hocevar S, Levec J (2003) *J Catal* 213:135
- Liu W, Flytzani-Stephanopoulos M (1996) *Chem Eng J* 64:283
- Otsuka K, Ushiyama T and Yamanaka I (1993) *Chem Lett* 1517
- Otsuka K, Wang Y, Sunada E, Yamanaka I (1998) *J Catal* 175:152
- Otsuka K, Wang Y, Nakamura M (1999) *Appl Catal A-Gen* 183:317
- Pantu P, Kim K, Gavalas GR (2000) *Appl Catal A-Gen* 193:203
- Fathi M, Bjorgum E, Viig T, Rokstad OA (2000) *Catal Today* 63:489
- Jalibert JC, Fathi M, Rokstad OA, Holmen A (2001) *Stud Surf Sci Catal* 136:301
- Kim T, Vohs JM, Gorte RJ (2005) *Ind Eng Chem Res* 45:5561
- Shah PR, Kim T, Zhou G, Fornasiero P, Gorte RJ (2006) *Chem Mater* 18:5363
- Zhou G, Shah PR, Kim T, Fornasiero P, Gorte RJ (2007) *Catal Today* 123:86
- Duwez P, Odell F (1950) *J Am Ceram Soc* 33:274
- Meriani S (1985) *J Mater Sci Eng* 71:369
- Yashima M, Takashina H, Kakihana M, Yoshimura M (1994) *J Am Ceram Soc* 77:1869
- Meriani S (1989) *Mater Sci Eng A-Struct* 109:121
- Duran P, Gonzalez M, Moure C, Jurado JR, Pascual C (1990) *J Mater Sci* 25:5001
- Tani E, Yoshimura M, Somiya S (1983) *J Am Ceram Soc* 66:506
- Yashima M, Morimoto K, Ishizawa N, Yoshimura M (1993) *J Am Ceram Soc* 76:1745
- Yashima M, Morimoto K, Ishizawa N, Yoshimura M (1993) *J Am Ceram Soc* 76:2865
- Yashima M, Ohtake K, Arashi H, Kakihana M, Yoshimura M (1993) *J Appl Phys* 74:7603
- Lamas DG, Fuentes RO, Fabregas IO, de Rapp MEF, Lascalea GE, Casanova JR, de Reca NEW, Craievich AF (2005) *J Appl Crystallogr* 38:867