Available online at www.sciencedirect.com

SCIENCE DIRECT®

Catalysis Today 91–92 (2004) 161–164

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Methane transformation into syngas over Ce–Zr–O systems: role of the surface/bulk promoters and oxygen mobility

T.G. Kuznetsova[a,*], V.A. Sadykov[a], S.A. Veniaminov[a], G.M. Alikina[a], E.M. Moroz[a], V.A. Rogov[a], O.N. Martyanov[a], V.F. Yudanov[a], I.S. Abornev[b], S. Neophytides[c]

[a] *Boreskov Institute of Catalysis SB RAS, Pr. Lavrentieva, 5, 630090 Novosibirsk, Russia*
[b] *Novosibirsk State University, Novosibirsk, Russia*
[c] *Institute of Chemical Engineering and High Temperature Processes, Patras, Greece*

Abstract

The surface and bulk oxygen mobility and reactivity of ceria-based solid solutions as related to the process of methane conversion into syngas can be tuned in a broad limits by bulk and surface promoters. Variation of the surface/bulk real structure of those complex oxides and their strong interaction with the surface promoters (Pt, Ni) appear to be responsible for those effects.

Keywords: Methane transformation; Syngas; Oxygen mobility

---

1. Introduction

The lattice oxygen of ceria-based systems was recently shown to selectively convert methane into syngas or hydrogen as dependent upon the chemical composition of the surface and lattice oxygen mobility [1,2]. Ce–Zr based systems have attracted much attention of researchers, since, due to their high oxygen mobility and storage capacity, they are used in state-of-the-art three-way catalysis for auto-exhaust treatment [3]. However, a lot still remains to be done to elucidate the effect of the real structure and chemical composition of those systems on the mobility and reactivity of their surface and lattice oxygen by using different reductants. In the previous work, to elucidate the reactivity of the surface and bulk oxygen of Ce–Zr-based oxide samples [2], we have applied a method based upon isothermal reduction of oxidized samples by CO in pulse and flow regimes. The results obtained by this method agreed well with those obtained by using another approaches. This work aims at widening the range of chemical compositions of ceria-based fluorite-like complex oxides as related to their reactivity, namely, to study the effect of the content and charge of substituting cations (Zr^{4+}, La^{3+}, Ca^{2+}), anions (F^-) and surface promoters (Pt or Pt + Ni) on the features of their reduction by CO, H_2, and methane. Polymerized complex method (PCM) has been chosen for the preparation of those samples materials, since it allows to obtain highly dispersed single phase of Ce–Zr–O solid solutions with zirconia content up to 50 mol% [4].

2. Experimental

Dispersed samples of ceria-based solid solutions were prepared by PCM and annealed at 700 °C [4]. Samples are denoted as CeZr–$Ce_{0.5}Zr_{0.5}$, CeZrLa$_x$–$Ce_{0.5-x/2}Zr_{0.5-x/2}La_x$, $x = 0.1$–0.3, CeZrCa–$Ce_{0.6}Zr_{0.2}Ca_{0.2}$ and CeZrCaF–$Ce_{0.6}$-$Zr_{0.2}Ca_{0.2}F_{0.2}$. Pt (1.4 wt.%) or Pt + Ni (0.7 + 0.7 wt.%) were supported by the incipient wetness impregnation from the water solutions of H_2PtCl_6 and nickel nitrate and annealed at 700 °C.

The X-ray phase analysis of samples was carried out using a HZG-4C diffractometer (Cu Kα radiation and a flat monochromator) in the range of 2θ angles equal to 1–70°. The unit cell parameter of ceria and modified composites was determined from the position of 3 1 1 diffraction peak.

The chemical composition of samples was analyzed by the atomic absorption spectroscopy (a Karl Zeiss Jena AAS1N spectrometer).

EPR and FMR spectra were recorded at a Bruker-200 X spectrometer at room temperature. Samples were reduced by

---

[*] Corresponding author.
E-mail address: tgkuzn@catalysis.nsk.su (T.G. Kuznetsova).

0920-5861/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2004.03.056

H_2 at 300 °C and kept in sealed ampoules. After FMR spectra recording, ampoules were opened, and spectra evolution under step-wise heating on air was monitored.

For samples pretreated in O_2 at 500 °C, isothermal reduction by CO (1% CO in He, pulse and flow modes); and methane (0.1% CH_4 in He, flow mode) and temperature-programmed reduction (TPR) by H_2 (10% H_2 in Ar, temperature ramp 10°/min up to 900 °C) and CH_4 (1% CH_4 in He, ramp 5°/min up to 900 °C) were carried out using microcatalytic installations and procedures described earlier [2]. The sample reduction degree was expressed in monolayers (one monolayer $= 10^{19}$ atoms/m^2).

3. Results and discussion

3.1. Bulk structure

Samples with a wide range of Ce substitution (up to 50 mol% Zr, 20 mol% Ca or 30 mol% La) and F addition (up to 20 mol%) show the same set of diffraction peaks as for ceria which are widened (even the first ones up to 1.5–2°) and shifted due to the formation of solid solutions. The lattice parameters of samples are given in Table 1. Only for $CeZrLa_{0.2}$ and $CeZrLa_{0.3}$ samples two mixed solid solutions of fluorite structure are formed. Since La solubility in ceria exceeds 30 mol% [5], this means that distortions of ceria lattice caused by incorporation of Zr cations decreases its stability to aliovalent cation substitution. However, for Ca cations with the ionic radius close to that of La, only single phase is formed in CeZrCaO system with Ce/Zr = 3. This suggests that oxygen vacancies generated due to Ca cations incorporation helps to release stresses caused by the cation sizes mismatch. Detailed analysis of the structural features of Ce–Zr system modified by different dopants is beyond the scope of this work and will be presented elsewhere. The most important task of the presented work is to prepare solid solutions with a homogeneous distribution of Ce and Zr to ensure reproducibility of results and to avoid effects of intergrain/interphase boundaries and such extended defects as microprecipitates on the lattice oxygen diffusion. The lattice parameter of CeZr is equal to 5.280 A, which is somewhat higher than the value of 5.25 A expected for the ideal solid solution of cubic ceria and zirconia. However, it is close to that of the ordered solid solution with the same 1:1 composition prepared by a high temperature reducing treatment [6]. Though two solid solutions of a fluorite structure are formed in samples with a large La content, the relative contribution of extended defects with typical sizes exceeding 80 Å (as estimated by SAXS data and ascribed earlier [4] to intergrain boundaries) is small.

Table 1
Lattice parameters, specific surface area, amount of oxygen (in monolayers) removed by H_2 and CH_4 in TPR experiments (*N*) and integral selectivity of methane transformation into syngas in TPR runs

Sample (lattice parameter, Å)	Surface area (m^2/g)	H_2-TPR, *N*	CH_4-TPR	
			S_{CO} (%)	*N*
CeO_2 (5.411)	19	3.4	–	–
CeZr (5.280)	65	1.4	74	2.3
$CeZrLa_{0.1}$ (5.331)	66	1.2	80	2.4
$CeZrLa_{0.2}$ (5.309, 5.440)	66	1.0	76	1.7
$CeZrLa_{0.3}$ (5.344, 5.479)	68	0.9	84	2.5
CeZrCa (5.358)	44	2.4	72	3.9
CeZrCaF (5.358)	58	1.5	–	–
Pt/CeZr	33	3.4	92	9.2
Pt/$CeZrLa_{0.1}$	43	2.1	91	6.9
Pt/$CeZrLa_{0.2}$	29	2.7	91	9.3
Pt/$CeZrLa_{0.3}$	41	1.8	91	6.9
Pt/CeZrCa	27	4.4	90	11.7
Pt/CeZrCaF	57	3.7	–	–

3.2. Oxygen mobility

3.2.1. Temperature-programmed reduction

Temperature-programmed reduction by hydrogen (H_2-TPR) is often used to characterize the reducibility of Ce–Zr samples [3]. For pure dispersed ceria samples prepared by PCM, the main peak of hydrogen consumption appears at 880 °C. Zr addition leads to the shift of ceria bulk reduction to lower (550 °C) temperatures. For CeZrCa sample, the start of the lattice oxygen reduction shifts to higher temperatures (a double peak at 590 and 630 °C). In the presence of La additional peak appears at lower (350 °C) temperatures. Pt and Pt + Ni supporting shifts the beginning of reduction to the range of 200–300 and 200–400 °C, respectively. The amount of oxygen removed by H_2-TPR in the series of Ce-based samples including those promoted by Pt is shown in Table 1.

For all Ce–Zr–O based systems including those promoted by Pt, both CO (partial oxidation product) and CO_2 (deep oxidation product) were detected in CH_4-TPR. While CO_2 evolution is observed in the wide temperature range up to 800 °C, the main peak of CO evolution (with concomitant formation of H_2 in 1:2 syngas ratio [2]) appears at 880 °C. Samples differ by the amount of removed oxygen which reaches a maximum for the CeZrCa system (Table 1). Selectivity of methane conversion to CO (syngas) increases with La addition and decreases for Ca-doped samples. For Pt-supported samples reducibility considerably increases reaching a maximum value for the same CeZrCa system. Pt supporting on promoted complex oxides also increases the selectivity to CO up to ∼90%. The main peak of CO formation appears at 495 °C for CeZr sample and further moves to 470 °C for sample with a maximum La content. On the contrary, for Pt/CeZrCa sample evolution of CO starts at 630 °C. Comparison of samples reducibility by H_2 and CH_4 (Table 1) shows that it is higher for methane as reductant. A rather good agreement between trends in the series of promoted samples is revealed for both reductants. Thus, in both series of TPR experiments over

Pt supported samples, La addition to support decreases the initial temperature of reduction, while Ca increases the amount of oxygen removed in a given temperature range.

3.2.2. *Isothermal reduction by CO*

In the previous work, reduction of Ce–Zr-containing samples by CO in the pulse and flow regimes has been used to elucidate the reactivity of the surface and bulk oxygen [2]. In the series of CO pulses fed to the oxidized surface, the rate of CO oxidation to CO_2 declines with the amount of removed oxygen, until it reaches a plateau when the amount of oxygen removed by a pulse is compensated by the oxygen migration from subsurface layer during the period of relaxation between pulses (540 s). The analysis of the reduction curves by using approaches developed in [2] allows to elucidate the specific surface reduction rate (W_{sp}), the amount of the reactive surface oxygen easily removed by CO pulses (N_o) and the effective rate constant of the oxygen diffusion exchange between the surface and the first subsurface layer (V_D). Under sample contact with the stream of reducing mixture (flow regime), the oxygen is removed from deeper layers. Here, the rate of reduction also declines until it reaches a nearly constant value determined by the oxygen supply from the bulk of particles. Since the latter process is characterized by the bulk oxygen diffusion coefficient (D), the latter parameter can be estimated provided the reduction process is not controlled by the surface reaction. Some characteristics of the oxygen mobility and reactivity for samples considered here are presented in Table 2. La addition causes decline of W_{sp} and V_D, whereas the amount of the surface reactive oxygen remains constant, and the coefficient of the bulk diffusion increases. More complex dependence is revealed for samples with supported Pt + Ni mixed active component. At least, the amount of reactive surface oxygen N_o and D increase due to supporting of active component, though the bulk mobility is leveled under La addition.

Table 2
Some characteristic of the oxygen mobility and reactivity of Ce–Zr-based systems at 500 °C estimated from the experiments of isothermal reduction by CO (1%)

Sample	W_{sp} (s^{-1})	N_o	V_D (s^{-1})	D ($\times 10^{21}$ $m^2 s^{-1}$)
CeZr	0.88	0.2	1.8	0.3
$CeZrLa_{0.1}$	0.28	0.2	1.9	0.6
$CeZrLa_{0.2}$	0.08	0.4	0.7	1.2
$CeZrLa_{0.3}$	0.14	0.25	1.2	1.1
Pt + Ni/CeZr	0.42	1.2	1.2	5.2
Pt + Ni/$CeZrLa_{0.1}$	1.6	0.5	1.5	3.0
Pt + Ni/$CeZrLa_{0.2}$	0.15	0.6	1.3	3.6
Pt + Ni/$CeZrLa_{0.3}$	0.36	0.5	1.6	4.2

W_{sp}, specific surface reduction rate by [2]; N_o, amount of surface reactive oxygen easily removed by CO pulses; V_D, effective rate constant of the oxygen diffusion exchange between the surface and the first subsurface layer [2]; D, coefficient of bulk diffusion.

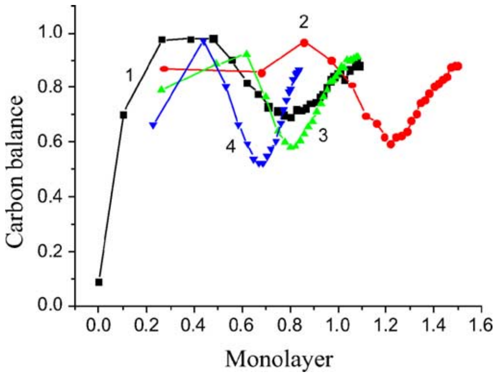

Fig. 1. The carbon balance vs. the amount of oxygen removed from the catalysts with Pt + Ni mixed active component supported on: CeZr (1), $CeZrLa_{0.1}$ (2), $CeZrLa_{0.2}$ (3), and $CeZrLa_{0.3}$ (4) in the course of their reduction at 500 °C by 0.1% CH_4 in He.

In the case of CO as reductant, La helps to increase the lattice oxygen mobility, which is indeed expected for this dopant known to enhance the oxygen mobility in ceria-based electrolytes [5]. The nature of the active component supported onto the surface was found to affect the estimated bulk oxygen mobility stronger than the chemical composition of the support. This suggests that in fact the rate-limiting stage is the surface reaction and not the bulk oxygen mobility which should thus to considerably exceed the values estimated here.

3.2.3. *Isothermal reduction by CH_4*

CH_4 oxidation by the oxygen of the catalyst with supported mixed Pt + Ni active component produces CO_2, CO, and H_2 as main products. As judged by the carbon balance and H_2/CO ratio variation in the course of the sample reduction by CH_4, carbon is formed as well. First CO_2 is formed with participation of the reactive surface oxygen, its content rapidly decreasing with time. CO_2 further appears in small amounts as a result of the deposited carbon oxidation. Selectivities to CO and carbon change in the way opposite to that of CO_2. Changes in the carbon balance in the series of samples with different La content are shown in Fig. 1. These data reveal the non-monotonous dependence of carbon balances on the amount of oxygen removed by CH_4. Here, doping of binary oxides by La favors more rapid

Table 3
Initial specific surface area of samples, coefficient of bulk diffusion and amount of oxygen consumed for methane combustion and the surface carbon oxidation.

Sample (surface area, m^2/g)	D ($\times 10^{21}$, $m^2 s^{-1}$)	O from R1	O from R2
Pt + Ni/CeZr (38)	0.6	0.14	0.03
Pt + Ni/$CeZrLa_{0.1}$ (50)	0.4	0.81	0.03
Pt + Ni/$CeZrLa_{0.2}$ (61)	1.0	0.47	0.01
Pt + Ni/$CeZrLa_{0.3}$ (56)	0.8	0.36	0.01

O from R1 ($CH_4 + [O] \Rightarrow CO_2 + H_2O$) or R2 ($C + [O] \Rightarrow CO_2$)—amount of oxygen removed by reaction 1 or 2, monolayers.

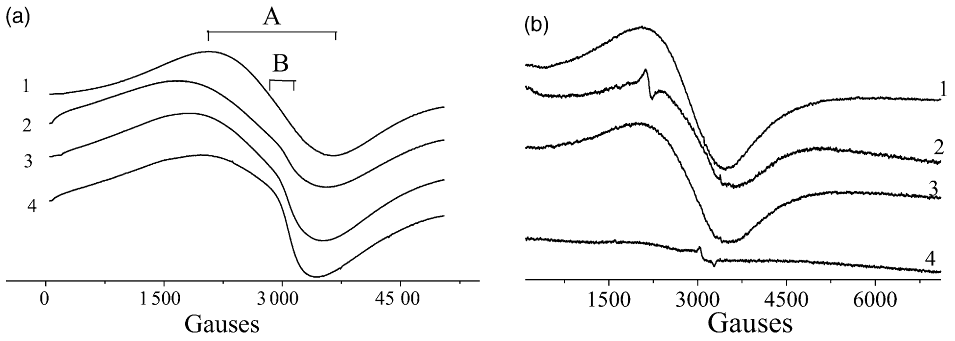

Fig. 2. FMR spectra of Pt + Ni supported over CeZr (1), $CeZrLa_{0.1}$ (2), $CeZrLa_{0.2}$ (3), and $CeZrLa_{0.3}$ (4) catalysts reduced in H_2 at 300 °C/2 h (a) and reoxidized at 150 °C by air (b).

carbon accumulation due to decreasing the surface oxygen reactivity (Tables 2, 3). On the other hand, a higher lattice oxygen mobility for La-doped samples (as judged by *D* values estimated from the experiments on samples isothermal reduction by CH_4, Table 3) helps to recover the carbon balance after main part of reduced nickel apparently responsible for the carbon build-up is blocked by deposited coke.

Kinetic features of methane oxidation by the lattice oxygen of ceria-based systems (specific rates, product selectivities, amount of the reactive oxygen supplied by the lattice diffusion) are strongly affected by change of the surface/bulk real structure and composition caused by promoters. La addition to Ce–Zr–O samples decreases reactivity of the surface oxygen, thus, improving syngas selectivity. Promotion by Pt + Ni increases the initial rates of reaction and the amount of reactive oxygen, while leveling the effect of the bulk promoters. Lower values of *D* determined from the CH_4 reduction in comparison with CO also suggest that the rate-limiting stage of CH_4 transformation is the surface reaction and not the bulk oxygen mobility.

La addition partly prevents sintering of catalysts after supporting Pt + Ni component (Tables 1 and 3) and during red-ox cycles. This facilitates formation of more dispersed active component. A high dispersion of metallic components on the surface of samples with Pt + Ni mixed active component supported on La-containing oxides and reduced by H_2 is indeed confirmed by FMR data. In these spectra two signals corresponding to large anisotropic ferromagnetic (A signal) and small (<100 Å) superparamagnetic (B signal) particles of Ni (or Ni + Pt alloy) are registered (Fig 2a). Small particles start to oxidize slowly under air even at 150 °C. For the Pt + $Ni/CeZrLa_{0.3}$ sample, this process is the fastest causing a rapid disappearance of both signals (Fig. 2b).

4. Conclusions

The surface and bulk oxygen reactivity and mobility of ceria-based solid solutions as related to the process of methane conversion into syngas can be tuned in a broad limits by bulk and surface promoters. Variation of the surface/bulk real structure of those complex oxides and their strong interaction with the surface promoters (Pt, Ni) appear to be responsible for those effects. Results of TPR experiments with different reductants reasonably agree as far as the effect of ceria-based solid solutions doping on the reactivity of the surface/bulk oxygen and its amount is concerned. Isothermal experiments allow to estimate parameters characterizing the oxygen mobility and reactivity and elucidate some mechanistic features of the surface reactions.

Acknowledgements

This work is in part supported by INTAS 01-2162 and ISTC 2529 Projects.

References

[1] K. Otsuka, E. Sunada, T. Ushiyama, I. Yamanaka, Stud. Surf. Sci. Catal. 107 (1997) 531.
[2] V.A. Sadykov, T.G. Kuznetsova, S.A. Veniaminov, V.V. Lunin, E. Kemnitz, A. Aboukais, React. Kinet. Catal. Lett. 76 (2002) 83.
[3] A. Trovarelli (Ed.), Catalysis by Ceria and Related Materials, Catalytic Science Series, vol. 2, Imperial College Press, 2002.
[4] T.G. Kuznetsova, V.A. Sadykov, E.M. Moroz, S.N. Trukhan, E.A. Paukshtis, V.N. Kolomiichuk, E.B. Burgina, V.I. Zaikovskii, M.A. Fedotov, V.V. Lunin, E. Kemnitz, Stud. Surf. Sci. Catal. 143 (2002) 659.
[5] H. Inaba, H. Tagawa, Solid State Ionics 83 (1996) 1.
[6] M. Sugiura, Catal. Surv. Asia 7 (2003) 77.