Fuel-rich methane combustion: Role of the Pt dispersion and oxygen mobility in a fluorite-like complex oxide support

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Abstract

For catalysts comprised of Pt supported onto dispersed complex fluorite-like oxides (ceria doped by Pr, Gd, Sm, or CeO_2–ZrO_2 doped by La, Gd or Pr), the effects of the oxygen mobility in supports and Pt dispersion on the performance in methane selective oxidation into syngas at short contact times were elucidated using combination of kinetic and spectroscopic methods. While in general any simple universal relation between the oxygen mobility, Pt dispersion and the rate of methane transformation into syngas was not found, for some series, a good correlation was observed agreeing with the bifunctional scheme of the methane selective oxidation into syngas.
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1. Introduction

Catalysts comprised of doped ceria, zirconia or ceria–zirconia oxides with supported Pt were recently shown to be very efficient and stable in the fuel-rich hydrocarbons combustion ensuring a high yield of syngas at short contact times [1,2]. This makes them promising for replacing expensive Rh/corundum foam catalysts first suggested for this application [3].

The role of Pt as the active component is mainly considered to be activation of the hydrocarbon molecule by the homolytic cleavage of the C–H bond thus generating hydrogen atoms and hydrocarbon fragments adsorbed on the metal particles [3,4]. The carbon build-up leading to coking and loss of activity is prevented due to rapid interaction of those fragments with the oxygen atoms supplied to the metal particle-oxide support perimeter via the surface diffusion thus generating CO and hydrogen [5]. Complex ceria-containing fluorite-like oxides (possessing required surface lattice oxygen mobility and reactivity along with the phase stability in strongly reducing conditions) appear to be the most promising oxide supports [1,2,6]. Incorporation of low-valence cations into the lattice of ceria or ceria–zirconia solutions is expected to create anion vacancies, thus improving the lattice oxygen mobility [7]. However, up to date, systematic studies of the effect of a dopant type and its content on the lattice oxygen mobility and surface properties of dispersed fluorite-like solid solutions are missing. Furthermore, no straightforward correlations have been obtained relating oxide properties with the performance of supported platinum group metals in the transformation of methane into syngas. Recent results of Wei and Iglesia [8–10] even suggest the absence of any bifunctional CH_4 reforming pathways for Pt group metals and Ni on such supports as ZrO_2,

γ-Al$_2$O$_3$, CeO$_2$–ZrO$_2$ (Zr/Ce = 4), MgO. This is explained by a kinetic scheme in which only C–H bond activation has kinetic relevance, while other steps occur much faster.

Some arguments in favor of the bifunctional scheme of methane fuel-rich combustion/partial oxidation (POM) can be obtained by comparing the specific rate of POM for catalysts with a close Pt dispersion but broadly varying surface/bulk oxygen mobility. This mobility can be estimated by dynamic methods either for standard oxidized state of samples (oxygen isotope exchange, temperature-programmed oxygen desorption) or for their partially reduced state (H$_2$ or CH$_4$ TPR). However, for proving the bi-functional scheme, estimation of the rate of the oxygen-containing species transfer between the Pt particles and the support in the course of catalytic reaction would be of crucial importance. This can be made by using kinetic transients, where relaxation curves fitting allows to estimate the rate constants of corresponding steps [11,12].

In the frame of this bi-functional scheme, another important factor is the Pt dispersion. This parameter determines both Pt efficiency in the C–H bond cleavage in methane molecule [8] as well as resulting flux of oxygen-containing species to the boundary between Pt clusters and support. IR spectroscopy of adsorbed CO test molecule sensitive not only to the number of accessible Pt sites, but to their clustering degree and charge state as well [13,14] can be applied for this purpose.

This work summarizes results of systematic studies of the role of the oxygen mobility in support, Pt dispersion and Pt-support interaction for ceria and ceria–zirconia systems doped with La, Sm, Pr or Gd and promoted with Pt as catalysts of POM. Detailed characterization of the samples real structure and surface properties has already been presented in a number of publications [14–25] and will be considered here only in the extent required to clarify the factors determining mobility/reactivity of the oxygen and catalytic activity in the reaction of methane selective oxidation into syngas.

2. Experimental

Samples of complex oxides including ceria doped with Gd, Sm, or Pr (Ce$_{1-x}$Me$_x$O$_{2-y}$, Me content x = 0–0.5) and Ce$_{0.5-x/2}$Zr$_{0.5-x/2}$Me$_x$O$_{2-y}$ (Me = La, Gd or Pr, x = 0–0.3) were prepared via the polymerized precursor (Pechini) route [1] with modifications of procedures described earlier [14,15,23,24] and calcined at 500–700 °C. All samples were nanocrystalline fluorite-like solid solutions, excluding La-doped ceria–zirconia system at xLa $\geq$ 0.2 comprised of two fluorite-like phases [15]. Pt (1.4 wt.%) was supported by the incipient wetness impregnation with H$_2$PtCl$_6$ solution followed by drying and calcination at 500 °C.

The surface features of samples (support sites and state of supported Pt) were characterized by Fourier transform infra-red spectroscopy (FTIRS) of CO or O$_2^-$ test species adsorbed at 77 K using a Shimadzu 8300 spectrometer and earlier described procedures [14,24].

BET specific surface area of samples (varied in the range of 35–150 m^2/g) was determined from the Ar thermal desorption data.

A dynamic ^{18}O-isotope exchange experiments in the temperature-programmed mode were carried out in the static installation with on-line-coupled quadruple mass spectrometer QMG421 I (Pfeiffer Vacuum GmbH) [26,27]. To characterize the oxygen mobility by using data obtained in the temperature-programmed mode, a dynamic degree of exchange normalized to the surface area of a sample was used [18,21,26]:

$X_s = \lambda_s\{(\alpha^0/\alpha) - 1\}$, where $\lambda_s = N/N_s$ (monolayers), N is the number of O atoms in the gas phase; N_s is the number of exchangeable oxygen atoms in the monolayer of an oxide, α^0, α are initial and current fraction of ^{18}O in the gas phase.

Experiments in the temperature-programmed mode for O$_2$ TPD, H$_2$ TPR, and partial oxidation of CH$_4$ were carried out in a flow quartz reactor using a kinetic installation equipped with GC, an on-line IR absorbance gas analyzer PEM-2M, TCD, an electrochemical sensor for O$_2$ and a polarographic sensor for H$_2$ monitoring with the data acquisition and processing through a PC as described in details elsewhere [16–24].

For the sample of Ce–Zr–La–O series containing 20% La, both with Pt and without it, steady-state isotopic transient kinetic analysis (SSITKA) experiments were carried out as well in the temperature range 650–850 °C. When the steady state was achieved under 2% ^{16}O$_2$ in Ar flow, it was replaced stepwise by the same one containing ^{18}O$_2$, the transient changes in the gas isotopic composition being continuously monitored by a VG-Gas Lab mass-spectrometer.

In relaxation experiments, 0.05 g of a catalyst was loaded into a tubular quartz reactor (L = 300 mm, i.d. = 3 mm) and heated up to 650 °C under flowing He. Prior to every experiment, a sample was oxidized in 2.2% O$_2$ + He flow (flow rate 5 ml/s) for 30 min. Reduction of a sample was carried out by contacting sample with a pure H$_2$ flow for 0.5 h at the same temperature. Before reaction mixture feeding, O$_2$ or H$_2$ were flushed by He purging for 2 min. Switches from He to reaction mixture and vice versa (flow rates were 5 ml/s for both mixtures) were performed with continuous monitoring of the gas phase composition by a QMS-200 (SRC) mass spectrometer and on-line chromatographic analysis. Reaction mixtures of 4.6% CH$_4$ (+2.2% O$_2$) in He were used in these switches.

3. Results and discussion

3.1. Catalytic activity in POM

Fig. 1 compares the specific rates of CH$_4$ consumption, H$_2$ and CO$_2$ generation for all studied series of samples estimated using the efficient first-order rate equation for the plug-flow reactor satisfactorily describing the experimental data [19,20,22]. A broad (by more than one order of magnitude) variation of these rates at the same Pt content and its comparable dispersion (vide infra) is quite clear, suggesting a structural sensitivity of this reaction. For all systems, catalysts performance both in model and realistic [20] feeds was stable, and no coking of catalysts was observed. Obviously, the support effect on the catalytic activity of Pt in POM is prominent, and support oxygen mobility could be among decisive factors. Hence, subsequent analysis is directed to elucidation of