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Partial oxidation of methane to synthesis gas over supported catalysts based on Pt-promoted mixed oxides

S.N. Pavlova*, N.N. Sazonova, J.A. Ivanova, V.A. Sadykov, O.I. Snegurenko, V.A. Rogov, I.A. Zolotarskii, E.M. Moroz

Boreskov Institute of Catalysis, Novosibirisk State University, Siberian Branch RAS, Pr. Lavrentieva 5, Pirogova 1, Novosibirsk 630090, Russia

Abstract

Alumina supported catalysts comprised of a ceria–zirconia solid solution and lanthanum nickelate promoted by Pt were tested in the partial oxidation of methane into synthesis gas under conditions (high temperature, short contact time, highly diluted gas mixture, small catalyst grains) providing acquisition of a catalyst intrinsic activity. The phase composition and reducibility of catalysts were characterized with XRD and TPR. The influence of the catalyst chemical composition, type of redox pretreatment and support phase composition on the activity has been studied. Prolonged relaxations of catalytic activity have been observed, and their nature is discussed taking into account the catalyst properties.

Keywords: Partial oxidation of methane; Syngas; $LaNi_{0.9}Pt_{0.1}O_x/Ce–ZrO_2/\alpha\text{-}Al_2O_3$

1. Introduction

Catalytic partial oxidation of methane (POM) at short contact times is now considered as an alternative to steam reforming of methane, in particular, for production of synthesis gas in compact reactors [1]. Ceria–zirconia solid solutions promoted by Ni and Pt possessing a high surface/lattice oxygen reactivity and storage capacity were shown to be effective systems for POM, steam reforming of methane and its partial oxidation into syngas by the lattice oxygen in reversible red–ox cycles [2,3]. Our previous work has shown that corundum monolith supported Ce–ZrO_2 solid solutions promoted by small amounts of Pt and Rh are more active in POM than supported pure precious metals [4]. However, these data were obtained in the autothermal mode at high reactant concentrations when all oxygen in the feed was consumed within a narrow inlet part of the monolith. Hence, to design effective and stable POM catalysts operating at temperatures ~900–1000 °C, an intrinsic activity of Ce–ZrO_2 containing active components is to be determined.

Recently, the use of perovskites $LaNi(Co)O_3$ promoted by small amounts of Pt, Rh, Ir as active components precursors was shown to increase the activity and selectivity as well as coking resistance of POM catalysts [5]. The aim of this work is to study the intrinsic activity of corundum-supported POM catalysts comprised of ceria–zirconia solid solution and lanthanum nickelate promoted by small amounts of Pt. The catalysts were studied under conditions (high temperature, short contact time, highly diluted gas mixture, diluted catalyst bed, small catalyst grains) providing acquisition of their intrinsic activity. The phase composition and reducibility of catalysts were also characterized with XRD and TPR.

2. Experimental

2.1. Catalyst preparation and characterization

As supports, microspheric $\alpha\text{-}Al_2O_3$ containing an admixture (~10 wt.%) of $\theta\text{-}Al_2O_3$ (designed as A_θ, 16 m^2/g, 100 μm mean particle diameter) and pure $\alpha\text{-}Al_2O_3$ (A) (4 m^2/g, 0.2–0.25 mm fraction) were used. The $Zr0_{0.8}Ce_{0.2}0_2$ secondary support (ZC) and the active components $LaNi_{0.9}Pt_{0.1}O_x$ (LNP) or $LaNiO_3$ + 0.2 wt.% Pt (LNP(0.2)) were successively supported by the incipient wetness impregnation as described in [5]. The ZC content in the catalysts was 5–10 wt.%, LNP content was 3–7 wt.%.

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* Corresponding author. Fax: +7-3832343056.
E-mail address: pavlova@catalysis.nsk.su (S.N. Pavlova).

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Table 1
Catalyst composition, perovskite particle sizes, type of pretreatment, CH_4, O_2 conversions, CO, CO_2 selectivity and H_2/CO ratio during POM at 900 °C

Catalyst	Composition	Perovskite particle size (nm)	Pretreatment	Conversion (%)		Selectivity (%)		H_2/CO
				CH_4	O_2	CO	CO_2	
A	α-Al_2O_3		Oxidation	3	3	73	27	1.3
LNP-A	3% LNP	18.5	Oxidation	5	10	7	93	0
			Reduction	94	99	99	1	2.0
LNP-ZC-A	3% LNP[a]	13	Oxidation	20	25	2	98	0
	5% ZC		Reduction	94[b]	99.5	98	2	2.2
A_θ	α-Al_2O_3 θ-Al_2O_3		Oxidation	3	7	28	72	0
LNP-A_θ	7% LNP	16.5	Oxidation	66	99.6	82	18	2.15
			Reduction	84	99.6	82	18	2.2
LNP-ZC-A_θ	7% LNP	10	Oxidation	63	99.5	82	18	2.2
	10% ZC		Reduction	92	99.5	98	2	2.0
LNP(0.2)-ZC-A_θ	7% LN 0.2% Pt	10	Oxidation	22[b]	77	5	95	0
	10% ZC		Reduction	45[b]	99	45	55	1.9

Feed composition: 1% CH_4 and 0.5% O_2 in He, feed velocity: 300 cm^3/min.

[a] LNP: $LaNi_{0.9}Pt_{0.1}O_3$; ZC: $Zr_{0.8}Ce_{0.2}O_2$.

[b] Conversions and selectivities after the induction period.

XRD spectra of the catalysts were recorded on an HZG-4C Freiberger Prazisionmechanik diffractometer with monochromatic Cu Kα irradiation. The mean crystallite sizes of Ce–Zr mixed oxide, $LaNiO_3$ and Pt were determined from the XRD line broadening measurements using the Scherrer equation. The H_2 TPR experiments were carried out as in [5]. The composition of the catalysts and their characteristics are presented in Table 1.

2.2. Catalyst testing

The catalysts were tested in the POM at an atmospheric pressure in a plug-flow quartz reactor of 5 mm inner diameter. The catalyst weight of 0.01 g was diluted with a quartz powder (0.25–0.25 mm, 0.4 g). The catalyst bed length was 20 mm. The empty reactor space was filled with the quartz sand. The temperature of the catalytic bed was measured by a thermocouple situated outside the reactor. Prior to testing, the catalysts were pretreated for 1 h at 900 °C either in the oxygen or in the flow of 30% H_2 in He. After pretreatment, the reaction mixture (1 vol.% CH_4, 0.5% O_2, He—balance) was supplied with the flow rate of 300 cm^3/min. The reaction products were analyzed by GC.

3. Results and discussion

3.1. Phase composition

According to XRD, $Zr0_{0.8}Ce_{0.2}0_2$ loaded onto both types of supports is a solid solution of the apparent cubic structure. Since Ce–ZrO_2 solid solution of this composition is known to be of a tetragonal structure [6] this means that splitting of diffraction peaks is masked due to small particle sizes causing broadening of reflexes. For samples based on A_θ, after subsequent supporting of perovskite, the ZC average crystallite size is slightly reduced from 12.5 to 9 nm. Pt-containing supported lanthanum nickelate possesses a perovskite structure which predominates in all the catalysts. Support modification by the Ce–Zr oxide favors a higher perovskite dispersion (Table 1). The broad lines of a low intensity corresponding to NiO are observed in the XRD patterns of LNP(0.2)-ZC-A_θ sample. For all samples but LNP-A_θ, the diffraction lines of Pt were not observed probably as a result of Pt incorporation into the perovskite structure. For LNP-A_θ sample, the appearance of large (∼45 nm) Pt particles evidences its partial segregation. This suggests a strong interaction of $LaNiO_3$ with A_θ thus preventing Pt incorporation into the perovskite structure.

Stoichiometric $LaNiO_3$ is known to have an ideal cubic perovskite structure [7], [JCPDS No. 33-0710]. A small deficiency of oxygen is sufficient to transform the cubic structure to the hexagonal one [7]. A variety of the hexagonal cell parameters given in the literature [JCPDS No. 34-1181; No. 34-1028; No. 34-0711] result from less pronounced splitting of the XRD peaks corresponding to the transformation of the cubic structure into the hexagonal one. For all catalysts, their X-ray diffraction patterns in general correspond to the $LaNiO_3$ perovskite phase of the hexagonal structure [JCPDS No. 34-1181]. However, the lines are sufficiently broad suggesting a small (10–20 nm) size of supported perovskite particles. Due to this broadening, the line splitting is not pronounced being reflected in profiles of only high-angle ($2\theta = 59$–60°) diffraction peaks. The lattice parameters of the supported perovskite are slightly different from those of bulk $LaNiO_3$ sample prepared in identical conditions. This implies that the structure of the supported perovskite is somewhat distorted due to its interaction with the support.

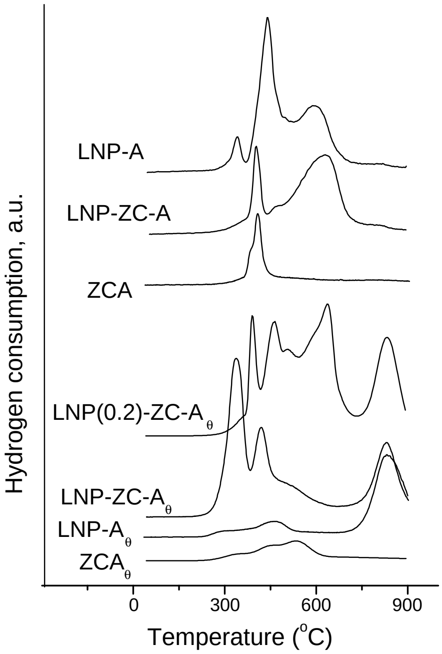

Fig. 1. TPR profiles of the catalysts.

3.2. *Temperature-programmed reduction*

The TPR data are presented in Fig. 1. The spectra of supported $Ce_{0.2}Zr_{0.8}O_2$ depend on the support type. ZC-A_θ has three peaks at 340, 440 and 530 °C, while reduction starts at temperatures below 300 °C. This feature suggests a high reactivity of the surface oxygen for a part of supported CeZr mixed oxide. Simultaneously, a part of the mixed oxide for this sample (a peak at 530 °C) is less easily reduced as compared with the ZC-A sample, where only one intense peak at 400 °C with a low-temperature shoulder is observed. Hence, interaction with more reactive A_θ support leads to appearance of both less reactive and more reactive particles of ceria–zirconia solid solution, probably, due to their structural features and size variation.

Reduction of supported lanthanum nickelate was found to occur at higher temperatures as compared with the bulk one [5,6], thus evidencing the effect of interaction with a support. Addition of Pt was shown to strongly affect the reduction of perovskites. For LNP-A, three peaks at 340, 450 and 600 °C are observed. The low temperature peaks can be assigned to removal of the surface oxygen followed by reduction of the lattice Ni^{3+} cations into Ni^{2+} state [7]. The peak at 600 °C corresponds to complete perovskite reduction to the metals (Ni, Pt) and La_2O_3. The spectrum of LNP-ZC-A shows two main peaks at 400 and 630 °C. The shift of the high-temperature peak to 630 °C and a smaller hydrogen consumption at temperatures below 500 °C as compared with LNP-A indicate that interaction with the secondary Ce–Zr support decreases the reactivity of supported lanthanum nickelate. A similar effect was observed for 15% Ni/Ce–ZrO_2 system [3].

The spectra of all catalysts supported on A_θ show the intense high-temperature peak at 830 °C evidencing a strong interaction between the perovskite and this support retarding reduction of the perovskite phase (Fig. 1). The spectrum of LNP-A_θ shows also two broad low intensity peaks situated at 280 and 460 °C. Note that reduction of Pt-doped lanthanum nickelate supported on A_θ starts at lower temperatures as compared with the same perovskite supported onto pure corundum. This implies that, as for supported Ce–Zr oxide system, for the complex perovskite oxide supported onto A_θ, interaction with support results in formation of particles with a low and high reactivity. When A_θ support is precovered by ZC complex oxide (LNP-ZC-A_θ), the low-temperature reduction of perovskite is strongly enhanced, while the position of the high-temperature peak remains unchanged. This suggests that secondary ZC support modifies the interaction between the alumina and perovskite enhancing reactivity of the surface and a part of the lattice oxygen of the perovskite.

Another factor strongly influencing the perovskite reduction is the mode of its doping by Pt. When Pt is supported after La–Ni perovskite (LNP(0.2)-ZC-A_θ sample), low- and middle-temperature reduction peaks are shifted upward. Earlier [5], similar spectra were observed for $LaNiO_x$ supported on A_θ either pure or precoated by Ce–Zr solid solution. This implies that doping by Pt enhances the reactivity of the surface/near-surface oxygen of a perovskite only when Pt is incorporated into its lattice.

3.3. *Catalytic activity*

Table 1 presents some data on the activity of studied catalysts and supports. In the reactor filled with quartz, no conversion of CH_4 and O_2 was observed. For supports and supported Ce–Zr solid solution, the methane and oxygen conversions are small. The catalytic performance clearly depends upon the catalyst composition and pretreatment. In general, the oxidized catalysts reveal poor activity as compared to the reduced ones. Among the oxidized catalysts, LNP-A_θ and LNP-ZC-A_θ show the most effective performance. For all other catalysts, methane conversions are rather low and the products of deep oxidation are mainly formed.

The activity and selectivity of Ni-containing catalysts in POM were known to depend on the catalyst surface oxidation state [8]. It is now generally agreed that the deep oxidation of methane mainly proceeds over NiO, whereas Ni^0 is responsible for the synthesis gas formation [9]. Methane is activated only over metal Ni while the oxygen activation can proceed with Ce–ZrO_2 oxide participation as well [3]. Thus, to obtain active POM catalysts, a metal Ni has to be formed as a result of the partial or complete decomposition of precursors—Ni-containing perovskites. Hence, the different activity of the oxidized catalysts can be due to different extent of perovskite reduction to the metal Ni by highly diluted reactant mixture. Furthermore, dispersion of

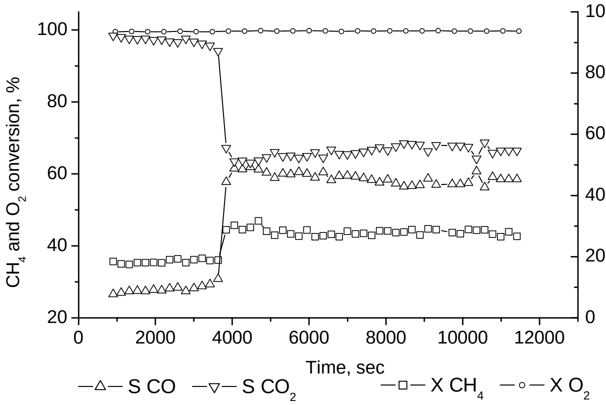

Fig. 2. CH_4 (□), O_2 (○) conversions, CO (△), CO_2 (∇) selectivities of prereduced LNP(0.2)-ZC-A_θ. 900 °C, 1% CH_4 and 0.5% O_2 in He, the feed velocity 300 cm^3/min.

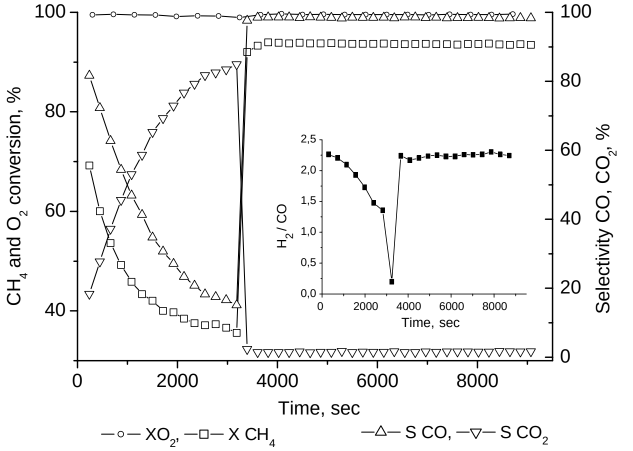

Fig. 3. CH_4 (□), O_2 (○) conversions, H_2/CO ratio and CO (△), CO_2 (∇) selectivities of prereduced LNP-ZC-A. 900 °C, 1% CH_4 and 0.5% O_2 in He, the feed velocity 300 cm^3/min.

formed metal Ni affects the POM catalyst activity [9]. A high activity of oxidized LNP-A_θ and LNP-ZC-A_θ clearly correlates with the easier reducibility of these systems as revealed by H_2 TPR, namely, with the reduction starting already below 300 °C. Hence, in the reaction mixture, the surface of these pre-oxidized catalysts is partly reduced, thus generating Ni^0 particles and ensuring realization of POM route.

High methane conversions and syngas selectivity (Table 1) are observed over prereduced catalysts but LNP(0.2)-ZC-A_θ. This is due to Ni^0 formation as a result of the perovskite decomposition. All highly active catalysts were prepared via $LaNi_{0.9}Pt_{0.1}O_x$ perovskite as a precursor, and the catalysts supported on a pure corundum are more efficient. A high performance of the latter catalysts correlates with their easier complete reduction as shown by H_2 TPR (Fig. 1). Hence, a higher surface concentration of the metal Ni particles is expected to be present on the surface of prereduced corundum-supported samples.

Figs. 2 and 3 show the conversions and selectivities on the reduced LNP(0.2)-ZC-A_θ and LNP-ZC-A samples as a function of the reaction time. For these samples, the induction period of POM reaction is observed. In the case of LNP(0.2)-ZC-A_θ (Fig. 2), the deep oxidation products are mainly formed during the induction period followed by the drastic increase in the methane conversion and syngas selectivity, CO and CO_2 selectivities becoming nearly equal. For LNP-ZC-A during the induction period (Fig. 3), a methane conversion and syngas selectivity first gradually decline then sharply rise.

Hence, an induction period is observed only for the catalysts containing Ce–Zr solid solution. It is well known that prolonged relaxation of catalytic activity cannot be caused by variation of the surface coverage by oxygen [10]. They are usually observed when such side processes as phase transformation, diffusion, or structural rearrangements induced by the sample stoichiometry variation occur.

For the reduced catalysts initially comprised of the supported metal Ni particles, the relaxation features depend on the active component composition. The rate of oxygen adsorption on a clean metal nickel surface is well known to be very high. Hence, prolonged relaxations observed for the reduced samples cannot be caused by changes in the nickel surface oxidation state. At the same time, oxidation of reduced Ce–Zr solid solution followed by changes in its structure [3] and carbonization of its surface proceed slowly [11]. Different dynamics during induction period as well as a different steady-state activity of LNP-ZC-A and LNP(0.2)-ZC-A_θ samples appear to be caused by the different surface state of these reduced catalysts which is reflected in their H_2 TPR features (Fig. 1).

4. Conclusion

The partial oxidation of methane to synthesis gas over corundum-supported active components comprised of Ce–Zr solid solution and Pt-doped lanthanum nickelate has been studied under conditions providing acquisition of the intrinsic catalytic activity. The redox properties of catalysts as revealed by H_2 TPR depend on the perovskite stoichiometry, nature of corundum-like support and the presence of Ce–Zr solid solution. The activity of catalysts depends on both the catalyst composition and their surface oxidation state. The prolonged relaxations of the reaction rate are observed over the catalysts containing Ce–Zr solid solution. For oxidized catalysts, relaxations appear to be mainly due to dynamics of the lanthanum nickelate reduction to metal Ni^0 conjugated with the formation of carbon species on the catalyst surface. In the case of reduced catalysts, they can be caused by oxidation of the reduced Ce–Zr solid solution followed by slowly occurring changes in its structure and the surface carbonization.

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