The Effect of the Nature of the Support on Catalytic Properties of Ruthenium Supported Catalysts in Partial Oxidation of Methane to Syn-Gas[1]

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Abstract—The effect of the carrier on catalytic properties of ruthenium supported catalysts in partial oxidation of methane (POM) was investigated. A variety of supports differed in texture and reducibility (Al_2O_3, SiO_2, TiO_2, Cr_2O_3, CeO_2 and Fe_2O_3) were used. The catalyst activity is governed by ruthenium phase formation ($RuO_2 \rightarrow Ru^0$), and it depends on redox properties of the support as well as support–ruthenium phase interaction. The activity of Ru supported catalysts decreases in the order $Al_2O_3 \approx SiO_2 > Cr_2O_3 > TiO_2 > CeO_2 > Fe_2O_3$. No significant effects of the specific surface area and porosity of catalysts on the methane conversion and selectivity of CO formation were found. The selectivity of CO_2 formation (total oxidation of CH_4) under conditions of POM (a ratio of $CH_4/O_2 = 2$) is associated with the contribution of reducible support oxides into the catalytic performance.

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Partial oxidation of methane has been extensively investigated for many years due to various advantages among which the low cost plays a significant role.

Irreducible (SiO_2, Al_2O_3, La_2O_3, Y_2O_3, MgO [1–3]) as well as reducible (ZrO_2, TiO_2, CeO_2 [4–6]) oxides can be used in partial oxidation of methane (POM) as supports for metal catalysts. Ruckenstein and Wang found that with irreducible supports higher activity and selectivity can be achieved than with reducible oxides. A possible reason is that a fraction of the active phase (ruthenium or nickel) is covered by oxygen from the support material [7, 8]. The strong metal–support interaction (SMSI) effects were observed also for TiO_2-based catalysts [9]. Experiments [9] with VIII group metals reported by Nakagawa et al. showed that for high activity in POM reaction the reduction of active phase is needed. A low activity of catalysts supported on reducible support is related to the presence of ruthenium oxide in the form of a surface oxide on the support which is difficult to reduce. The existence of the SMSI effects was proved by Ruckenstein and Wang [6, 7] who found SMSI in the case of catalysts on irreducible supports. They observed that the nature of the supports as well as the calcination temperature influence the formation of perovskite ($LaRhO_3$) or spinel ($MgRh_2O_4$) like structures which can be involved in redox cycle of POM reaction [9]. The authors compared the effects of support precursors on

reaction yield and found that the kind of precursor has no significant influence on the catalytic activity of rhodium supported catalysts [9], while modifying their stability and resistance to carbonaceous deposits.

The influence of the carrier on catalytic properties of platinum and palladium supported catalysts in POM reaction was studied by Choundary et al. [10]. They found that activity of platinum catalysts was higher than that observed with palladium systems. The order of decreasing activity for supported platinum catalysts was: $Gd_2O_3 > Dy_2O_3 > Er_2O_3 \geq Sm_2O_3 > Pr_6O_{11} \geq Nd_2O_3$.

Literature data suggest that the yield of syn-gas depends upon the conditions of the process, the method of catalyst preparation, the nature and the amount of an active phase. Correspondingly, the comparison of experimental data from different works is difficult or nearly impossible. For this reason, it seems important to compare the behavior of ruthenium catalysts dispersed on different oxides (Al_2O_3, SiO_2, TiO_2, Cr_2O_3, CeO_2, Fe_2O_3) in POM.

EXPERIMENTAL

Catalyst Preparation

Ruthenium supported catalysts were prepared according to the usual wet-impregnation procedure. Commercial oxides, such as silica, alumina, titania, ceria, chromia and Fe_2O_3 were used as supports. Ruthenium was introduced from an aqueous solution

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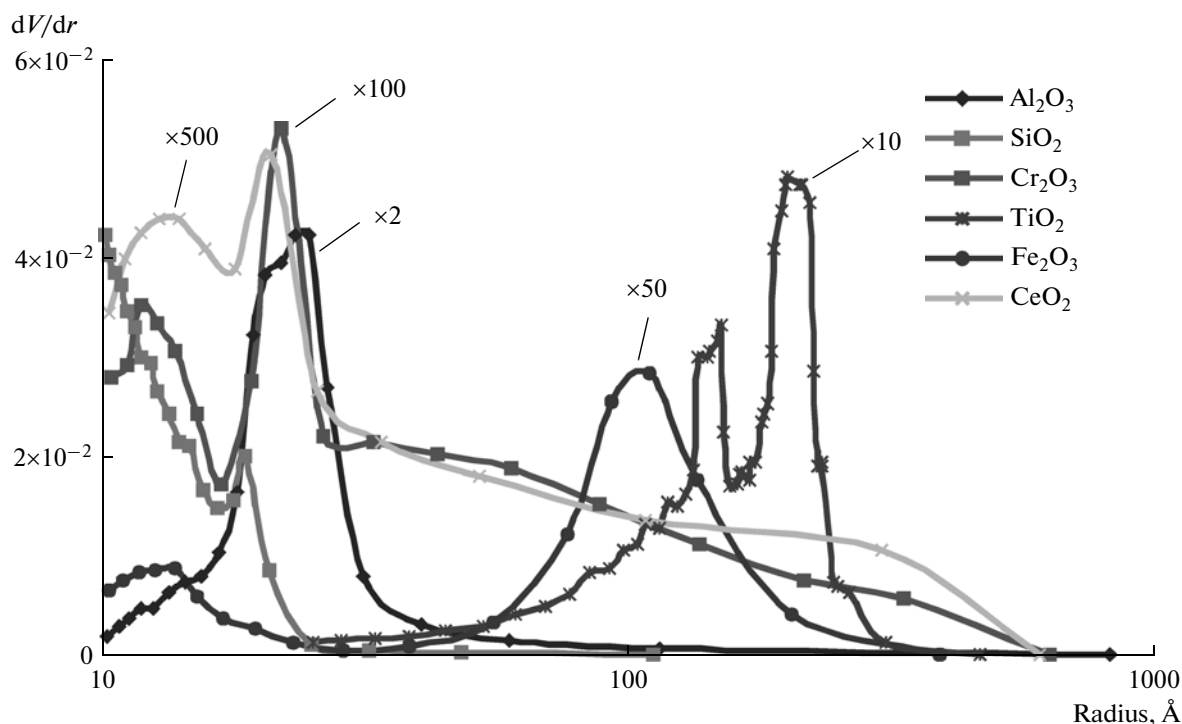[1] The article is published in the original.

Fig. 1. Pore- size distribution of different supports.

of RuCl$_3$. Two sets of catalysts containing 0.5 and 5% of ruthenium were prepared. The catalysts were dried and then calcined at 400°C for 4 h in air.

Methods of Characterization

Temperature programmed reduction (TPR-H$_2$) of supports and ruthenium supported catalysts was conducted using the automatic unit (TPO-TPR system AMI-1 Altamira Instruments) in the H$_2$ flow at 10°C/min to 900°C. The samples (ca. 0.1 g) were reduced in a 60 cm^3/min stream of hydrogen (5% H$_2$ + 95% Ar) or methane (5% CH$_4$ + 95% He). Thermal

The surface area of different supports preheated in air at 500 and 900°C for 5 h

Support	Specific surface area, m^2/g	
	500°C	900°C
SiO$_2$	650	450
Al$_2$O$_3$	130	75
TiO$_2$	80	20
CeO$_2$	25	8
Fe$_2$O$_3$	12	<1
Cr$_2$O$_3$	20	3

conductivity detector (TCD) or mass spectrometer was used.

The BET surface area and porosity (Dollimore–Heal method) associated with supports calcined at 500 and 900°C were determined using the commercial Sorptomatic 1900 unit. Prior to the low temperature nitrogen adsorption–desorption cycle, the samples were preheated at 250°C for 12 h.

The activity tests in POM reaction were carried out in a flow quartz reactor loaded with 0.1 g catalyst samples. Both reactants—methane (5% CH$_4$ + He) and oxygen (5% O$_2$ + He)—were fed in a gaseous stream of CH$_4$ and O$_2$ (molar ratio = 2) with a flow rate of 100 cm^3 min^{-1}. The reaction was studied in a temperature range of 25 to 900°C.

The gas chromatography analysis of reactants and products mixture (CH$_4$, O$_2$, CO$_2$, CO) was carried out using GC Varian 3300 (Varian Inc) instrument equipped with CTR-1 column (helium as a carrier gas, 35°C) and TCD detector (130 mA, 120°C). The analysis of hydrogen was carried out employing the CHROM-4 gas chromatograph unit (Laboratorni Pristroje Praha) packed with 4 Å molecular sieve, argon, 110°C). The data were monitored by a thermal conductivity detector (100 mA, 120°C).
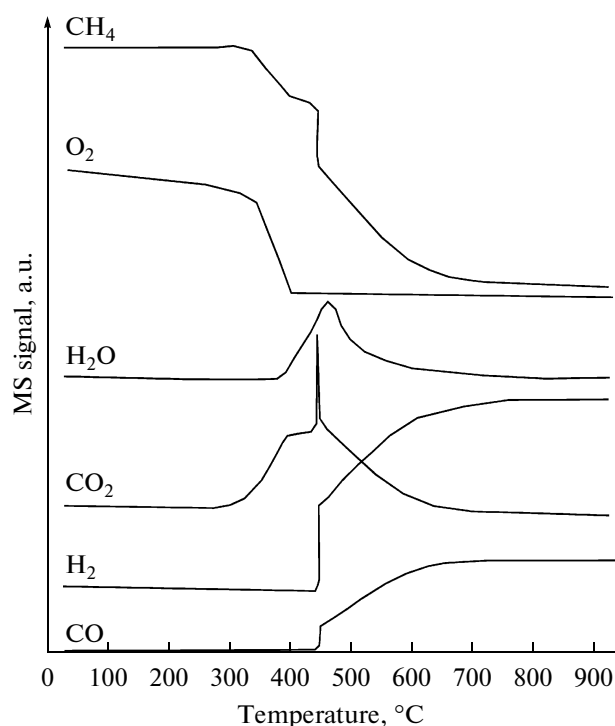
Fig. 2. TPSR reactants concentration profiles for 5% Ru/Al_2O_3 catalyst heated at 10°C/min in the POM reaction.

RESULTS AND DISCUSSION

The effect of calcination temperature on the specific surface area of various supports is shown in the table. There are considerable differences among oxides as evidenced by a wide range of values of surface area recorded for the supports calcined at 500°C (20–650 m^2/g) and for the supports preheated at 900°C (1–450 m^2/g). The increasing calcination temperature results in a decrease of specific surface area that is especially pronounced for oxides Cr_2O_3 or Fe_2O_3 which seem to be very sensitive to sintering. When specific surface areas of oxides and their catalytic activity are compared, no evident relation between activity in POM reaction and support surface area can be traced. The pore-size distribution in samples of various supports is presented in Fig. 1. The differences in the porosity of the oxides with pore sizes in the range of 20 to 600 Å are fairly discernable.

The preliminary catalytic activity tests in the POM reaction indicated that pure supports show no catalytic activity. Only for Cr_2O_3 a negligibly small activity could be observed [11].

The profiles of the temperature programmed surface reaction (TPSR) for the 5%Ru/Al_2O_3 catalyst are given in Fig. 2. In the 300–450°C temperature range full oxidation of methane occurs:
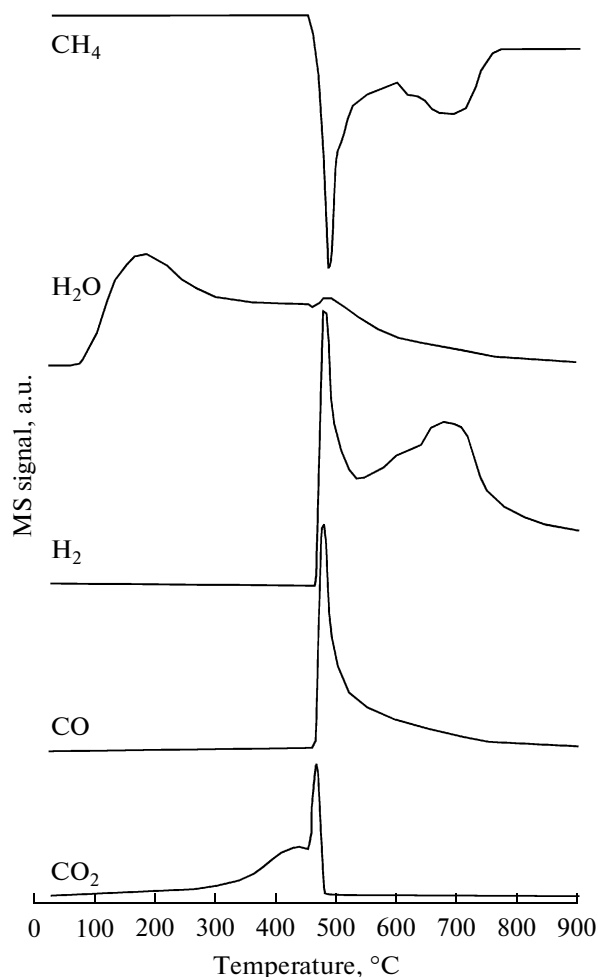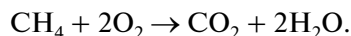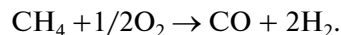
$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O.$$

Fig. 3. TPR-CH_4 profiles for 5% Ru/Al_2O_3 catalysts.

At a temperature near to 450°C the concentrations of reactants change considerably and the evolution of carbon monoxide and hydrogen in POM reaction is observed:

$$CH_4 + 1/2O_2 \rightarrow CO + 2H_2.$$

This rather rapid ignition effect is associated with the reduction of ruthenium oxide by methane according to equitation:

$$2RuO_2 + CH_4 \rightarrow 2Ru + CO_2 + 2H_2O,$$
$$3RuO_2 + 2CH_4 \rightarrow 3Ru + 2CO + 4H_2O.$$
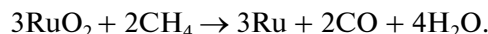
In the temperature range 450–750°C the selectivity towards CO_2 decreases due to enhancement of methane conversion in the POM reaction indicating that the POM reaction occurs on the surface of metallic ruthenium.

This suggestion was confirmed by the TPR-CH_4 experiment. An example of a typical TPR-CH_4 run on 5% Ru/Al_2O_3 catalyst is presented in Fig 3. Based on the TPR profile, the rapid methane consumption occurs at 480°C. At the same temperature the peaks due to CO and CO_2 evolution are observed. Above
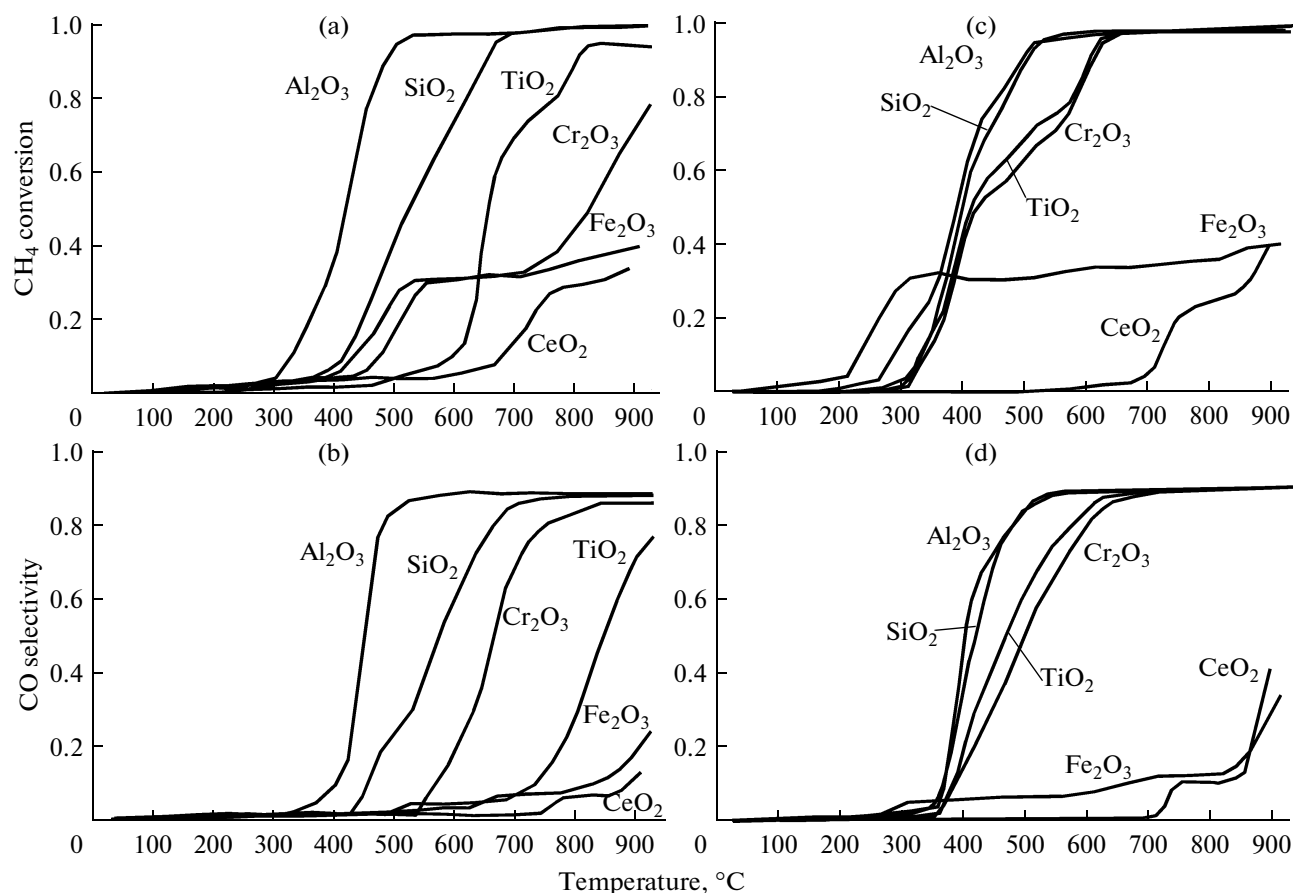
Fig. 4. Temperature dependences of methane conversion and selectivity to carbon monoxide for 0.5% Ru (a, b) and 5% Ru (c, d) supported catalysts.

500°C only the thermal decomposition of methane can be traced as evidenced by evaluation of hydrogen and simultaneous consumption of methane (see CH_4 and H_2 profiles). This process took place according to equation:

$$CH_4 \rightarrow C + 2H_2.$$

The effects of rapid consumption of CH_4 and evaluation of H_2, CO, CO_2, H_2O at 470°C can be identified during POM reaction and at the same temperature in reactions that accompany TPR-CH_4 processes. Occurrence of both reactions in the course of ruthenium oxide reduction indirectly confirm the analysis of TPR-CH_4 profiles. During those processes the simultaneous release of CO, CO_2, water and CH_4 consumption were observed.

However, results obtained for supported catalysts suggest that support also plays important role in this process.

The results of activity tests of 0.5 and 5% Ru catalysts are given in Figs. 4a, 4b and 4c, 4d, respectively. As can be readily seen, for the major part of the supports the increasing ruthenium loading causes a significant shift of catalyst ignition temperature toward

lower values. At the same time a 100% CO selectivity can be achieved at reduced temperatures. The comparison of different catalysts with the same ruthenium loading leads to a general conclusion that the nature of the support plays an important role in POM reaction. Obviously, semireducible and reducible oxides are unsuitable as supports for the preparation of catalysts active in this reaction. Comparison of selectivity to CO on Ru-supported catalysts allows us to conclude that the highest activity shows the catalysts supported on irreducible supports such as alumina or silica whereas the catalysts supported on ceria are the least favorable systems. This conclusion is based on the differences in the behavior of various supports in the reoxidation of ruthenium phase by the oxygen from the support.

From the results outlined above the following conclusions can be made:

(1) The activity of Ru-supported catalysts in POM reaction is governed by ruthenium phase formation ($RuO_2 \rightarrow Ru^0$), and it depends on redox properties of the support as well as support—ruthenium phase interaction.

(2) The order of decreasing activity for Ru-supported catalysts is: $Al_2O_3 \approx SiO_2 > Cr_2O_3 > TiO_2 > CeO_2 > Fe_2O_3$. It reflects the increasing reducibility of the support. The degree of methane conversion and the selectivity to CO formation are practically independent on the porosity and the specific surface area of the catalyst.

(3) The selectivity to CO_2 formation (total oxidation of CH_4) under the conditions of POM reaction at a ratio of $CH_4/O_2 = 2$ is related to the involvement of reducible support oxides in the catalytic transformations.

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