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Catalytic properties of nanostructured Pt and Ru metal clusters over alumina promoted by CeO_2

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Abstract

0.5%Pt-0.5%Ru/2%Ce/(θ + α)-Al_2O_3, reduced by H_2 at 1173 K, presents a mixture of Pt and Ru (3–30 nm) nanoparticles in reduced and partially oxidised condition surrounded by larger formations of surface compound $CeAlO_3$ with perovskite structure and oxide Ce_6O_{11} (15–80 nm). High conversion of CH_4 and selectivity for CO and H_2 (close to 100%) at short contact times ($2.35–8 \times 10^{-3}$ s) are observed by using that catalyst in catalytic partial oxidation of CH_4 to synthesis-gas at 1173 K and atmospheric pressure. Methane is activated on Pt and Ru metal clusters while oxygen is activated on Ce oxide nanostructures.

Keywords: Clusters; Metals; Nanostructures; X-ray diffraction; Transmission electron microscopy

1. Introduction

Nano-size catalysts containing noble metals and applications of nanotechnology for development of the catalysts for catalytic partial oxidation (CPO) of CH_4 into synthesis-gas are a focus in heterogeneous catalysis during the last decade [1–4]. Recently, Pt and Ru containing catalysts were investigated extensively in reaction of CPO at short contact times [2,5]. Pt-Ru-Ce-catalysts are effective in complex purification of waste gases of internal combustion engines from CO, NO and C_3H_6 (C_3H_8) in the presence of oxygen [6].

It was established [7] that reduced Pt-Ru-Ce-catalyst is a mixture of CeO_2, $CeAlO_3$ and unconnected superfine metal particles of platinum and ruthenium. Ruthenium can be easily converted to RuO_2 and again reduced to Ru at low temperatures (433–443 K). It is probable that the stabilization of Pt and Ru in an oxidizing atmosphere is provided due to formation of surface compound $CeAlO_3$ with perovskite structure with interaction of the carrier (Al_2O_3) with cerium ions and ruthenium.

The aim of this work was the investigation of the activity and structure of low-percentage catalysts based on Pt-Ru-Ce due to easy reducibility and stabilization of Ru in the presence of cerium in reaction of partial oxidation of methane into synthesis-gas ($CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2$) at short contact times.

2. Experimental

The catalyst was prepared by consecutive impregnation of dispersed (θ + α)-Al_2O_3 (particle size between 40 and 50 μm) with water solutions of salts $Ce(NO_3)_3{\cdot}6H_2O$, $Ru(OH)Cl_3$ and $H_2PtCl_6{\cdot}6H_2O$ with subsequent heating in air at 873 K for 3 h. The catalyst was reduced in a mixture of $H_2/Ar = 40$ vol.%/60 vol.% within 1 h at 1173 K before the CPO of methane.

Initial reaction mixture ($CH_4/O_2/Ar = 1.5$ vol.%/0.75 vol.%/97.75 vol.%) was supplied into reactor. An Agilent 6890N gas chromatograph equipped with an FID and TCD was employed for the on-line analysis of the products.

Phase structure of catalysts was recorded using X-ray diffraction (XRD) DRON-4-7, operating at 25 kV and 25 mA and employing Co Kα radiation, covering 2θ between 5 and 80°. Morphology, particles size, chemical composition of initial and final catalysts after 56 h were performed on transmission electron microscope TEM-125 K with enlargement up to 133,000 times by replica method with extraction and micro diffraction. Carbonic replicas were sputtered in a vacuum universal station, and carrier of the catalysts was dissolved in HF. Identification of micro diffraction patterns were carried out using the ASTM cart index (1986).

3. Results and discussion

The activity of pre-reduced 0.5%Pt-0.5%Ru/2%Ce/(θ + α)-Al_2O_3 catalyst in catalytic oxidation of methane was investigated at 1173 K and short contact times (τ) of 2.35–8 ms. Alteration of CH_4 conversion (X_{CH_4}), selectivity for CO (S_{CO}),

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Table 1
Alteration of CH_4 conversion, selectivity by CO, H_2, CO_2 and H_2/CO depending on duration of experiment at $T = 1173$ K on 0.5%Pt-0.5%Ru/2%Ce/(θ + α)-Al_2O_3 catalyst

Time (h)	X_{CH_4} (%)	S_{CO} (%)	S_{H_2} (%)	S_{CO_2} (%)	H_2/CO
0.2	84.3	95.8	98.7	4.2	2.06
0.6	77.1	97.2	96.8	2.8	1.99
1.0	72.9	95.1	99.5	4.9	2.09
1.7	58.6	93.9	100	6.1	2.13
2.7	57.1	87.5	100	12.5	2.13

H_2 (S_{H_2}) and H_2/CO depending on duration of experiment are presented in Table 1. It was shown that CPO of CH_4 resulted in selective formation of synthesis-gas (H_2/CO = 1.99–2.13) and decrease of methane conversion from 84.2 to 57.1%. Alterations of CH_4 conversion and selectivity for CO and H_2 depend upon the contact time (τ) of Pt-Ru catalyst and are presented in Fig. 1. The highest conversion of methane (100%) and selectivity for CO and H_2 (99.6 and 100%) were observed at $\tau = 3.25$ ms ($W = 1.17 \times 10^6\ h^{-1}$). An insignificant amount of CO_2 ($S_{CO_2} = 0.4\%$) was detected in the products.

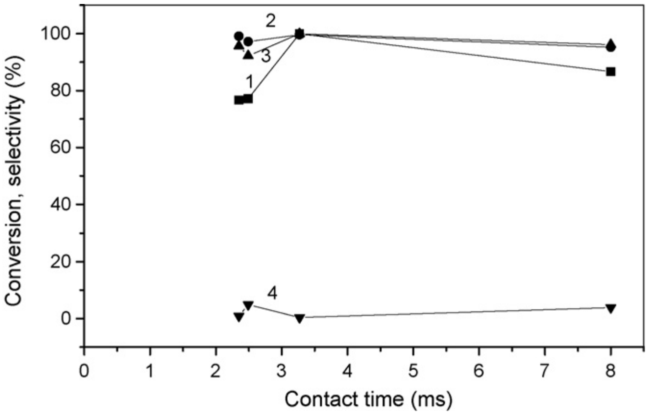

Fig. 1. Catalytic conversion of CH_4 to synthesis-gas on 0.5%Pt-0.5%Ru/2%Ce/(θ + α)-Al_2O_3 at different contact times. $W = 1{,}440{,}000\ h^{-1}$, $CH_4:O_2 = 2$, $T = 1173$ K. (1) X_{CH_4}; (2) S_{CO}; (3) S_{H_2}; (4) S_{CO_2}.

0.5%Pt-0.5%Ru/2%Ce/(θ + α)-Al_2O_3, reduced in H_2 at 1173 K is a mixture of CeO_2, Ce_6O_{11}, surface compound $CeAlO_3$ with perovskite structure and nanostructured clusters of Pt and Ru in reduced and partially oxidised condition according to XRD.

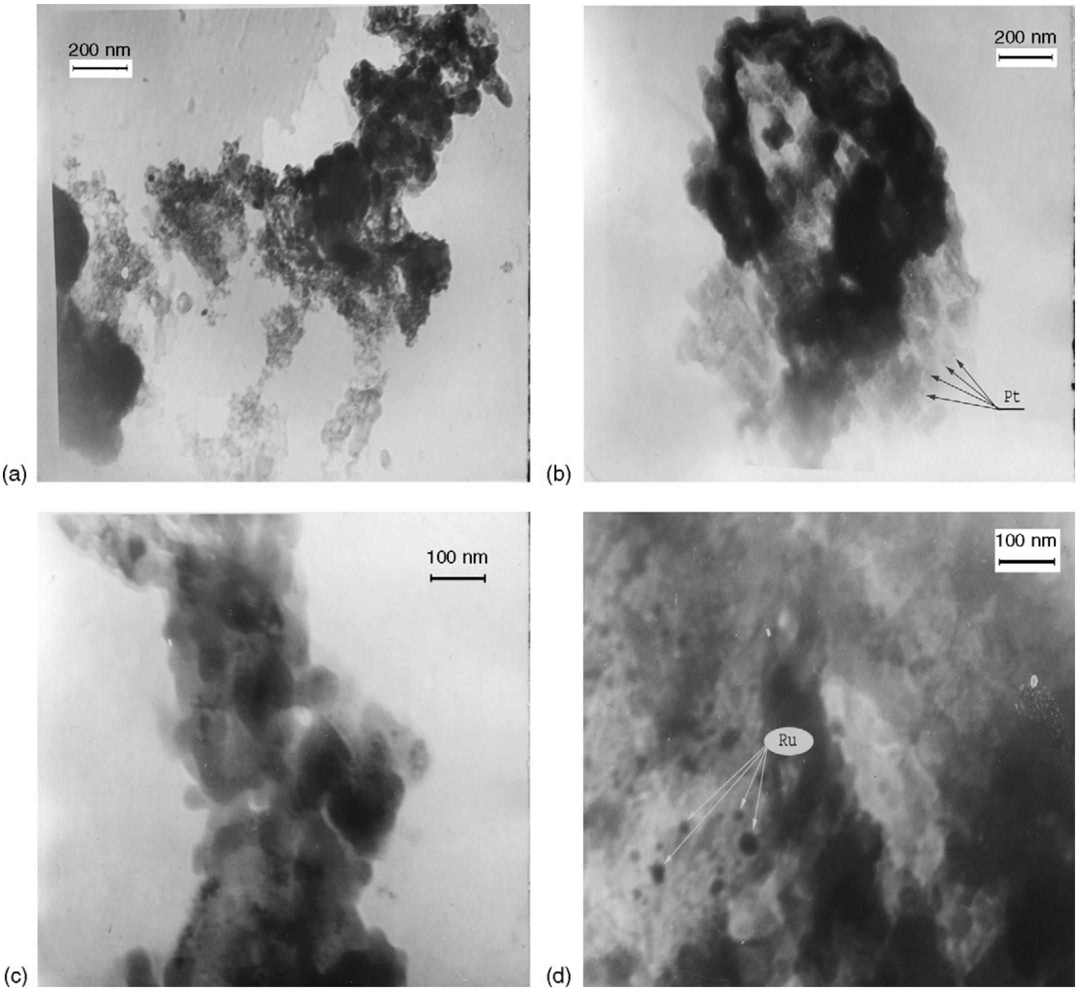

Fig. 2. TEM images of various phases of the fresh 0.5%Pt-0.5%Ru/2%Ce/(θ + α)-Al_2O_3 and reduced catalyst in H_2 at 1173 K (a and b) and with CPO during 8.5 h (c and d).

TEM images of various phases of fresh 0.5%Pt-0.5%Ru/2%Ce/(θ + α)-Al_2O_3 catalyst and reduced in H_2 at 1173 K (a and b) and after CPO during 8.5 h (c and d) are shown in Fig. 2.

The large-sized aggregates of semi-transparent 6–8 nm sized particles of Ce_6O_{11} phase are presented in Fig. 2a. Typical morphology of the Pt nanoparticles is shown in Fig. 2b. Pt presents single 3–4 nm sized particles which are distributed on the surface of the carrier.

Enlargement of Ce_6O_{11} nanoparticles up to 80 nm (Fig. 2c) occurred in reducing atmosphere after processing in reaction conditions. The dense nanoparticles of metallic ruthenium with size 10–20 nm are presented in Fig. 2d.

4. Conclusion

0.5%Pt-0.5%Ru/2%Ce/(θ + α)-Al_2O_3, reduced in H_2 at 1173 K partially oxidises methane into synthesis-gas at short contact times with high conversion of methane and selectivity for CO and H_2 (close to 100%) at $\tau = 3.27$ ms due to the presence of nanoparticles of Pt and Ru. Increasing of contact time reduced slightly the conversion of CH_4 to 82% and selectivity by CO and H_2. The ratio H_2/CO was close to 2. Such ratio is ideal for synthesis of methanol and hydrocarbons. The results confirm well-known data about high selectivity of ruthenium in the case of injecting of CeO_2 and CPO of CH_4 with $X_{CH_4} = 74\%$ [8]. In our investigation the promotion of Ru by Pt and supported over stabilised 2%Ce/θ-Al_2O_3 at high selectivity raises the degree of methane conversion up to 100% at short contact times. The data indicate formation of Pt°, Ru°, Ce_6O_{11} and $CeAlO_3$ clusters. It is suggested that improvement of reaction parameters over mixed Pt-Ru catalyst on 2%Ce/θ-Al_2O_3 could be caused by division of activation functions of reactants: CH_4-on Pt°, O_2-on Ru° or Ce_6O_{11}. It is possible that surface $CeAlO_3$ perovskite promotes stabilisation of Pt and Ru on carrier (Al_2O_3).

References

[1] H.H. Kung, M.C. Kung, Catal. Today 97 (2004) 219.
[2] I. Balint, A. Miyazaki, K. Aika, J. Catal. 220 (2003) 74.
[3] F. Basile, G. Fornasary, M. Gazzano, A. Kienemann, et al., J. Catal. 217 (2003) 245.
[4] R. Jin, Y. Chen, W. Li, W. Cui, et al., Appl. Catal. A: Gen. 201 (2000) 71.
[5] P. Pantu, G.R. Gavalas, Appl. Catal. A: Gen. 223 (2002) 253.
[6] N.M. Popova, N.A. Antonova, E.M. Moroz, Kinet. Katal. 38 (1997) 757.
[7] N.M. Popova, N.A. Antonova, A.S. Sass, E.M. Moroz, et al., Kinet. Katal. 38 (1997) 749.
[8] H. Nishimoto, K. Nakagawa, et al., Catal. Lett. 89 (2002) 161.