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Production of Synthesis-Gas from Methane on Ni-Containing Nanosized Catalysts

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Introduction

Great attention is paid to the processes of production of synthesis gas by means of selective catalytic oxidation (SCO) of methane and other alkanes in the last 10-15 years. It is known that the alloys based on noble metals provide high activity and efficiency of the catalysts at space velocities from $500 \cdot 10^3$ to $900 \cdot 10^3$ h⁻¹. Ni and Ni-based catalysts based on precious metals which provide complete conversion of methane to synthesis gas over a long period without loss of activity compared to the oxide and perovskite catalysts without activation of the noble metals are the best. We have carried out a investigation of low-percentage nano-sized Pt-Ru and Ni-Cu catalysts in these processes.

Materials and Methods

The catalysts were prepared by impregnation of dispersed Al₂O₃ (prepared by Co-impregnation between 180-210 μm) by water solutions of metal nitrates with subsequent heating in air at 503K (6 h), 873K (1 h) and 1123K (1 h). The catalysts were reduced in a mixture of H₂, Ar = 40:60 (vol %) at 1173K before the SCO of CH₄ or C₂H₆. Initial reaction mixture (CH₄, O₂, Ar = (1-4):2): (0.6-0.8): (197-99) (vol %) was supplied into reactor with space velocity $0.45 \cdot 10^4$ h⁻¹. An Agilent 6890N gas chromatograph equipped with a flame ionization detector and thermal conductivity detector was employed for the on-line analysis of products. Phase structure of catalysts was recorded on XRD (D8 Advance, Siemens) at 25 kV and 25 mA, employing Cu-K_α radiation, scanning 2θ between 5 and 30°. Morphology, particles size, chemical composition of initial and spent catalysts for 50 h were performed on TEM-EDS with enlargement up to 133000 times by replica method with extension and area diffraction. Catalysts pellets were sintered in vacuum at 1100°C, and curves of catalytic activity were discussed in HR identification of micro diffraction patterns were carried out by means of ASTM card index (1986).

Results and Discussion

Determination of the active phase composition of catalysts by studying of oxidation of 3.4% C₂H₆ in the presence of 0.4% O₂ at 1173K on short contact time were conducted. The process is carried out entirely (X_{CO} = 100%) with the formation of synthesis gas without by-products (H₂, CO = 2.0) with high selectivity by H₂ and CO only at molar ratio of Pt-Ru = 2:1, 1:1 (0.68 at % Pt, 0.32 at % Ru, 0.55 at % Pt, 0.45 at % Ru) for series of Pt, Ru, and Pt-Ru catalysts with 0.5 Torr initial ratio of elements. SCO reaction proceeds by direct route. Optimal conditions for preparation and pre-treatment of 9% Ni-Cu/0.2% Ce/0.1-Al₂O₃ catalyst with the number of physical and chemical methods have been established: T = 1173K, CH₄:O₂ =

2:1, t = 2.15-1.27 ms, V = (1.17-1.31)·10⁴ h⁻¹. The degree of methane conversion reaches 80-100%, the selectivity of CO and H₂ formation 99.0-100 and 99.0-100%, respectively, and traces of CO₂ (0.005%) are also formed. Disappearance of synthesis-gas of optimal composition H₂:CO = 2.0 is possible at a ratio of CH₄:O₂ = 1, in other cases the ratio H₂:CO is in the range of 1.65-1.84 due to lack of H₂ in the products. The kinetic models have allowed assume that the SCO of methane can be carried out individually, using O₂ as oxidant and combining it with the steam conversion on the short contact times.

According to numerous reports, the SCO reaction can occur by two mechanisms: 1) consecutive - through the deep oxidation of CH₄ to CO₂ and H₂O and its subsequent steam and dry reforming; 2) direct - through complete dissociation of CH₄ and oxygen of the surface. The selective oxidation of CH₄ or catalyst begins in the first few minutes and proceeds almost without the formation of CO. The contact time does not affect the composition of the formed products. This indicates that the reaction proceeds through the dissociative adsorption of CH₄. It is assumed that SCO reaction is carried out by direct mechanism due to the absence of complete oxidation products at multisecond contact times on the Pt-Ru_{0.5}Si_{0.5}(e⁻)/0.1Al₂O₃ and Ni-Cu/Ce²⁺ (e⁻)/0.1Al₂O₃ catalyst. Activation at 0.5 Torr of CH₄ on Pt²⁺ for the Pt-Ru catalysts on Si²⁺ for Ni-Cu-Ce samples with the formation of H₂ and fragments of CH₄ rather than followed by recombination of H₂ atoms into H₂ molecule and the oxidation of C to CO due to surface oxygen and bulk oxide of RuO₂ on copper oxide. TPO and TPO (O₂) which mainly formed in the presence of O₂ in the mixture even at 573K, is carried out. Ru on the reduced state also carries out the dissociation of H₂, but at a slower rate, partially oxidizes to Pt²⁺ Ru_{0.5}, even at 573K, which reduces the selectivity of the process. At the same time Au¹⁺ is easily reduced to Au⁰ according to the TPR data at 773-553K, and the copper oxide - Cu²⁺ to metallic copper. Ru or Cu were introduced into the catalyst in order to equalize the rate of C₂ formation with rates of oxygen activation for the oxidation of C₂ into CO. Oxidation of C₂ can occur on Pt due to the structural oxygen of PtO₂ which is slow. Here it is believed that the surface. The oxygen of various acids can be involved in the oxidation of CO to C₂ particles. The introduction of CeO₂ accelerates the dissociation of O to PtO, but the O from PtO is not enough. As the copper is predominant in the composition of Ni-Cu-Ce oxides, it is likely the rate of oxidation of carbon particles exceeds the rate of their formation. Carbon accumulation does not occur: the balance of carbon is equal to 100%; due to this fact. The presence of Pt-Ru and Ni-Cu oxides in Pt-Ru and Ni-Cu-Ce contacts greatly facilitates the interaction of C₂ with C₂ because of the possible separate adsorption and activation of oxygen on different parts of the cluster: C₂⁺ or Pt²⁺(Ni²⁺) and O₂ on Ru²⁺(Cu²⁺), as well as because that the exchange in the oxides and the transfer of electron proceed at high speeds.

The ability of Ni-Cu-Ce catalyst to absorb the formed atomic hydrogen in its volume is important for the mechanism of SCO of CH₄. It is known that the dissolved hydrogen is released from Ni, Fe, Co etc. their alloys in those parts of the surface where chemisorbed strongly-bonded hydrogen. It occurs at T_{max} = 1123-1163K in the case of Ni-Cu-Ce catalyst.

Significance

Thus, the new thermo-stable high-performance catalysts for selective production of synthesis gas from methane were developed, the relationship of physical and chemical characteristics of catalysts with their catalytic properties was revealed, and the mechanism of the process was proposed.