



CHISA
2016
PRAGUE
PRES 2016

22nd International Congress of Chemical
and Process Engineering
CHISA 2016

19th Conference on Process Integration,
Modelling and Optimisation for Energy
Saving and Pollution Reduction
PRES 2016

organized by

ČSCHI ČESKÁ SPOLEČNOST CHEMICKÉHO INŽENÝRSTVÍ
CZECH SOCIETY OF CHEMICAL ENGINEERING

Prague, Czech Republic, 27 August - 31 August 2016



CD-ROM - ABSTRACTS

Development of composite materials by combustion synthesis for catalytic methane reforming into hydrocarbons and synthesis-gas

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Processing of natural gas into motor fuel in the XXI century has become one of the major problems of oil and gas chemistry. Currently, only steam methane reforming process is implemented in the industry for the production of synthesis gas. However, the processes of partial oxidation and carbon dioxide reforming of methane, which are not implemented in practice and are performed at high temperatures, attract a great attention of researchers in recent years. Resistant to temperature extremes and thermal shocks is one of the most important requirements for this kind of catalysts. It is desirable to have a high thermal conductivity to reduce the possibility of local overheating.

Works on research of intermetallic compounds of transition metals as a contact mass for the conversion of methane were carried out. The method of self-propagating high temperature synthesis (SHS) was used for the synthesis of catalysts. Catalysts of this type are characterized by thermal stability, mechanical strength and high thermal conductivity. SHS is a heterogeneous combustion process, which proceeds without the participation of oxygen with low energy consumption, high efficiency and rapidity. Self-propagating mode of chemical interaction is realized at local initiation, which moves along the mixture. In this case, almost no gas is released. The very high temperature develops in the reaction zone.

The catalysts of oxidative and carbon dioxide reforming of methane were prepared by SHS method from powder mixtures of metal oxides. Self-propagating combustion wave was initiated after pressing the batch and preheating to 400-600°C. The temperature of the combustion front has evolved to 830-1150°C, the specific surface area of the synthesized catalyst decreased to 0.5-0.8 m²/g, and the temperature operating range of catalyst began from 700°C. Experiments on the catalytic reforming were carried out on flow type installation at atmospheric pressure in a tubular quartz reactor with a fixed catalyst bed.

Mixtures of salts (Ni(NO₃)₂ - Co(NO₃)₂ - Al(NO₃)₃ - Mg(NO₃)₂) are used for the synthesis of catalysts. The reactions resulting in the formation of spinels NiCo₂O₄, Co₂AlO₄ and CoAl₂O₄ and intermetallic compounds AlCo, AlNi₃ occur at preparation of samples by solution combustion synthesis. Figure 1 presents data on the catalysts with 50% Co, which show that the magnesium ions are almost completely replaced by cobalt ions in the MgAl₂O₄ spinel. As a result, the CoAl₂O₄ and Co₂AlO₄ spinels are formed in the reaction products.

Investigation of the activity of catalysts based on the initial mixture of Ni(NO₃)₂ - Co(NO₃)₂ - Al(NO₃)₃ - Mg(NO₃)₂ produced in the solution combustion synthesis process was carried out in the reaction of carbon dioxide conversion of methane. 100% methane conversion at 750°C was carried out on the catalyst with 47% Ni(NO₃)₂, whereas the conversion of CO₂ reached 81.7% at a temperature of about 900°C. Hydrogen yield reached 99.2%, yield of CO - 99.1% in the ratio of H₂/CO = 1.2. The activity corresponded to 0.96 mol H₂/g Cat × h and 0.78 mol CO/g Cat × h.

Tests have shown that the maximum conversion of CO₂ at 750°C was observed on the catalyst with 50% Ni(NO₃)₂ in the initial mixture. Catalysts with 50% Co(NO₃)₂ have

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maximum activity by CO and H₂. 100% conversion of CH₄ and CO₂, and 100% yield of H₂ and CO at a ratio of H₂/CO = 0.9 - 1.2 and the activity of 1.70 mol H₂/g Cat × h and 1.47 mole CO/g Cat × h observed with increasing of space velocity on the catalyst with 50% of Co(NO₃)₂ in the starting material. However, the catalysts with 50% Co(NO₃)₂ in the starting material have insufficient stability over time due to coking, associated with the formation of the NiAl₂O₄ spinel. Thus, the lower the concentration of spinel, the higher the stability of catalyst over time.

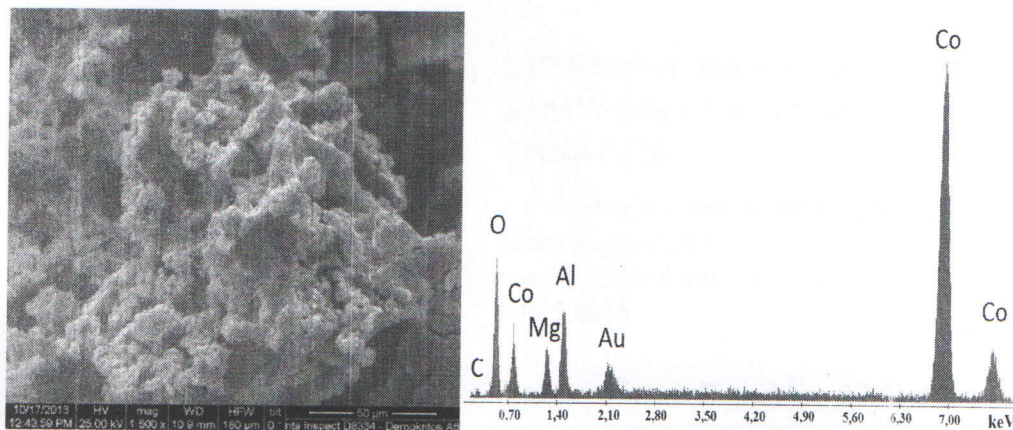


Figure 1. Electron-microscopic picture and results of chemical analysis (EDS spectrum) of catalyst 50% Co(NO₃)₂ + 36,15% Al(NO₃)₃ + 13,85% Mg(NO₃)₂ + 37% urea from the area indicated on the image.

Stability of the catalyst with 50% Ni(NO₃)₂ depending on the time at a space velocity of 3300 h⁻¹ was investigated. It should be noted that the catalyst retained its high catalytic activity. At the end of the 8 h of CH₄ conversion was 92.6%, the conversion of CO₂ - 94.3%, yield of H₂ reached 91.9% and CO yield - 93.5%, the ratio of H₂/CO close to 0.9 and the activity per hydrogen was 6.05 mol H₂/g Cat × h, and the activity per CO - 6.10 mol CO/g Cat × h. This catalyst is needed regeneration after 8 h of continuous operation. The catalyst of similar composition is active and selective for the partial oxidation of methane to synthesis gas. The highest results were obtained on reduced catalyst samples.

Thus, effective catalysts for the production of synthesis gas from methane of natural gas as a result of studies have been developed. The modern method of self-propagating high temperature synthesis and solution combustion method were used for the synthesis of catalysts. XRD and scanning electron microscopy of samples with chemical analysis before and after catalysis indicated on single-phase of produced systems and the absence of significant changes in the phase composition after experiments. The activity of catalysts obtained in the solution combustion process was examined in carbon dioxide reforming of methane and partial oxidation of methane to synthesis gas.

The work was supported by the Ministry of Education and Science of the Republic of Kazakhstan (Grant No 0247/GF4).