

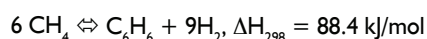
Direct catalytic conversion of biomethane with CO₂ and H₂O towards hydrogen and hydrocarbons

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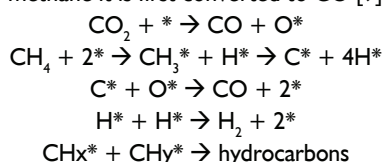
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Introduction

The direct catalytic conversion of methane (dehydrocondensation DHC) was intensively studied for the last decade by several groups of researchers, mostly from Japan [1–4], China [5], USA [6], and Hungary [7] and Russia. Following endothermic reaction represents methane direct conversion to benzene and hydrogen without participation of oxygen:

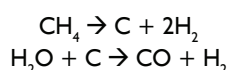


The most effective catalyst for this process is Mo/ZSM-5. Oxygen-free conditions used for this reaction result in high benzene selectivity (up to 80%). Nowadays, methane is mostly used for heating purposes, as a transport fuel (CNG) and for chemical synthesis. DHC is a promising process from the point of view of petrochemical feed stocks synthesis, hydrogen production for fuel cells and possible conversion of the waste and difficult accessible resources of natural gas like clathrate (methane hydrate), coal bed methane, post fermentation biogas, land fill and recently shale gas to liquid fuels, to chemicals and easily transportable liquid products. In this work DHC reaction of biomethane with content of 2% CO₂ (or CO) and 0.5% H₂O is presented, which are one of undesired byproducts of fermentation in biogas plant. DHC reaction is thermodynamically limited, thermodynamic equilibrium conversions for this reaction amount 12% methane conversion at 973K [8]. This work focuses on the application of biomethane contained CO₂ or/and CO, H₂O for synthesis hydrogen, benzene and other hydrocarbons. The content of CO₂ and H₂O in biomethane stream for his reaction was not optimized in this work. It is normally accepted that Brønsted acid sites, molybdenum species and their location, and the zeolite channel structure are important for catalytic performance. The molybdenum carbide species have been identified as the active center for methane activation, whereas surface acid sites are responsible for aromatization of the intermediates [1]. DHC reaction also leads to coke formation, causing catalyst deactivation. The presence of CO₂ and H₂O in biomethane stream is important in DHC reaction because they can act as a “scavenging” agents of carbon deposits. The mechanism is explained below. When CO₂ is added to methane it is first converted to CO [9]:



Here (*) is a vacancy, and O*, H*, CH_x*, CH_y* are chemisorbed surface species.

The addition of small amounts of water (up to 2.2%) was shown [10] to improve the activity and stability of 6% Mo/ZSM-5 catalyst. The positive effect of water is related to the following reactions:



Where C stands for carbon in the carbonaceous residues.

Recently the reformer with 6% Mo/ZSM5 was applied in biogas demonstration plant on Hokkaido in Japan. 200 Nm³/day of biogas was reformed, and 134 Nm³/day of hydrogen and 8.6 l/day of benzene were

produced [11]. Moreover, to control coking and to regenerate the catalyst for the dehydroaromatization reaction, hydrogen was circulated through the catalyst for 1 h every 24 h, as a result, the formation rates of hydrogen and benzene were kept for a long time [11]. Unreacted methane was circulated through catalyst bed after separation in membrane filter. We have to remember that reaction is thermodynamically limited up to 12% of conversion of methane.

Experimental

Mo and Re/H-ZSM5 catalysts were prepared from commercial zeolite NH₄ZSM-5 (SiO₂/Al₂O₃ = 40; surface area, 421 m²/g; Tosoh Co.). H-type of ZSM-5 (H-ZSM-5) was obtained by calcinations of ammonium form of the zeolite at 773K for 5h. The resulting material was used for preparation of catalysts. Mo or Re/H-ZSM5 catalyst containing 10 wt% of metal was prepared by incipient wetness impregnation of H-ZSM5 with an aqueous solution of (NH₄)₆Mo₇O₂₄ × 4H₂O (Merck., purity 99.9%) or NH₄ReO₄, respectively. The resulting material was dried at 393K overnight and calcined at 773K for 5h. The loading amount of 10% Re/H-ZSM5 and 10%Mo/H-ZSM5 after calcinations was quantitatively measured by ICP analysis and amounted to 5 and 6 wt%, respectively.

The catalytic tests were carried out at 0.3 MPa under flowing a feed gas mixture of methane/Ar with 2% CO₂ and 0.5% H₂O in a continuous flow system with a quartz reactor of 8 mm i.d. charged with 0.33 g of catalyst pellets of 20–42 mesh in flow of He (35 ml/min) and reduced at pure H₂ (35 ml/min) at 583K for one hour before reaction. The feed gas mixture of 90% CH₄ (including CO₂ and H₂O) and 10% Ar (as an internal standard) was introduced into the reactor at 15 ml/min (space velocity of methane = 2500 ml g-cat⁻¹ h⁻¹) through a mass flow controller (Bronkhorst hi-tech) after flashing with He at 973K for 30 min. Hydrocarbon products including C₂–C₄ alkanes (and/or alkenes) and condensable C₆–C₁₂ aromatics such as benzene, toluene, xylene, naphthalene, and methylnaphthalene in a sampling loop of a six-way sampling valve heated at 533K were analyzed by an on-line FID gas chromatograph and separated on a Porapak-P column. Other products such as H₂, Ar, CO, CH₄, and CO₂ were analyzed by another on-line TCD gas chromatograph with an activated carbon column. Using an internal standard analyzing method of 10% v/v Ar in the feed gas, the conversion of methane, selectivity of hydrocarbon products, and amount of coke formed on the catalysts were evaluated according to the mass balance for carbon.

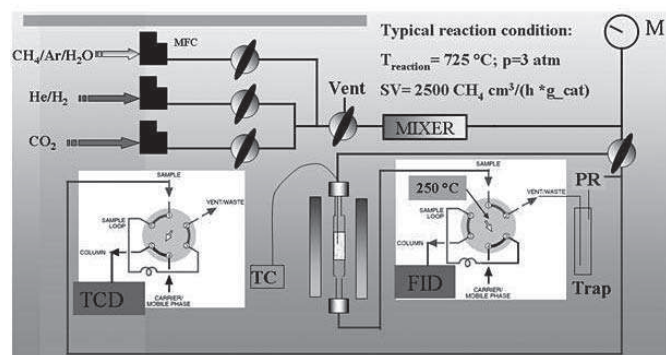


Fig.1. The scheme of flowing apparatus

Results and Discussion

Figure 2 shows catalytic performance of Mo and Re/H-ZSM5 in the presence of CO₂ and H₂O and without these oxidants only for Re/H-ZSM5 (Fig. 2c) in the DHC reaction of methane at 998K under 0.3MPa. Conversion of methane in the range 9 ÷ 10% on Mo or Re/H-ZSM5 in the presence of oxidants showed high stability and selectivity towards benzene, for Mo catalyst the highest activity in benzene production was observed. On the other hand Re catalysts possessed higher activity in naphthalene production. It is worth to notice that selectivity to coke formation was decreasing during all tests for Mo and Re catalyst as well. It is easy to observe that the change in coke selectivity is related with selectivity towards benzene. The decrease in selectivity of coke compensates the increase in selectivity towards benzene. There's no doubt that coke deposits block the pore mouths regions of zeolite with time on stream. The effect of CO₂ (and possibly H₂O) is similar to that of CO studied by Ohnishi et al. [1] with isotopic carbon oxide ¹³C. About 80% of carbon atoms in the formed benzene were ¹³C atoms. The amount of the carbonaceous deposits with high oxidation temperature (T > 500 °C) was found to decrease in the presence of CO. Probably with using CO₂ and H₂O in methane stream we observe the same effect. The reaction of methane without oxidants (Fig. 2c) shows unstable work of catalyst, increasing amount of C2 hydrocarbons with decreasing at the same time amount of benzene.

The following conclusions can be made on the basis of the above-presented results. Methane DHC reaction can be carried out over Mo and Re/ ZSM-5 with benzene selectivity 60 ÷ 80% and total methane conversion up to 12%. DHC reaction can be considered as a process for rational utilization of the natural gas, oil-associated gas, post processing biomethane and others. It is also a simply method for valorization of low value and difficult for exploration sources of methane e.g. coal bed methane, which is causing death accidents of miners.

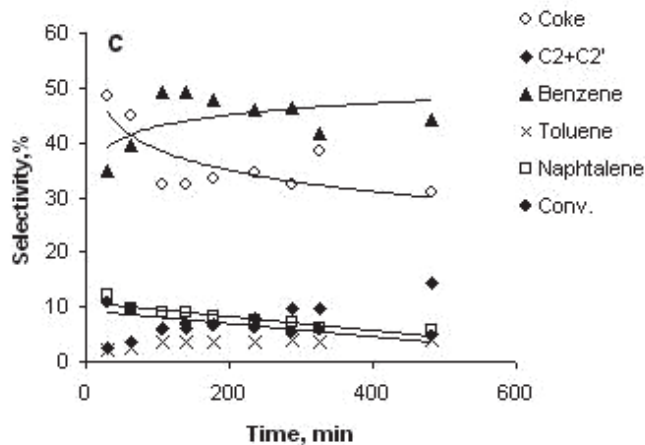
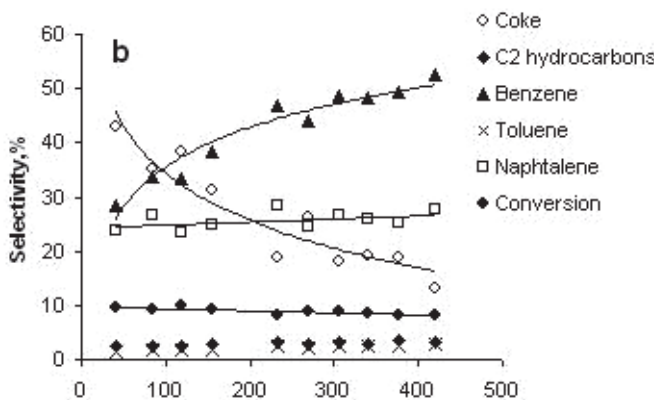
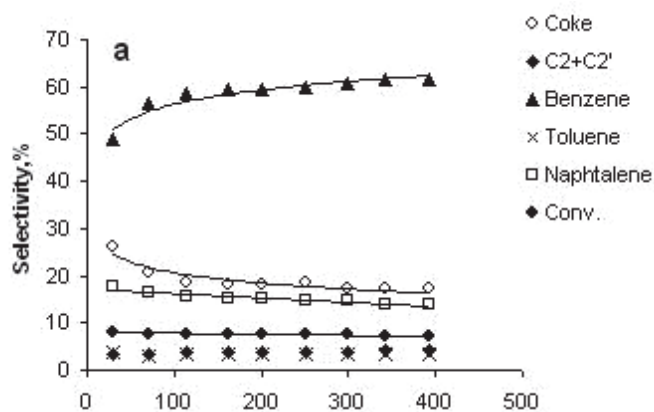


Fig. 2. Selectivity and conversion at 998 K, 0.3 MPa on (a) 10% Mo/ZSM-5 catalyst with CO₂ (2%) and H₂O (0.5%) in methane stream, (b) 10% Re/ZSM-5 catalyst with CO₂ (2%) and H₂O (0.5%) in methane stream, (c) 10% Re/ZSM-5 catalyst without CO₂ and H₂O in methane stream. The molar ratio H₂/benzene at the end of reaction amounted 12, 14 and 13, respectively

Translation into English by the Author

Literature

- Ohnishi R., Liu S., Dong Q., Wang L., Ichikawa M.: J. Catal. 1999, **182**, 92.
- Shu Y., Ma H., Ohnishi R., Ichikawa M.: Chem. Commun. 2003, **86**.
- Malinowski A., Ohnishi R., Ichikawa M.: Catalysis Letters 2004, **96**, 3-4, 141-146.
- Patent JP2002336704 Japan Steel Works LTD, 26 Nov. 2002, Ichikawa M., Ohnishi R., Malinowski A., Ikeda K., Yagi K.: The European Patent Office: <http://ep.espacenet.com>.
- Shu Y., Xu Y., Wong S., Wang L., Guo X.: J. Catal. 1997, **170**, 11.
- Weckhuysen B.M., Wang D., Rosynek M.P., Lunsford J.H.: J. Catal. 1998, **175**, 347.
- Solymsi F., Cserényi J., Szöke A., Bánsági T., Oszkó A. J.: J. Catal. 1997, **165**, 156.
- Wang D., Lunsford J.H., Rosynek M.P.: J. Catal. 1997, **169**, 347.
- Liu Z., Nutt M.A., Iglesia E.: Catal. Lett. 2002, **81**, 271.
- Liu S., Ohnishi R., Ichikawa M.: J. Catal. 2003, **220**, 57.
- Shudo Y., Ohkubo T., Hideshima Y., Akiyama T.: Int. J. of Hydrogen Energy 2009, **34**, 4500.

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