SiC mixed catalysts for hydrogen and benzene production via methane non-oxidative aromatization

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ABSTRACT

Novel bimetallic catalysts prepared by incipient wetness co-impregnation of a ZSM-5 zeolite support were formulated and tested for use in the methane non-oxidative aromatization to hydrogen and aromatic species. A novel 100% hydrogen-selective custom designed catalytic membrane reactor was utilized. In order to increase catalyst efficiency and lifetime, α-SiC size 2μm crystallites were added in order to increase thermal distribution for this highly endothermic reaction (600-750°C). *In-situ* Fourier transform infrared spectroscopy (FTIR) analysis of the reactants and products as well as X-ray photoelectron spectroscopy (XPS) of fresh, activated, spent, unpromoted and promoted (with α-SiC) Mo/ZSM-5 catalysts have been performed. Conversion data will also be provided.

This reaction is considered a novel technology. Most of the literature concentrates on the production of benzene rather than hydrogen using these forms of catalysts. Modifications to produce high purity fuel cell grade hydrogen along with benzene are considered; these modifications include the technology, the design of the test-bed and the reactor itself. The balanced chemical reaction is shown below. The reaction is highly endothermic, operating in the temperature range between 600-850°C.

$$6CH_4 \xrightarrow{Mo/HZSM-5} C_6H_6 + 9H_2 (\Delta H = 523 kJ/mol)$$

Oxygen-free methane aromatization was carried out over three different types of catalysts: Mo/ZSM-5, Ru-Mo/ZSM-5 and Pd-Mo/ZSM-5 in a catalytic membrane reactor. The 0.5% Ru-3% Mo/ZSM-5 catalyst, prepared by incipient wetness co-impregnation, considered highly selective toward benzene production [1]. Methane aromatization was evaluated under two sets of conditions: (i) without hydrogen permeation in a fixed-bed conventional catalytic reactor (CR) and (ii) with hydrogen permeation in a catalytic membrane reactor (CMR) [1].

The effect of adding SiC single crystalline particles in the catalyst matrix will be presented. This will include XPS analysis of fresh, activated and spent catalyst as well as methane conversion to hydrogen and other high H/C ratio hydrocarbons. A proposed mechanism will also be presented.

REFERENCES

1. M. Iliuta and F. al Larachi, *Methane Nonoxidative Aromatization over Ru-Mo/HZSM-5 in a Membrane Catalytic Reactor, Ind. Eng. Chem. Res.* **41**, 2371-2378 (2002).

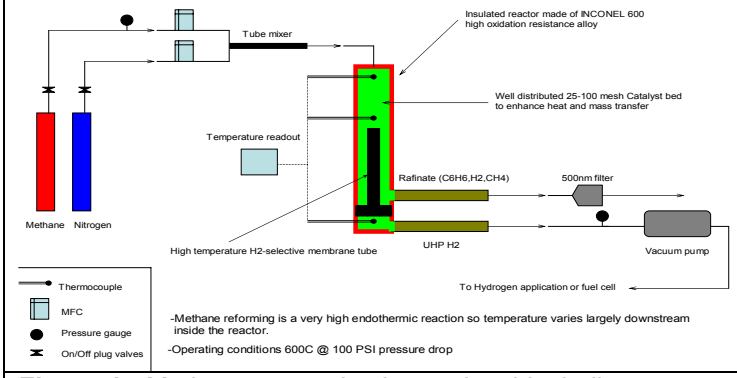


Figure 1: Methane aromatization project block diagram.

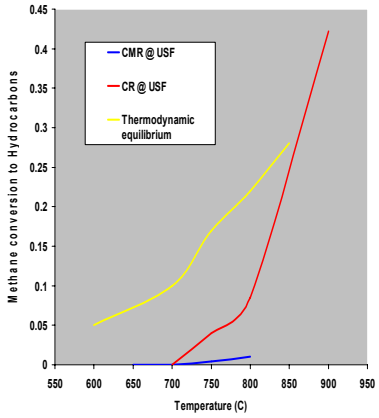


Figure 2: Methane conversion to benzene VS. temperature using both fixed-bed catalytic and catalytic membrane reactors.

Mo in a high oxidation state (+6) promotes
Heterolytic dissociation of C-H bond

$$CH_4 \xrightarrow{Heterolytically} CH_3^+ + H^-$$

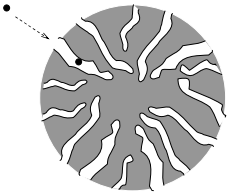
Catalytically active center

$$CH_2 = MoO_3 \qquad CH_2 = MoO_3$$

dimerization

$$C_2H_4$$

Methane molecule



ZSM-5 Zeolite particle

Reaction intermediate

Figure 3: A proposed mechanism of the methane reaction.

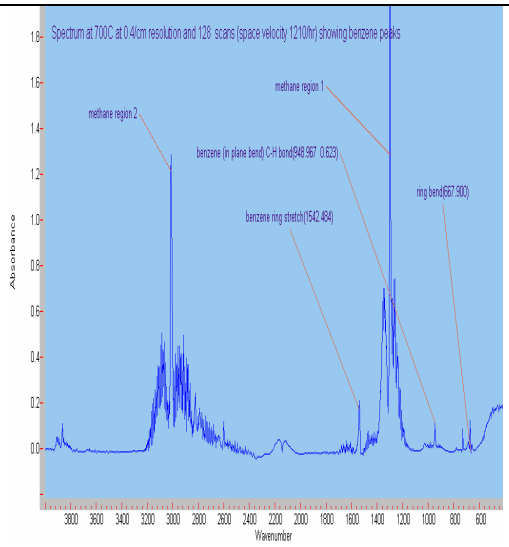


Figure 4: An FTIR spectrum at 700°C showing methane and benzene peaks.