Journal of Natural Gas Chemistry

Journal of Natural Gas Chemistry 12(2003)123–134

SCIENCE PRESS

Characterization and Activity of Cr, Cu and Ga Modified ZSM-5 for Direct Conversion of Methane to Liquid Hydrocarbons

Nor Aishah Saidina Amin[1,*], Didi Dwi Anggoro[1,2]

1 Faculty of Chemical and Natural Resources Engineering, Universiti Teknologi Malaysia, 81130 Skudai, Johor, Malaysia;
2 Department of Chemical Engineering, University of Diponegoro, 23589 Semarang, Indonesia

[Manuscript received April 02, 2003; revised May 09, 2003]

Abstract: Direct conversion of methane using a metal-loaded ZSM-5 zeolite prepared *via* acidic ion exchange was investigated to elucidate the roles of metal and acidity in the formation of liquid hydrocarbons. ZSM-5 (SiO_2/Al_2O_3=30) was loaded with different metals (Cr, Cu and Ga) according to the acidic ion-exchange method to produce metal-loaded ZSM-5 zeolite catalysts. XRD, NMR, FT-IR and N_2 adsorption analyses indicated that Cr and Ga species managed to occupy the aluminum positions in the ZSM-5 framework. In addition, Cr species were deposited in the pores of the structure. However, Cu oxides were deposited on the surface and in the mesopores of the ZSM-5 zeolite. An acidity study using TPD-NH_3, FT-IR, and IR-pyridine analyses revealed that the total number of acid sites and the strengths of the Brönsted and Lewis acid sites were significantly different after the acidic ion exchange treatment. Cu loaded HZSM-5 is a potential catalyst for direct conversion of methane to liquid hydrocarbons. The successful production of gasoline *via* the direct conversion of methane depends on the amount of aluminum in the zeolite framework and the strength of the Brönsted acid sites.

Key words: characterization, activity, modified ZSM-5, methane, direct conversion, liquid hydrocarbons

1. Introduction

Direct catalytic conversion of methane, the principal component of natural gas, to liquid fuels and chemicals of commercial importance remains an intensely sought-after goal. Many researchers have studied the applicability of HZSM-5 and modified ZSM-5 zeolites to the conversion of methane to liquid hydrocarbons [1–9], but the results of their research are still confined to low conversion and selectivity.

The direct partial oxidation of methane to liquid hydrocarbons was reported by Han *et al.* [1,2]. However, methane conversion and liquid hydrocarbon selectivity were too low, and the major product was CO_x (CO and CO_2). They concluded that only Cu, Ni, Zn and Ga-ZSM-5 catalysts could produce liquid hydrocarbons from methane oxidation if the methane or ethane dehydrogenation and olefin oxidation functions of the metals are in balance.

An important intermediate step in the methane and oxygen reaction to produce liquid fuels is the formation of ethylene. Ethylene is then converted to benzene or liquid hydrocarbons over the zeolite support through acid catalyzed oligomerization and cyclization reactions [4–8]. For ethylene oligomerization over ZSM-5, both Brönsted and Lewis acid sites were observed to be active, although Lewis sites have a small advantage in suppressing coke formation [9]. The strong Brönsted acid sites eliminated coke or aromatic formation and allowed only oligomerization to proceed [9]. The amount of framework aluminum is related to the number and strength of the Brönsted acid sites [10,11], an important criteria in ethylene conversion to liquid hydrocarbons [11].

In another study, Pak *et al.* [12] reported a reaction of methane with oxygen that led to a high liquid

* Corresponding author. Tel: 607-5535588; Fax: 607-5581463; Email address: r-naishah@utm.my