Direct oxidation of methane to value-added products using N_2O over Fe-ZSM-5, Fe-Beta and Fe-FER catalysts

Guangyu Zhao, Eric Kennedy*, Michael Stockenhuber
The University of Newcastle, Callaghan, NSW, 2308, Australia
**Corresponding author: Eric.Kennedy@newcastle.edu.au*

Abstract:

Direct oxidation of methane to C_1-oxygenates (methanol and formaldehyde) has received extensive attention in the field of chemical engineering and catalysis. Currently, the primary direct methane oxidation process is conducted at either high temperatures (600°C–900°C) or low temperatures (< 200°C), and suffers from the drawbacks of unsatisfactory selectivity. In this study, characterization and activity of Fe-ZSM-5, Fe-Beta and Fe-FER catalysts were investigated, aiming to study the feasibility of producing C_1-oxygenates in the gas phase catalytically at moderate temperature (350°C) and in an effort to clarify the reaction mechanisms involved.

Keywords: direct methane oxidation, C_1-oxygenates, active sites.

1. Introduction

In past decades, the direct oxidation of methane to higher value products has been widely studied[1]. However, direct oxidation of methane at high temperature (600°C–900°C) by oxygen (usually in air) produces C_1-oxygenates at low yields, typically lower than 4.0%[2], and addition of NO_X to the reaction was reported to decrease reaction temperature slightly but has little influence on selectivity and yield of product [3]. Methane conversion under mild conditions (< 200°C) could enhance selectivity of C_1-oxygenates, but the process has not been developed which can be considered to economically viable, with a sufficiently high methanol selectivity or in a closed catalytic cycle[4]. Therefore, methane oxidation under moderate temperatures (350°C) was carried out in this study, in an effort to produce methanol and formaldehyde in gas phase catalytically.

2. Experimental

Helium, N_2O and methane were fed in a stainless steel tubular reactor continuously with a ratio of 65:28:7 at 350°C, and gas products were analyzed by online Varian micro GC and Shimadzu IR. In situ FTIR, Nitrogen adsorption measurements, TPD and CO chemisorption were used to characterize involved catalysts. All the catalysts were prepared by incipient wetness impregnation method with 2.0% of iron.

3. Results and discussion

As shown in Table 1, iron dispersion of the catalysts ranged from 14.0%–16.0%, and nitrogen adsorption measurements results indicated that the order of pore size of the catalysts is Fe-Beta>Fe-FER>Fe-ZSM-5.

To obtain the specific iron species on the catalysts, IR spectroscopy of NO adsorption was applied and a comparison of the spectra of the catalysts is presented in Fig. 1. Two Fe-related bands were observed over Fe-FER at 2186, 1870 with shoulders at 1912, 1896 and 1820 cm^{-1}. According to published data, the band at 2195 cm^{-1} assigned to NO^{δ}_2 which resulted from oxidation of NO by oxidized iron sites[5]. Bands at 1916 and 1816 cm^{-1} are normally assigned to di-nitrosyl on isolated Fe^{2+} sites[6]. For the primary band at 1870 cm^{-1} with shoulder at 1896 cm^{-1}, G. Mul *et al.* assigned a band at 1874 cm^{-1} with a shoulder at 1892 cm^{-1} to NO adsorbed on extra-framework Fe-O-Al species[7], which are suggested to be the active sites of N_2O decomposition and methanol generation[8]. However, the shoulder around 1896 cm^{-1} is less prominent for the Fe-Beta and Fe-ZSM-5 catalysts.

Furthermore, methane conversion, N_2O decomposition and products selectivity over Fe-ZSM-5, Fe-Beta and Fe-FER were compared at 350°C. As shown in Table. 1, Fe-FER obtained 2.0% of methane conversion and 13.4% of N_2O decomposition, which were the highest among the three catalysts. In addition, methanol and formaldehyde were produced under these experimental conditions, and the selectivity of C_1-oxygenates over Fe-FER, Fe-Beta and Fe-ZSM-5 were 31.6%, 11.2% and 7.8%, respectively. The results confirmed that Fe-FER contained more extra-framework Fe-O-Al species and hence enhanced N_2O decomposition and methanol generation. It should be noted that the selectivity of ethylene over Fe-ZSM-5 reached to 31.1%, which was much higher as compare to that over Fe-FER and Fe-Beta. It is asserted that ethylene was generated via the methanol to olefins (MTO) reaction scheme. According to Khadzhiev *et al.*, appropriate pore size and a low concentration of Lewis sites in the catalysts were the two key factors for the MTO reaction[9]. In comparison with other catalysts, Fe-ZSM-5 has smaller pore size as shown in Table. 1, and lower Lewis sites which can be inferred from Fig. 2, and hence resulted in higher ethylene selectivity.

Table 1. Textual properties, iron dispersion and reaction results over the catalysts

	Fe-ZSM-5	Fe-FER	Fe-Beta
Pore size (nm)	4.3	6.2	8.4
Iron dispersion (%)	14.0	16.0	14.5
Methane conversion (%)	1.4	2.0	1.3
N_2O decomposition (%)	7.4	13.4	9.2
selectivity of C_1-oxygenates	7.8	31.6	11.2
Selectivity of ethylene	31.1	2.0	2.0

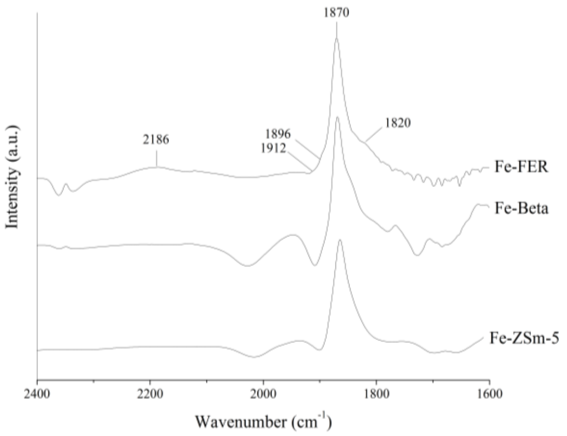

Figure 1. . FTIR spectra of NO adsorption on the catalysts

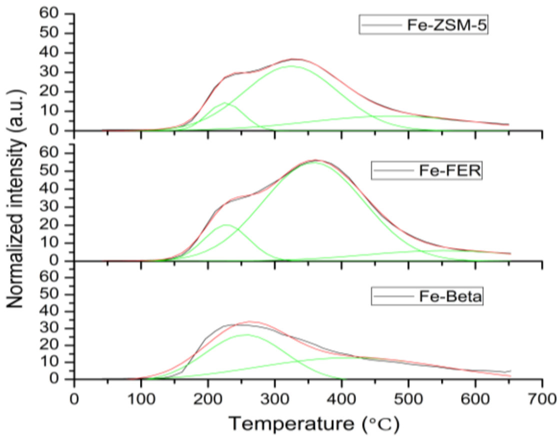

Figure 2. Normalized NH_3-TPD profiles of the catalysts

4. Conclusions

Methane conversion, N_2O decomposition and product selectivity were investigated over Fe-FER, Fe-Beta and Fe-ZSM-5 catalysts. Fe-FER attained the highest level of methane conversion and the highest C_1-oxygenates selectivity among these catalysts. The band of 1870 cm^{-1} with a shoulder at 1896 cm^{-1} in FTIR spectra indicated the existence of extra framework Fe-O-Al species on Fe-FER, and these species are critical for N_2O decomposition and methanol generation. Besides, textual properties and acid sites would also affect the selectivity of products.

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