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DIRECT PARTIAL OXIDATION (DPO) OF METHANE TO HIGHER HYDROCARBONS BY MODIFIED H-ZSM5 CATALYST

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Abstract

The oxidation of methane has been studied in a flow system as a function of the chemical composition of zeolite catalyst using nitrous oxide as oxidant. It is concluded that methanol is a primary oxidation product which may undergo further oxidation to formaldehyde and to carbon oxides. However, it may also undergo conversion over the acidic catalyst to higher hydrocarbons. Reaction with nitrous oxide resulted in the production of carbon oxides, methanol, formaldehyde, C_2- C_4, C_5- C_7 nonaromatics, and aromatics. The effect of Fe_2O_3 and Al_2O_3, with or without, over HZSM5 on products was studied.

Keywords: HZSM5, methane, higher hydrocarbons, partial oxidation

INTRODUCTION

Methane conversion to higher hydrocarbons has acquired great relevance in the past years because of the enormous surplus of natural gas in the world. Due to some characteristics of methane such as strong C-H bonds, its high symmetry and the absence of any functional groups, the activation of methane is not an easy process. Over the past decade indirect routes of conversion by obtaining syngas ($CO + H_2$) were the chosen way to produce hydrocarbons. HHC (higher hydrocarbons) can be obtained from syngas either directly (Fischer – Tropsch process) or through the steps of methanol synthesis (Mobil process) [1-3].

Direct conversion of methane into HHC and hydrogen is not thermodynamically allowed in a one-step reaction, because of a positive change of Gibbs free energy. So oxidants like oxygen or chlorine, have been used to lower the ΔG value, converting H_2 into more stable products (H_2O, HCl). However, in that case the first product of oxidative conversion of methane is methanol, which is convertible to higher hydrocarbons. One way to solve this problem is the application of a bifunctional catalyst with acid–base properties that would enhance methanol conversion into liquid hydrocarbons. HZSM5-Zeolite, whose activity in the synthesis of liquid hydrocarbons from methanol is well known [3], which was found to be active for the oxidation of methane by nitrous oxide at temperature of 570 K [4]. The effect of other catalyst and oxidants has been investigated earlier [4-8]. In this paper catalytic properties of HZSM5 with and without added Al_2O_3 and Fe_2O_3 is described in methane activation process.

EXPERIMENTAL

HZSM5-Zeolites with SiO_2/Al_2O_3 ratio of 80 was prepared according to standard procedure [9]. The synthesized samples were washed in distilled water, calcined in dry air at 823 K for 12 h. Decationization of zeolites was carried out by ion exchange using ammonium chloride solution followed by drying and calcinations of samples at 823 K for 8 h. To examine the iron oxide - zeolite for their catalytic properties the HZSM5 catalyst with 0.5%Fe was prepared by impregnation of HZSM5 catalyst with $Fe(NO_3)_3$ solution at pH=3, followed by drying of catalyst and calcinations for 3 h at 823 K. Also to examine the influence of the aluminum oxide over HZSM5-Zeolite, HZSM5 catalysts and FeHZSM5 were physically mixed by 35 wt.% Al_2O_3. These catalysts were prepared by pelletizing zeolite powders without binder at pressure of 5×10^2 atm. The pellets then were crushed and sized between sieves with 1.20 mm and 0.60 mm holes.

Catalytic tests were carried out in a stainless steel flow reactor, containing 6 cm^3 catalyst and operating at a total pressure of l atm. The reactor temperature was increased under nitrogen atmosphere and reaction carried out at 673 K and l atm in CH_4/ N_2O molar ratio equal to 3.077 and GHSV equal to 0.554 s^{-1}. No other reagents, diluents or gas promoters were used. Gas analysis was performed by on-line gas chromatography using a 3 m chromosorb–101 column in a temperature-programmed mode.

RESULTS AND DISCUSSION

The catalyst compositions used in this study are shown in Table 1. The variation of the methane conversion with time *vs*. the catalyst is shown in Fig. 1, which shows that the methane conversion was decreased rapidly with respect to time, while for Z_1 and Z_2 catalysts the conversion goes through a maximum. In comparison with Z_1 catalyst, the higher conversion of Z_2 catalyst at the beginning of the reaction can be related to the presence of Fe_2O_3. As methanol is a primary oxidation product from methane, it seems that the presence of Fe_2O_3 apparently lowers the activation energy of methane to methanol conversion:
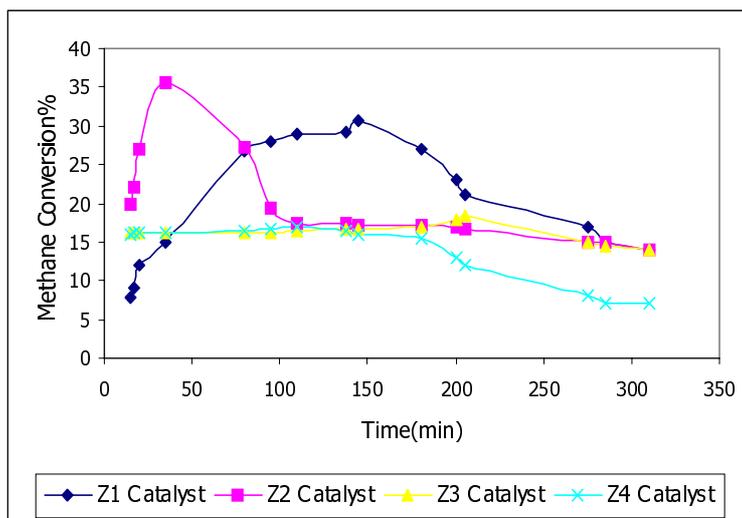
$$N_2O + Fe_2O_3 \longrightarrow N_2 + O.Fe_2O_3$$

$$R + O.Fe_2O_3 \longrightarrow RO + Fe_2O_3$$

Fig. 1. Variation of methane conversion with time for used catalysts
Condition: Temp.= 673 K ; P= 1 atm ; CH_4/N_2O=3.077 ; GHSV=0.554 s^{-1}

The higher oxidation activity of N_2O in the presence of Fe_2O_3 may increase the deactivation rate of Z_2 catalyst as compared to the Z_1 catalyst. As is shown in Fig. 1, the conversion for Z_3 and Z_4 proceedes more steadily, although the degree of conversion is less than for Z_1 and Z_2. This may be related to the presence of Al_2O_3, which was mixed with HZSM5 and resulted in the fall of catalyst activity.

Table 1

Catalysts composition

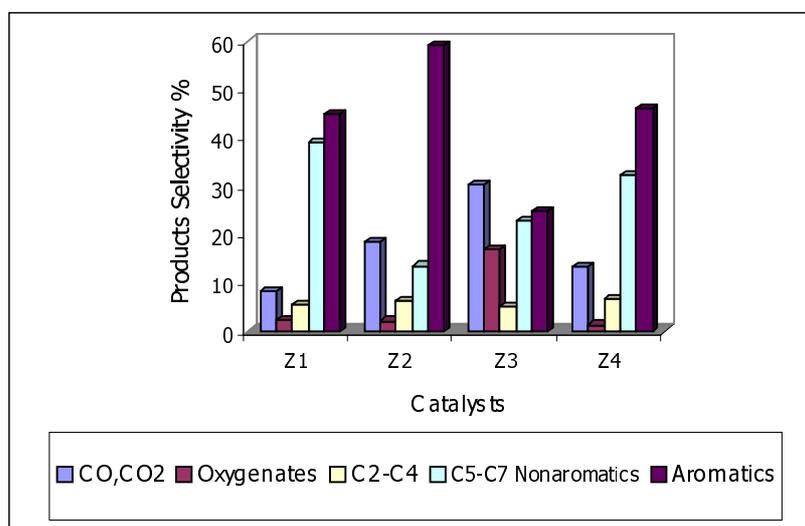| Catalyst	Composition of catalyst
Z_1	HZSM5
Z_2	FeHZSM5
Z_3	65 wt.% HZSM5+ 35 wt.%Al_2O_3
Z_4	65 wt.% FeHZSM5+ 35wt.%Al_2O_3

Fig. 2. Selectivity of products over the catalysts
Condition: Temp.= 673 K ; P= 1 atm ; CH_4/N_2O=3.077 ; GHSV=0.554 s^{-1}

Figure 2 displays the influence of the catalyst on the products. Apparently, the amount of oxygenates, such as CO_x, methanol and formaldehyde, increase greatly with addition of Al_2O_3 to HZSM5, as compared to pure HZSM5. This was anticipated because of the acidic sites of zeolite decreased upon addition of Al_2O_3. As is elucidated in Fig. 5, the reaction proceeds *via* methanol formation, and there are two reaction paths after methanol formation. The first path is the conversion to CO_x *via* formaldehyde and the second one is the conversion of methanol to higher hydrocarbon by acidic sites of zeolite. Methanol conversion to higher hydrocarbons was performed by acidic sites of zeolite *via* aromatization of light olefins (C_2-C_4). Also, as it was explained before [7], route 5 is considered to be a step, where methane is converted to CO_x *via* other

intermediates. Of stages 2 and 3, the latter was also increased and resulted in the formation of more oxygenated products, but addition of small amounts of Fe_2O_3 to this mixture (Z_4 catalyst) significantly decreases the selectivity to oxygenates. Therefore, it seems that the presence of Fe_2O_3 not only leads to an increase of conversion rate of methane to methanol, but also affects the conversion of methanol to HHC (Fig. 5. stage 2). In other words a comparison between Z_1 and Z_2 products shows that the presence of Fe_2O_3 increases the selectivity of CO_x and decreases the selectivity to C_5-C_7 products. The increase of CO_x production can be attributed to fast deactivation of the catalyst in the presence of Fe_2O_3. This phenomenon also reveals that free [O⁻] can be scavenged by hydrogen molecules and converts them to H_2O and therefore decreases the formation of C_5-C_7 products.

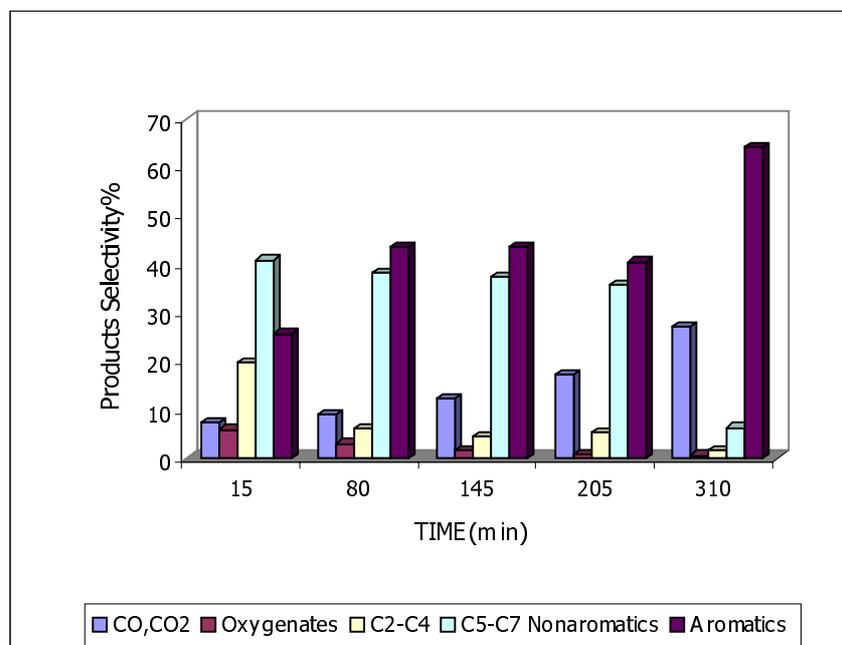**Fig. 3.** Variation of products selectivity with time over Z_1 catalyst
Condition: Temp.= 673 K ; P= 1 atm ; CH_4/N_2O=3.077 ; GHSV=0.554 s^{-1}

Figures 3 and 4 show the variation of production against time for Z_1 and Z_2 catalysts. In both catalysts, selectivity of CO_x increases fast, however the selectivity of C_5-C_7 products decreases, which is due to catalyst deactivation. The increase of the [O⁻] on the surface due to catalyst deactivation, attracts

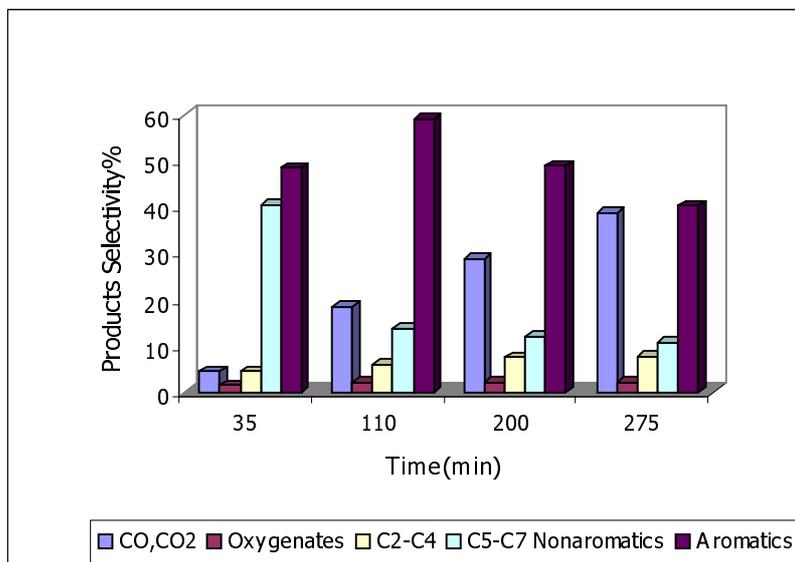**Fig. 4.**Variation of products selectivity with time over Z_2 catalyst
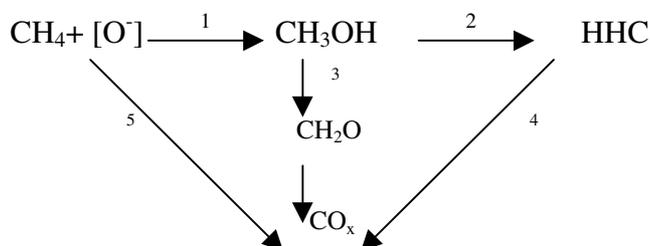Condition: Temp. 673 K ; P= 1 atm ; CH_4/N_2O=3.077 ; GHSV=0.554 s^{-1}

Fig. 5. Scheme of oxidative conversions of methane over ZSM5 catalysts

hydrogen ions, which were obtained from different processes and therefore reduces the selectivity of C_5-C_7 alkanes. However, excess surface of [O⁻] activates route 4 and therefore, reduces HHC production. The reduction of oxygenates selectivity for Z_1 catalyst indicates the significance of route 3 for CO_x production as compared with route 4, but the steady production of this compound on catalyst Z_2 may be attributed to the significance of path 2 to 4 in

CO_x production. From activation energy considerations, it seems that the presence of Fe_2O_3 makes path 2 to 4 more favorable, but due to the interaction of radical particles it seems that route 5 has a similar significance for both catalysts, while the decrease of the selectivity to aromatics formation in Z_2 catalyst compared to Z_1 catalyst supports this theory.

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