Catalytic Methane Conversion to Methanol on Cu-SSZ-13

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Abstract: Direct methane conversion to methanol is achieved catalytically using N_2O as oxidant at temperatures as low as 270 °C. The methanol production rates on Cu-SSZ-13 on a per gram basis was found to be more than twice the rate on Cu-mordenite and more than four times the rate on Cu-ZSM-5, reaching 33 μmol g^{-1} h^{-1} on Cu-SSZ-13 with a methanol selectivity of 40%.

Keywords: Cu-SSZ-13, methane activation, methane.

1. Introduction

Direct conversion of methane to chemicals and fuels has been a long-standing challenge for the field of catalysis. The large energy barrier for homolytic cleavage of the C-H bond of methane in contrast to the lower energy of the C-H bonds in the desired products—methanol and formaldehyde—renders the selective conversion of methane very difficult; facile over-oxidation of the products is unavoidable at the conditions where methane activation is possible. Copper exchanged zeolites (Cu-ZSM-5 [1] and Cu-mordenite [2,3]) were found to convert methane to methanol selectively following a 3-step cyclic process: (i) oxidation of the Cu-zeolite with O_2 at relatively higher temperatures (450 °C) to create reactive copper-oxo species, (ii) methane activation at moderate temperatures (120–200 °C) and (iii) admission of a solvent to extract methanol from the surface.

The ultimate goal for methane activation is to catalytically (at one step) and selectively convert methane into methanol. The temperature differences between the oxidation of Cu-zeolites and methane activation render the catalytic process difficult. In this study, we report successful activation of Cu-zeolites at temperatures lower than 300 °C using N_2O (thus preventing over-oxidation reactions to some point) and catalytic methanol production at ambient pressure using methane, N_2O and water vapor.

2. Experimental

SSZ-13 (Si/Al = 12) was synthesized using a protocol reported elsewhere [4]. Na-mordenite (Si/Al = 5) was purchased from Tricat (TZM 1011). NH_4-ZSM-5 (Si/Al = 11.5) was purchased from Zeolyst (CBV 2314). Copper (II) ion-exchange was performed by exchanging H- or Na-form of the zeolites in copper (II) acetate (Aldrich, 98% purity) aqueous solution at 25 °C for 12 h. The amount of copper (II) acetate in the solutions varied depending on the mass of the zeolite and targeted Cu/Al ratio [5]. The hydrated samples (0.300 ±0.005 g and particle size between 250 – 425µm) were tested for CH_3OH formation using a reactor system described elsewhere (ID = 7 mm).[6] CH_3OH was analyzed using a gas chromatograph (GC) (Agilent 7890A) with a flame ionization detector and a HP-PLOT Q column (Agilent19091P-Q04, 30 m x 0.32 mm x 0.02 mm). CO and CO_2 were analyzed using a thermal conductivity detector of Agilent 7890A with a HayeSep Q column (Agilent G3591-81121, 12 ft 1/8” 2 mm). Hydrated Cu- zeolites were saturated at 20 °C by 120 cm^3 min^{-1} $CH_4/N_2O/He/H_2O$ flow with designated compositions for 15 min. The feed mixture containing $CH_4/N_2O/He$ was diverted through a water-containing saturator kept at 25 °C. Temperature of the samples was increased to reaction temperatures with a heating rate of 5 °C min^{-1}.

3. Results and discussion

Catalytic experiments were conducted in the temperature range of 250–300 °C using a gas composition consisting of 30% CH_4, 30% N_2O and 3% H_2O (balance He). Steady state CH_3OH production rates were observed over Cu-SSZ-13 approximately 50 minutes after the desired reaction temperature was reached, no deactivation was observed for the duration of the measurements (up to 23 hours). CH_3OH, CO and CO_2 were observed as the main products of the catalytic CH_4 oxidation with CH_3OH selectivity between 16% and 24% for temperatures between 250 °C and 270 °C.

Table 1. Catalytic CH_4 conversion and methanol production data on Cu-SSZ-13, Cu-mordenite and Cu-ZSM-5^{a}

Sample	**Cu Concentration (g^{-1})**	**Temperature (°C)**	**CH_4 Conversion (%)**	**CH_3OH Rate (μmol CH_3OH g^{-1} h^{-1})**	**CH_3OH Selectivity (%)**
Cu-SSZ-13	0.50	250	0.016	12	24
Cu-SSZ-13	0.50	270	0.055	28	16
Cu-SSZ-13	0.50	300	0.75	55	2.3
Cu-SSZ-13	0.22	270	0.022	33	40
Cu-mordenite	0.17	270	0.013	10	24
Cu-mordenite	0.83	270	0.063	2	1
Cu-ZSM-5	0.54	270	0.67	6	0.3

a Standard reaction conditions: 0.300–0.005 g catalyst weight; feed 30% CH_4, 30% N_2O, 3% H_2O balance helium (30.4 kPa CH_4, 30.4 kPa N_2O, 3.2 kPa H_2O, 37.3 kPa He); flow rate: 120 cm^3 min^{-1}, WHSV = 19 650 g_{feed} g_{cat}^{-1} h^{-1}

In addition to the observed higher methanol selectivity values, methanol production rate on Cu-SSZ-13 was observed to be more than four times than the rate on Cu-ZSM-5 at 270 °C. For Cu-SSZ-13, a decreasing trend in methanol selectivity was observed with increasing reaction temperatures. In addition to the decreased temperatures, increased H_2O pressure, increased methane pressure and decreased N_2O pressure were observed to result in increased methanol selectivity values [5]. Increasing N_2O pressures resulted in increased CH_4 conversion but decreased methanol selectivity indicating a larger rate order of N_2O for over-oxidation of methanol.

4. Conclusions

Catalytic methanol production from methane at low temperatures and ambient pressure on Cu-SSZ-13 was demonstrated here. Catalytic methanol production yields reaching 55 μmol g^{-1} h^{-1} are promising for ambient pressure. Observed higher methanol selectivity values for higher methane and H_2O pressures and lower N_2O pressures imply possibility of achieving higher methanol selectivity values with parameter optimization studies. For Cu-SSZ-13 and Cu-mordenite, lower Cu concentrations resulted in both higher methanol production rates and higher methanol selectivity values, indicating the importance of the design of the catalysts to prevent unwanted over-oxidation reactions.

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