Reaction of nitrous oxide with methane to synthesis gas: A thermodynamic and catalytic study

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ABSTRACT

The aim of the present study is to explore the coherence of thermodynamic equilibrium predictions with the actual catalytic reaction of CH_4 with N_2O, particularly at higher CH_4 conversions. For this purpose, key process variables, such as temperature (300 °C–550 °C) and a molar feed ratio ($N_2O/CH_4 = 1$, 3, and 5), were altered to establish the conditions for maximized H_2 yield. The experimental study was conducted over the Co-ZSM-5 catalyst in a fixed bed tubular reactor and then compared with the thermodynamic equilibrium compositions, where the equilibrium composition was calculated via total Gibbs free energy minimization method.

The results suggest that molar feed ratio plays an important role in the overall reaction products distribution. Generally for N_2O conversions, and irrespective of N_2O/CH_4 feed ratio, the thermodynamic predictions coincide with experimental data obtained at approximately 475 °C–550 °C, indicating that the reactions are kinetically limited at lower range of temperatures. For example, theoretical calculations show that the H_2 yield is zero in presence of excess N_2O ($N_2O/CH_4 = 5$). However over a Co-ZSM-5 catalyst, and with a same molar feed ratio (N_2O/CH_4) of 5, the H_2 yield is initially 10% at 425 °C, while above 450 °C it drops to zero. Furthermore, H_2 yield steadily increases with temperature and with the level of CH_4 conversion for reactions limited by N_2O concentration in a reactant feed. The maximum attainable (from thermodynamic calculations and at a feed ratio of $N_2O/CH_4 = 3$) H_2 yield at 550 °C is 38%, whereas at same temperature and over Co-ZSM-5, the experimentally observed yield is about 19%.

Carbon deposition on Co-ZSM-5 at lower temperatures and CH_4 conversion (less than 50%) was also observed. At higher temperatures and levels of CH_4 conversion (above 90%), the deposited carbon is suggested to react with N_2O to form CO_2.

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1. Introduction

N_2O in the troposphere is a comparatively non-reactive molecule, however, its presence in the stratosphere layer (12–50 km, from the surface of earth) can actively absorb infrared radiation, and is more potent as compared to most common greenhouse gases, CH_4 and CO_2 [1,2]. For reference, N_2O global warming potential (GWP) is 15 and 310 times that of CH_4 and CO_2, respectively [3]. The atmospheric concentration of N_2O in pre-industrial age was roughly constant at about 270–288 ppbv [4]. However, present-day human activities, such as use of fertilizers, chemical

productions, fuel combustion (both stationary and mobile), and sewerage treatment are releasing more than 7 million ton of N_2O per year into environment [5]. The photolysis of N_2O leads to the production of stratospheric NO_x, and subsequently results in the chemical destruction of O_3 (ozone) molecule [6–8].

The catalytic reduction of N_2O with CH_4 is an extensively studied reaction [3,4,9]. CH_4 is a major component of natural gas and is commercially used for synthesis gas production [10]. On the other hand, concerns over feedstock supply have maintained interest in processes that are aimed at the production of synthetic fuels. One approach to produce synthetic fuels is via synthesis gas production. Large quantities of natural gas are potentially available for production of synthetic fuels, but the selective catalytic conversion of natural gas (which is primarily CH_4) remains elusive. The conversion of CH_4 into valuable chemicals is also a major driver of

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significant research programs [11,12]. While N_2O supply is limited compared to natural gas, still significant amounts of N_2O are found as a by-product of adipic acid manufacturing, ammonium nitrate, and nitric acid production. N_2O emission as in the mentioned manufacturing processes is of sufficient concentration to be used as an oxidant.

As a whole, CH_3OH, CH_2O, C_2H_6, C_2H_4, and H_2 are valuable chemicals that can be formed from CH_4 [13]. A number of research groups are focussing their research on the development of catalysts for direct (bypassing synthesis gas production) conversion of CH_4 to fuels and chemicals [14]. On the other hand, there are various approaches to indirect conversion methods, in which CH_4 is first converted into synthesis gas which is then transformed into various useful chemicals [15].

Synthesis gas ($CO+H_2$) is used for the production of valuable chemicals and fuels [16,17]. There are three well established technologies, catalytic partial oxidation, steam reforming and auto-thermal reforming, for the conversion of natural gas to synthesis gas [18]. Among these technologies, catalytic partial oxidation and auto-thermal reforming of CH_4 are regarded as more energy efficient technologies [19–23]. The catalytic partial oxidation of CH_4 or other hydrocarbons is a reaction operated under oxygen deficient conditions [24], while auto-thermal reforming of CH_4 is a combination of combustion/partial oxidation and steam reforming reactions [25]. In auto thermal reforming, the energy required for the reaction of CH_4 and steam is supplied by CH_4 combustion (exothermic reaction) [26].

In the 1980s, the Lunsford and Somorjai research groups (amongst others) studied the reaction of CH_4 with N_2O to form CH_3OH and CH_2O over supported MoO_3 and V_2O_5 oxide catalysts. The catalytic selectivity (to CH_3OH and CH_2O) was highest at low reactant conversion, and thus these processes were constrained to very low product yields [27–30]. In general, the mechanistic paths for selective or complete oxidation of CH_4 are dependent on the state of reactive oxygen species formed on the catalytic sites [31]. Iwamoto et al. (1983) investigated the reaction of benzene with N_2O for phenol formation and subsequently developed a pilot scale production facility [32,33].

Thus far, a limited number of research papers have reported the study of the reaction of CH_4 with N_2O forming synthesis gas [23,34]. Recently the zeolite, Co-ZSM-5 was found to be an active catalyst for this reaction [35]. The reaction (CH_4 with N_2O) over H-ZSM-5 did not produce H_2, signifying the importance of cobalt at exchange sites for synthesis gas formation [35]. Additionally, the experiments conducted by Panov and collaborators and other research groups also suggest that, the acidic sites on H-ZSM-5 play no role in N_2O activation, in fact the presence of small concentration of iron (few hundred ppm) causes N_2O activation [36,37]. To our knowledge, a thermodynamic analysis of the reaction of CH_4 with N_2O has not been published. The current paper outlines the results of a thermodynamic and catalytic study of N_2O reaction with CH_4. This study is focussed on presenting a comparison of the thermodynamic predictions and the reaction observed experimentally, i.e., the effectiveness of the Co-ZSM-5 catalyst. The effect of temperature (300–550 °C) and molar feed ratio ($N_2O/CH_4 = 1$, 3, and 5) for improving H_2 yield was systematically examined.

2. Methodology

2.1. Thermodynamic analysis of the reaction

A non-stoichiometric approach was used for the calculation of equilibrium compositions of the reacting system [38–40]. The Gibbs free energy minimization method determines the species composition such that the simulation minimizes the total free energy of the reaction system, subject to elemental abundance. At fixed conditions of temperature and pressure, the reactants having a higher Gibbs free energy than the products will adjust the net reaction in the forward direction. The reaction species are at equilibrium, when the differential of Gibbs free energy at given conditions of temperature and pressure is zero [41].

$$\left(dG^t\right)_{T,p} = 0 \tag{1}$$

The total Gibbs free energy is the sum of chemical potential of each reacting species.

$$G^t = \sum_{i=0}^{N} n_i \mu_i \tag{2}$$

The Gibbs free energy of each species is shown in Eq. (3) [42].

$$\mu_i = \Delta G_i^\circ + RT ln \frac{\hat{f}_i}{f_i^\circ} \tag{3}$$

where the symbols G_i°, $\hat{f}_i$, and f_i° represent standard-state Gibbs free energy, partial fugacity and standard state fugacity of species i, respectively. The total Gibbs free energy (Eq. (4)) is minimized at any specified temperature and pressure, and constraint by elemental abundances, for finding reacting species at equilibrium conditions [41].

$$G^t = \sum_{i=0}^{N} n_i \Delta G_i^\circ + \sum_{i=0}^{N} n_i RT \, ln \frac{\hat{f}_i}{f_i^\circ} \tag{4}$$

The thermodynamic reaction study of CH_4 with N_2O was conducted using commercial software (COSILAB version 2004) [43]. This software has an inbuilt thermodynamic database to calculate the equilibrium compositions at predetermined temperatures and pressures. The species considered in simulation calculations are CH_4, N_2O, N_2, NO, NO_2, CO_2, CO, H_2O, H_2, C_2H_4, C_2H_2, CH_3OH, and (solid) carbon.

3. Experimental

3.1. Reactor studies

The catalytic conversion of CH_4 with N_2O was studied over Co-ZSM-5 in a fixed bed tubular reactor. A wet deposition method, as described in our previous study, was used for the preparation of Co-ZSM-5 catalyst [35]. The reaction of the feed (N_2O/CH_4, 95% helium diluent) was examined at three different reactant feed ratios (1:1, 3:1, and 5:1) over this catalyst. The oxidation reaction is exothermic and the gas temperature can differ from the catalyst surface temperature significantly [44,45]. In the present reaction study, a highly diluted feed stream composed of 95% of helium in reactant feed (N_2O/CH_4), with the helium effectively obviated the formation of hot spots over the catalyst bed [45].

Catalyst mass used in a tubular reactor was 0.250 g, having a fixed space time velocity of 0.92 ($m^3 \, kg^{-1} \, min^{-1}$), and was sieved between 250 μm and 450 μm. The temperature range was between 300 °C and 550 °C. Analysis of the product gas composition was carried out following 25 min of reaction at each studied temperature (attaining kinetic steady state). Analysis and quantification of the reaction products was carried out using a micro GC (Varian 490-GC). The catalytic performance of catalyst was measured on the basis of CH_4 and N_2O conversions [46]. The H_2 yield was calculated using Eq. (5).

$$H_2 \text{ yield } (\%) = \frac{(H_2/2)}{(CH_4)_{in}} \times 100 \tag{5}$$