

Reaction of nitrous oxide with methane to produce synthesis gas (CO + H₂); a thermodynamic and catalytic analysis

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Abstract

A thermodynamic and kinetic (experimental) study of N₂O with CH₄ to synthesis gas (H₂+CO) formation was investigated under various reaction conditions. The experimental study was carried out over Co-ZSM-5 as catalyst in a fixed bed reactor. The effect of temperature (270 °C - 570 °C) and molar feed ratio (N₂O/CH₄ = 1, 3, and 5) was examined in order to determine conditions for maximizing H₂ yield. The results show that for the molar feed ratios (N₂O/CH₄) of 1 and 3, N₂O is the limiting reactant. The thermodynamic and kinetic analyses of the reaction having a limiting N₂O reactant in reactant feed (N₂O/CH₄) shows that H₂ yield steadily increased with increase in temperature and the level of CH₄ conversion. Furthermore, the maximum attainable (from thermodynamic calculations) H₂ yield at 550 °C is about 20%. While thermodynamic predictions of H₂ yield drops to zero in presence of excess of N₂O in reactant feed (N₂O/CH₄ = 5). Over Co-ZSM-5 catalyst and with a molar reactant feed ratio (N₂O/CH₄) of 5, the H₂ yield first increases to 10 % with rise in temperature and then drops to zero at relatively higher range of temperatures (above 425 °C). The synthesis gas production from partial oxidation of CH₄ with N₂O may not be an alternative route to existing industrial practice; however, the fractional substitution of O₂ with N₂O in the partial oxidation of CH₄ could lead to emission reductions. This will also give a new route for H₂ generation.

Keywords: Gibbs free energy minimization, N₂O, CH₄, and synthesis gas.

Introduction

Recently, environmental and feedstock concerns have created renewed interest in processes that involve the production of synthetic liquid fuels. This increased interest has led the requirements of synthesis gas production. Due to high global warming, where N₂O is a major contributor to greenhouse gas emissions, any mitigation system involving production of useful feed stocks from N₂O are of high interest. In 1980s, Lunsford and Somorjai research groups (amongst others) studied the reaction of CH₄ with N₂O to form methanol and formaldehyde over supported MoO₃ and V₂O₅ oxide catalysts. The selectivity (methanol and formaldehyde) was better at lower reactants conversion (Liu, Iwamoto et al. 1982, Liu, Liu et al. 1984, Khan and Somorjai 1985, Zhen, Khan et al. 1985). In general, the selective or complete oxidation of CH₄ is dependent on the nature of reactive oxygen species present over the catalyst (Panov, Dubkov et al. 2006). Iwamoto et al., (1983) investigated the reaction of benzene with N₂O for phenol formation and subsequently developed a

pilot scale production facility for phenol production (Iwamoto, Hirata et al. 1983, Parmon, Panov et al. 2005).

In addition to N_2O as a possible reactant, it is important to consider CH_4 , which is the major component of natural gas (SAGE Publications). Fortunately, there are still large quantities of unutilized natural gas at different parts of the world (Lunsford 2000). The conversion of CH_4 to valuable chemicals is a major driver of significant research programs (H.E. Curry-Hyde 1994, A. Parmalian 1998). As a whole, methanol, formaldehyde, ethane, ethylene, H_2 are some of the important chemicals formed from CH_4 (Holmen 2009). A number of research groups are focussing their research on the development of catalysts for direct (without forming synthesis gas) conversion of CH_4 to fuels and chemicals (Alvarez-Galvan, Mota et al. 2011). On the other hand there are different other approaches of indirect conversion methods, in which CH_4 is first converted in to synthesis gas and then in to various useful chemicals (Lunsford 2000). In this study, we conducted a thermodynamic predictions and kinetics of the conversion of N_2O and CH_4 in to synthesis gas.

Synthesis gas ($CO+H_2$) is used for the production of valuable chemicals and fuels (Vannice 1976, Van Der Laan and Beenackers 1999). There are three well established technologies, catalytic partial oxidation, steam reforming and auto-thermal reforming, for the conversion of natural gas in to synthesis gas (Holladay, Hu et al. 2009). Among these technologies, catalytic partial oxidation and auto-thermal reforming of CH_4 are regarded as more energy efficient technologies for the synthesis gas production (Armor 1999, Freni, Calogero et al. 2000, Ferreira-Aparicio, Benito et al. 2005, Song 2006, Zhu, van Ommen et al. 2006). The catalytic partial oxidation of fuel (CH_4 or other hydrocarbon) is a reaction in oxygen deficient conditions (Christian Enger, Lødeng et al. 2008). While Auto-thermal reforming of CH_4 is a combination of combustion and steam reforming (Song and Guo 2006). In this process (auto-thermal reforming) energy required for the reaction of CH_4 and steam is supplied by the combustion of CH_4 (Gunardson and Abrardo 1999).

So far very limited numbers of research papers have been published on the study of the reaction of CH_4 with N_2O to form synthesis gas (Wood, Reimer et al. 2004, Zhu, van Ommen et al. 2006). The zeolite Co-ZSM-5 was found to be an active catalyst for this reaction (Khan, Kennedy et al. 2014). While the same reaction (CH_4 with N_2O) over H-ZSM-5 support didn't form H_2 , signifying the importance of cobalt at exchange sites for synthesis gas formation (Khan, Kennedy et al. 2014). Based on our analysis of the current literature, a thermodynamic analysis of the reaction of CH_4 with N_2O has not been published. For this reason, the current paper outlines the results of thermodynamic and catalytic study of N_2O reaction with CH_4 for the production of synthesis gas (H_2+CO), which was carried out at various reaction conditions. The effect of temperature (270 °C - 570 °C) and molar feed ratio ($N_2O/CH_4 = 1, 3, \text{ and } 5$) for improving H_2 yield was systematically examined.

Methodology

Thermodynamic analysis of the reaction

The Gibbs free energy minimization method was used for determining the species composition such that the simulation minimizes the total free energy of the reaction system subject to elemental abundances. At fixed conditions of temperature and pressure, the reactants having a higher Gibbs free energy than the products will move the net reaction in forward direction. The reaction species are at equilibrium, when the differential of Gibbs free energy at given condition of temperature and pressure is zero (Smith 2005).

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

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

$$G^t = \sum_{i=0}^N n_i \mu_i \quad (2)$$

The Gibbs free energy of each species is shown in equation 3 (Wang, Wang et al. 2009).

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

While 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 (equation 4) is minimized at any specified temperature and pressure for finding reacting species at equilibrium conditions (Smith 2005).

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

The thermodynamic reaction study of CH_4 with N_2O was conducted using COSILAB (ROTEXO. GmbH & Co. KG.2004). The software has an inbuilt thermodynamic data base to calculate the equilibrium compositions at defined temperature and pressure. The considered species 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 C (carbon).

Experimental section

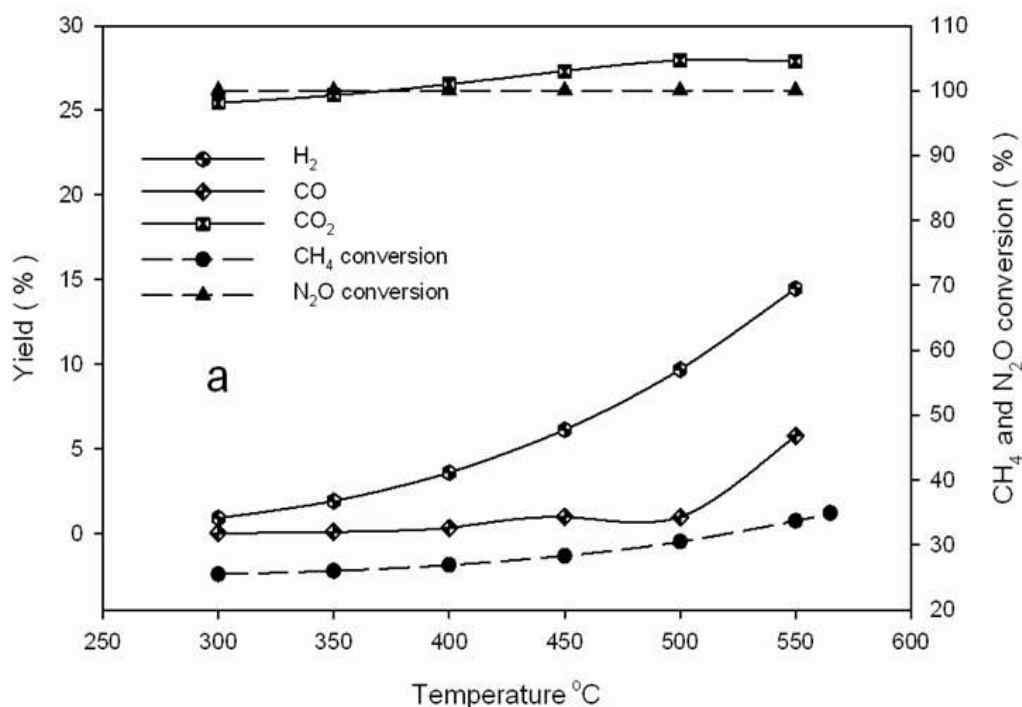
The catalytic conversion of CH_4 with N_2O was studied over Co-ZSM-5 in a fixed bed tubular reactor. A wet deposition method, as described in our previous study, was used for the preparation of Co-ZSM-5 catalyst (Khan, Kennedy et al. 2014). The reactant feed ($\text{N}_2\text{O}/\text{CH}_4$, 95 % helium diluent) was mixed well and the reaction was examined at three different reactant feed ratios (1:1, 3:1, and 5:1) over the catalyst. The oxidation reaction is an exothermic reaction and the gas temperature can differ from the catalyst surface temperature by several hundred degrees (van Looij, van Giezen et al. 1994, Horn, Williams et al. 2006). Since the catalytic conversion of CH_4 with N_2O is an oxidation reaction, therefore in our present reaction study, we adopted a diluted feed stream composed of 95 % of Helium in reactant feed ($\text{N}_2\text{O}/\text{CH}_4$). The presence of Helium in the reactant feed effectively obviated the formation of hot spots on the catalyst bed (van Looij, van Giezen et al. 1994). The experimental runs contained 0.250 g of catalyst, and the catalyst was sieved between 250 μm to 450 μm . The temperature range was kept between 270 °C to 570 °C. Analysis and quantification of the reaction products was carried out by using a micro GC (Varian 490-GC). The catalytic performance of catalyst was measured on the basis of CH_4 and N_2O conversions. The H_2 yield was calculated by using equation 5.

$$\text{H}_2 \text{Yield (\%)} = \frac{(n\text{H}_2)}{2 \cdot (n\text{CH}_4)} \quad (5)$$

Results and Discussion

Figure 1 shows the thermodynamic prediction (a) and experimental (b) results of reaction having a reactant feed molar ratio ($\text{N}_2\text{O}/\text{CH}_4$) of 1:1. Conversion of N_2O is thermodynamically a favorable reaction, and virtually 100 % conversion to product species is predicted, at studied range of temperature as shown in Figure 1 (a). The formation of H_2 and CO from CH_4 is thermodynamically favorable at high temperatures (Amin and Yaw 2007, Christian Enger, Lødeng et al. 2008). Our simulations show that H_2 yield increases consistently with rise in temperature and with higher levels of CH_4 conversion. It is observed that with increase in temperature from 300 °C to 550 °C, the H_2 yield increased from 1 % to 15 %. According to our thermodynamic analysis, at higher temperatures carbon oxides are formed in preference to H_2O . Thus, the overall H_2 yield increases with increase in temperature. CH_4 conversion at 300 °C is about 26 %, whereas it steadily increases to 37 % at 550 °C. The formation of CO is discernable above 500 °C. The yield of CO_2 remains between 24 % and 27 %.

The reaction of CH_4 with N_2O over Co-ZSM-5 is shown in Figure 1(b). It is generally accepted that the mechanism of synthesis gas formation changes with catalysts, and sometimes even for the same catalyst different pathways may follow, depending on the state of catalyst and reaction conditions (Christian Enger, Lødeng et al. 2008). We propose a direct mechanism (pyrolysis – oxidation) which will be presented in separate study. The H_2 yield at 555 °C is about 12%. CH_4 conversion is based on the availability of oxidant (N_2O), and therefore conversion of CH_4 is limited to 36 %. The increase of catalyst bed temperature progressively increases the rate of reactants conversion. The reaction is kinetically limited at temperatures below 450 °C. While the reaction approaches to equilibrium predictions at higher temperatures of 450 °C - 570 °C. In contrast to thermodynamic simulations, the formation of CO is observed at about 380 °C. Above 400 °C the yield of CO remains constant at about 5 %.



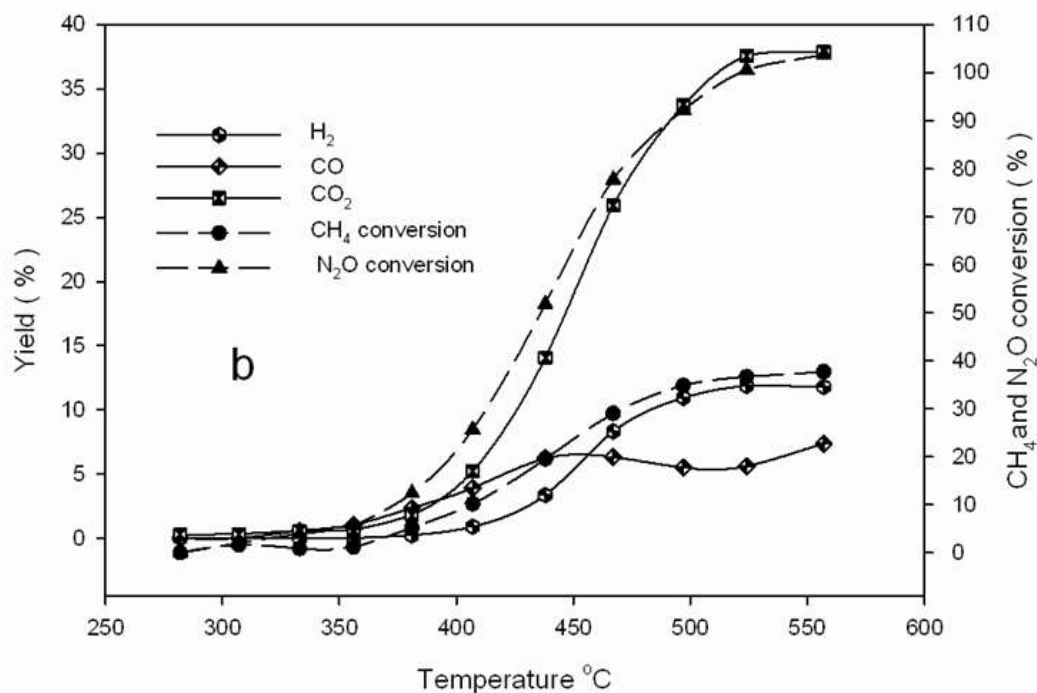


Figure 1: Reaction of CH₄ with N₂O (N₂O/CH₄ = 1); effect of temperature on yield of H₂, CO, and CO₂. Thermodynamic predictions (a); and experimental conversions over Co-ZSM-5 (b)

The effect of increase of oxidant concentration (N₂O/CH₄ = 3:1) in the reactant feed is shown in Figure 2. Even with an increase of N₂O concentration in the feed (N₂O/CH₄) molar ratio from 1:1 to 3:1, the N₂O is still a limiting reactant. The reactants (N₂O and CH₄) conversion and product (H₂, CO₂, and CO) yield predicted from thermodynamic calculations is shown in Figure 2a. The increase of the N₂O concentration in the reactant feed increases the CH₄ conversion to 87 % at 550 °C. With increase of temperature progressively increases the yield of H₂, CO₂, and CO in product stream. According to the predicted results, the H₂ yield at 300 °C is 1 % while it increases up to 20 % at a temperature of 550 °C. The N₂O conversion remains at 100 % at studied range of temperatures.

According to Figure 2b, CH₄ conversion rises up to 78% by increasing molar ratio of reactant feed (N₂O/CH₄) to 3:1 over Co-ZSM-5 at about 557 °C. The conversion of CH₄ with N₂O steadily increases with rise in temperature until the 100 % consumption of limiting reactant (N₂O). The activity of Co-ZSM-5 catalysts starts at about 333 °C and converts CH₄ to CO₂, CO, and carbon. The CH₄ carbonization reaction as part of direct mechanism occurs at lower range of temperatures (CH₄ → C_s+ 4H)(Horn, Williams et al. 2006). Therefore apart of formation of CO_x from CH₄ conversion, carbon is also deposited over the Co-ZSM-5 catalyst. The rise in temperature from 280 °C steadily increases CO₂ yield up to 500°C. The CO₂ yield remains stable with increasing the temperature from 500 °C to 525 °C, while CO and H₂ yield increases at same rate as seen in Figure 2b. However at about 557 °C, there is an abrupt increase in CO₂ yield from 77% to 87%. This sudden increase in CO₂ yield is due to oxidation of deposited carbon over catalysts. The oxidation of deposited carbon will be explained in later part of this paper. The formation of H₂ starts at about 407 °C and progressively increases with temperature and CH₄ conversion. The maximum H₂ yield with 100 % limiting reactant (N₂O) conversion at 557 °C is about 19 %.

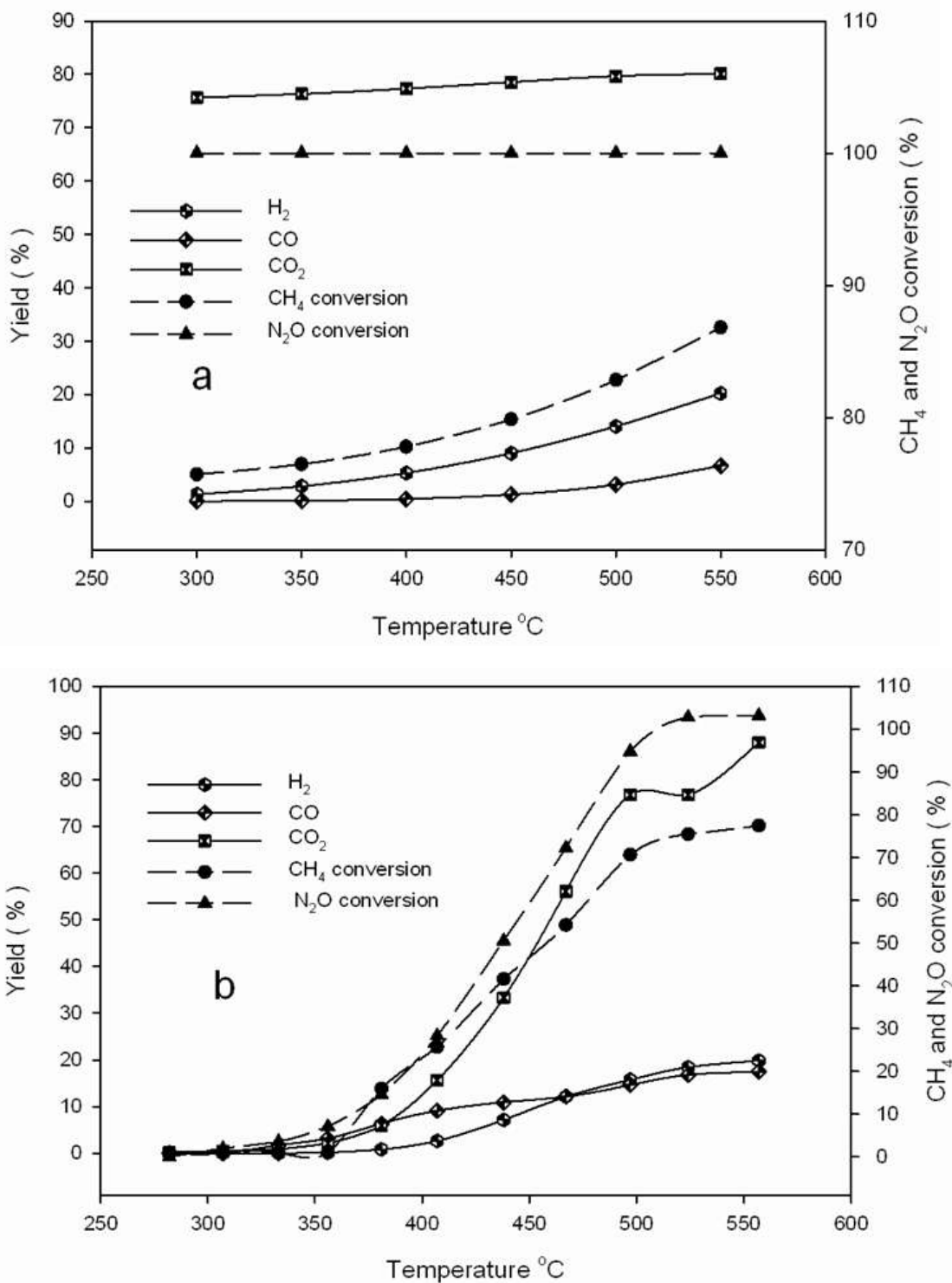
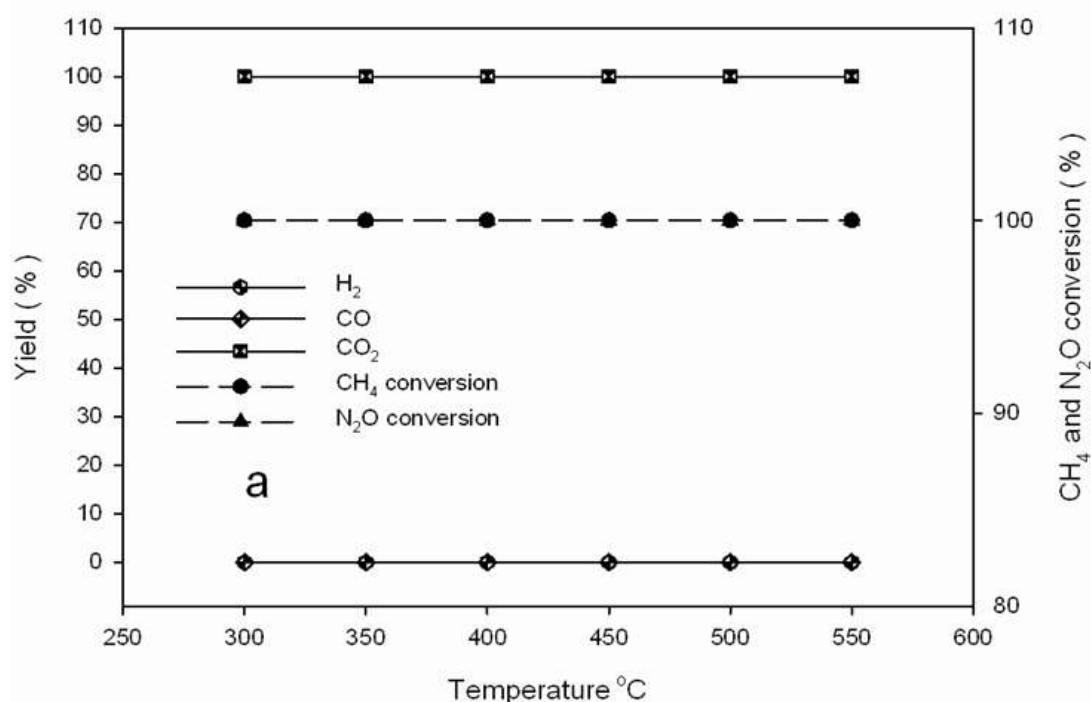


Figure 2: Reaction of CH₄ with N₂O (N₂O/CH₄ = 3); effect of temperature on yield of H₂, CO, and CO₂. Thermodynamic prediction (a); and experimental conversions over Co-ZSM-5 (b)

Figure 3 shows the CH₄ and N₂O reaction at higher reactant feed (N₂O/CH₄) ratio of 5:1. From the data (Fig 3a) it can be observed that excess of N₂O leads to complete combustion of CH₄ to form CO₂ and H₂O. The excess of oxidant in the system diminishes the formation of H₂ and CO. The conversion of CH₄ and N₂O remains at 100 % over the range of temperatures studied.

A similar reaction profile was observed in the reaction of CH_4 with N_2O over Co-ZSM-5 with a higher feed ($\text{N}_2\text{O}/\text{CH}_4 = 5:1$) molar ratio, as shown in figure 3b. At 287 °C conversion of CH_4 is observed and it is mainly converted into CO_2 . The increase in temperature from 227 °C to 424 °C gradually increases the yield of CO_2 , CO , and H_2 . The conversion of CH_4 and N_2O at 424 °C is 79 % and 50 % respectively. With further increase in temperature the N_2O reactivity increases and with 100 % CH_4 conversion we obtain 80 % of N_2O conversion. At a temperature higher than 424 °C, the free oxygen from N_2O dissociation reacts with H_2 and CO and forms H_2O and CO_2 . The H_2 and CO yield drops to zero when CH_4 conversion reaches 100 %. Furthermore, due to presence of excess of N_2O in reactant feed, besides oxidation of CO and H_2 , the deposited carbon reacts with N_2O and thus oxidizes to CO_2 . The yield of CO_2 shown at about 527 °C in Figure 3b is therefore combined yield based on CH_4 inlet feed, which is about 115 %.



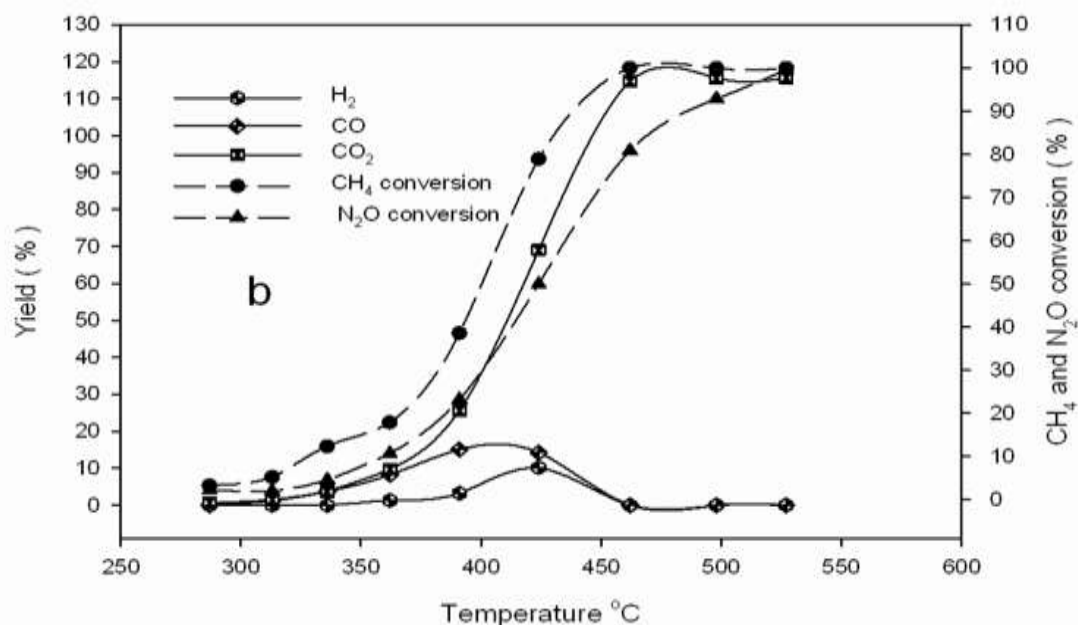


Figure 3: Reaction of CH₄ with N₂O (N₂O/CH₄ = 5); effect of temperature on yield of H₂, CO, and CO₂. Thermodynamic prediction (a); and experimental conversions over Co-ZSM-5 (b)

The experimental data as given in Figure 1b, 2b, 3b were repeated at least 3 times at each studied temperature. For every fixed temperature, the reaction of CH₄ with N₂O was allowed to react over the Co-ZSM-5 catalyst for at least 20 min before analyzing the gaseous product stream. The repeatability of the results was quite good. Figure 4 shows the error bar analysis of CO₂ yield for reaction feed (N₂O/CH₄) having a molar ratio of 5 as earlier shown in Figure 3b.

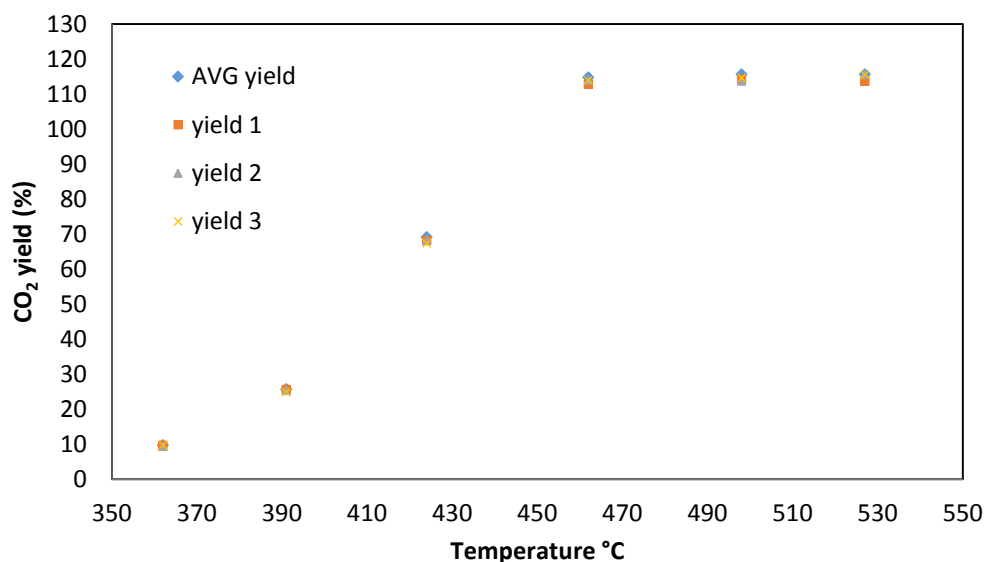


Figure 4: Effect of temperature on CO₂ yield for a feed ration (N₂O/CH₄) of 5; repeatability of examined data.

Conclusions

The reaction of CH₄ with N₂O was analyzed thermodynamically and conducted experimentally with varying molar feed (N₂O/CH₄) ratios at temperature ranges from 270 °C- 570 °C. The conversion of CH₄ over Co-ZSM-5 is dependent on the oxidant partial pressure (N₂O). At about 550 °C, the experimental reaction data approach the conversion and selectivity data, to the one as predicted

from thermodynamic simulations. An increase in the feed ($\text{N}_2\text{O}/\text{CH}_4$) molar ratio from 1:1 to 3:1 increases the H_2 yield and CH_4 conversions. Based on thermodynamic simulations, the maximum H_2 yield of 20% was observed for a feed ($\text{N}_2\text{O}/\text{CH}_4$) ratio of 3:1. The maximum H_2 yield was calculated at 550 °C. N_2O was used as a limiting reactant in the feed, and it partially oxidizes CH_4 to synthesis gas. Excess ratio of N_2O ($\text{N}_2\text{O}/\text{CH}_4 = 5:1$), combusts H_2 and CO to H_2O and CO_2 respectively.

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Biography



Naseer Ahmed Khan completed his Bachelor and Master degrees in Chemical Engineering from NWFP University of Engineering & Technology Peshawar, Pakistan in 2003 and 2008 respectively. He is currently pursuing his research in catalytic science, mainly focusing the effective utilization of zeolites under the supervision of Dr. Michael Stockenhuber, Prof. Eric M. Kennedy, and Prof. Bogdan Z. Dlugogorski.

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