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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\textsubscript{4} with N\textsubscript{2}O, particularly at higher CH\textsubscript{4} conversions. For this purpose, key process variables, such as temperature (300 °C–550 °C) and a molar feed ratio (N\textsubscript{2}O/CH\textsubscript{4} = 1, 3, and 5), were altered to establish the conditions for maximized H\textsubscript{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 N₂O conversions, and irrespective of N₂O/CH₄ 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 H₂ yield is zero in presence of excess N₂O (N₂O/CH₄ = 5). However over a Co-ZSM-5 catalyst, and with a same molar feed ratio (N₂O/CH₄) of 5, the H₂ yield is initially 10% at 425 °C, while above 450 °C it drops to zero. Furthermore, H₂ yield steadily increases with temperature and with the level of CH₄ conversion for reactions limited by N₂O concentration in a reactant feed. The maximum attainable (from thermodynamic calculations and at a feed ratio of N₂O/CH₄ =3) H₂ 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 CH₄ conversion (less than 50%) was also observed. At higher temperatures and levels of CH₄ conversion (above 90%), the deposited carbon is suggested to react with N₂O to form CO₂.

**Keywords**: Gibbs free energy minimization; N₂O; CH₄; Synthesis gas

1. Introduction

N₂O in 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, CH₄ and CO₂.
[1, 2]. For reference, N₂O global warming potential (GWP) is 15 and 310 times that of CH₄ and CO₂, respectively [3]. The atmospheric concentration of N₂O 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 N₂O per year into environment [5]. The photolysis of N₂O leads to the production of stratospheric NOₓ, and subsequently results in the chemical destruction of O₃ (ozone) molecule [6–8].

The catalytic reduction of N₂O with CH₄ is an extensively studied reaction [3, 4, 9]. CH₄ 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, and 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 CH₄) remains elusive. The conversion of CH₄ in to valuable chemicals is also a major driver of significant research programs [11, 12]. While N₂O supply is limited compared to natural gas, still significant amounts of N₂O are found as a by-product of adipic acid manufacturing, ammonium nitrate, and nitric acid production. N₂O emission as in the mentioned manufacturing process is of sufficient concentration to be used as an oxidant.

As a whole, CH₃OH, CH₂O, C₂H₆, C₂H₄, and H₂ are valuable chemicals that can be formed from CH₄ [13]. A number of research groups are focussing their research on the development of catalysts for direct (bypassing synthesis gas production) conversion of CH₄ 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\(_2\)O to form CH\(_3\)OH and CH\(_2\)O over supported MoO\(_3\) and V\(_2\)O\(_5\) oxide catalysts. The catalytic selectivity (to CH\(_3\)OH and CH\(_2\)O) 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\(_4\) is 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\(_2\)O 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\(_2\)O 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\(_2\)O) over H-ZSM-5 did not
produce H₂, 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 suggests that, the acidic sites on H-ZSM-5 play no role in N₂O activation, in fact the presence of small concentration of iron (few hundred ppm) causes N₂O activation [36,37]. To our knowledge, a thermodynamic analysis of the reaction of CH₄ with N₂O has not been published. The current paper outlines the results of a thermodynamic and catalytic study of N₂O reaction with CH₄. 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 (N₂O/CH₄ = 1, 3, and 5) for improving H₂ 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 determine 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].
\( (dG)_{T, p} = 0 \)  \hspace{1cm} (1)

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

\[
G^T = \sum_{i=0}^{N} n_i \mu_i \hspace{1cm} (2)
\]

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

\[
\mu_i = \Delta G^\circ_i + RT \ln \frac{\hat{f}_i}{\hat{f}_i^0} \hspace{1cm} (3)
\]

Where the symbols \( \Delta G^\circ_i \), \( \hat{f}_i \), and \( \hat{f}_i^0 \) 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 [41].

\[
G^T = \sum_{i=0}^{N} n_i \Delta G^\circ_i + \sum_{i=0}^{N} n_i RT \ln \frac{\hat{f}_i}{\hat{f}_i^0} \hspace{1cm} (4)
\]

The thermodynamic reaction study of CH\(_4\) with N\(_2\)O 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$_2$O, N$_2$, NO, NO$_2$, CO$_2$, CO, H$_2$O, H$_2$, C$_2$H$_4$, C$_2$H$_2$, CH$_3$OH, and (solid) carbon.

3. Experimental

3.1. Reactor studies

The catalytic conversion of CH$_4$ with N$_2$O 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$_2$O/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$_2$O/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 ℃ to 550 ℃. 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$_2$O conversions [46]. The H$_2$ yield was calculated using equation 5.

$$H_2 \text{ yield (\%)} = \frac{(H_2/2)}{(CH_4)_{in}} \times 100 \quad (5)$$
4. Results and discussion

Figure 1 compares the thermodynamic prediction (a) and experimental (b) results of the reaction between N\textsubscript{2}O and CH\textsubscript{4} (molar ratio N\textsubscript{2}O/CH\textsubscript{4}= 1/1). Conversion of N\textsubscript{2}O is a thermodynamically favourable reaction, and virtually 100% conversion to product species is predicted, in the studied temperature range (Figure 1.a). Thermodynamic analysis highlights that, at elevated temperatures, CO\textsubscript{2} formation is favoured over H\textsubscript{2}O production [24,47], and consequently the overall H\textsubscript{2} yield increases at elevated temperatures. CH\textsubscript{4} conversion at 300 °C is calculated to 26%, and increases steadily to 49% at 550 °C. The formation of CO is discernible above 450 °C. The predicted CO\textsubscript{2} yield increases slightly from 26% to 30% with increasing temperature from 300 °C to 450 °C, while a further increase in temperature (> 450 °C) lowers the CO\textsubscript{2} yield.

The experimentally measured yields and conversions of CH\textsubscript{4} and N\textsubscript{2}O over the Co-ZSM-5 are shown in Figure 1.(b). The H\textsubscript{2} yield at 550 °C is about 12%. CH\textsubscript{4} conversion is limited by the concentration of oxidant (N\textsubscript{2}O) in reacted feed, and a maximum conversion level of CH\textsubscript{4} is 37% and directly follows the N\textsubscript{2}O conversion trend. As expected, an increase in catalyst bed temperature progressively increases the level of reactant conversion. Below 450 °C, the reaction is kinetically limited, while the reaction approaches equilibrium product distribution, for N\textsubscript{2}O conversion, at temperatures in the range of 525 °C–550 °C. It is evident that below 525 °C, the reaction in the flow reactor is not at thermodynamic equilibrium. At temperatures higher than 525 °C, the equilibrium conversions are close to the observed catalytic conversions of both CH\textsubscript{4} and N\textsubscript{2}O. CH\textsubscript{4} conversion (40%) is slightly lower at 550 °C as compared to the predicted conversion. In contrast to thermodynamic simulations, CO is observed at lower temperatures of 350 °C, and increases up to 450 °C where the yield of CO
remains constant at roughly 5%. Even more important, the CO$_2$ yield is significantly increased over the catalyst compared to the thermodynamically predicted value. The thermodynamically predicted results suggest a reduction of CO$_2$ yield at 550 °C, a consequence from a reduced oxygen availability. This is also in line with increased CO$_2$ concentration for the more N$_2$O rich mixtures (please also see below). Due to the lower CH$_4$ conversion observed experimentally, the reduced oxygen availability is less important resulting in a higher CO$_2$ concentration (compared to CO). The CO$_2$/CO ratio experimentally was found 7:1 at temperatures above 500 °C, whereas thermodynamic analysis predicts a 1.3:1 ratio. Consequently, we can conclude that the Co-ZSM5 catalyst is a better catalyst for the activation of N$_2$O than CH$_4$. 
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 increasing N₂O concentration on the reactant conversion is shown in Figure . The conversion of reactants (N₂O and CH₄) and product (H₂, CO₂, and CO) yield predicted from thermodynamic calculations is shown in Figure (a). For a (N₂O/CH₄) 3:1 mixture, thermodynamic calculation predicts a similar N₂O conversion as for the 1:1 mixture and significantly increased conversion of CH₄ (almost double conversion of CH₄ compared to the (N₂O/CH₄=1/1). This is again in line with oxygen availability being most determining for the equilibrium position. At a temperature of 550 °C, the CH₄ conversion increased from 49% to 97% (as predicted earlier from a feed ratio of 1:1 as shown in Figure 1.a). The thermodynamic analysis reveals that an increase in temperature steadily increases the H₂, CO₂, and CO yield. The H₂ yield at 300 °C is 4%, increasing to 38% at a temperature of 550 °C.
As shown in Figure (b), CH$_4$ conversion rises to 78% by increasing the feed ratio (N$_2$O/CH$_4$) to 3:1 over Co-ZSM-5 at the highest temperature studied; 550 °C. The conversion of CH$_4$ with N$_2$O steadily increases with a rise in temperature, until approximately 100% consumption of limiting reactant (N$_2$O) is observed. N$_2$O conversion has reached equilibrium again at temperatures higher than 500 °C. CH$_4$ conversion, similar to the richer mixture, does not reach the equilibrium values even at 550 °C indicating the excellent ability of CoZSM-5 to activate N$_2$O but less so CH$_4$. The activity of Co-ZSM-5 catalyst commences at approximately 350 °C and converts CH$_4$ to CO$_2$, CO, and carbon (carbon formation is based on mass balance estimation, also please see below). The CH$_4$ carbonization reaction occurs at lower CH$_4$ conversion and range of temperatures (CH$_4$ → C$_x$ + 4H) [44]. An increase in temperature above 300 °C results in a steady increase in the CO$_2$ yield. The CO$_2$ yield remains constant between 500 °C to 525 °C, while CO and H$_2$ yield increases at the same rate as seen in Figure (b). However, at about 550 °C, there is an abrupt increase in CO$_2$ yield, from 77% to 87%. This sudden increase in CO$_2$ yield is most likely due to oxidation of carbon which was deposited on the catalyst at lower temperatures. The oxidation of deposited carbon will be discussed in a later section of this paper. The formation of H$_2$ starts at about 400 °C and progressively increases with temperature and CH$_4$ conversion. The maximum H$_2$ yield detected at the conversion of 100% of the limiting reactant (N$_2$O) at 550 °C amounts to about 19%.
Figure 2. Reaction of CH$_4$ with N$_2$O (N$_2$O/CH$_4$ = 3); effect of temperature on yield of H$_2$, CO, and CO$_2$. Thermodynamic prediction (a), and experimental conversions over Co-ZSM-5 (b).
Figure shows the CH$_4$ and N$_2$O reaction at higher reactant feed (N$_2$O/CH$_4$) ratio of 5/1. Based on the thermodynamic calculation of the data (Figure a), it is predicted that an excess of N$_2$O in the feed leads to complete combustion of CH$_4$ into CO$_2$ and H$_2$O. An excess of oxidant in the feed diminishes the selectivity to H$_2$ and CO. The conversion of CH$_4$ and N$_2$O remains at 100% over the studied range of temperatures.

Somewhat surprisingly, at lower temperatures (< 425 °C), a similar reaction profile (as given in Figure 1.b and Figure b) was observed for the reaction of CH$_4$ with N$_2$O over Co-ZSM-5 with a higher feed (N$_2$O/CH$_4$= 5/1) molar ratio, as shown in Figure (b). At approximately 300 °C, conversion of CH$_4$ is observed which is mainly converted into CO$_2$. Increasing the reaction temperature from 300 °C to 425°C gradually increases the yield of CO$_2$, CO, and H$_2$. The conversion of CH$_4$ and N$_2$O at 425 °C is 79% and 50%, respectively (kinetically limited reaction). Above 425 °C, the CH$_4$ conversion reaches approximately 100%, while N$_2$O remains at about 90%. Thus the catalytic CH$_4$ conversion reaches levels predicted thermodynamically at 450 °C, whereas for N$_2$O (thermodynamic estimates), it is about 500 °C (100% N$_2$O conversion). It is interesting to note that at 400°C– 425°C partial oxidation to form synthesis gas is significant (in contrast to the thermodynamic predictions), and this coincides with the temperature of optimal benzene to phenol conversion using N$_2$O [48,49]. An increase in temperature (above 425 °C) appears to oxidize any intermediate species which are necessary for synthesis gas formation, and therefore the H$_2$ and CO yield drops to zero. Furthermore, due to presence of excess of N$_2$O in reactant feed, the deposited carbon (this carbon was deposited at lower ranges of temperature) reacts with N$_2$O and oxidizes to CO$_2$. Excess oxidant also results in the formation of O$_2$ at 425 °C, which was observed at...
$\text{N}_2\text{O}/\text{CH}_4 = 5$. The yield of $\text{CO}_2$ shown at about 500 °C in Figure (b) is therefore a combined yield, based on $\text{CH}_4$ inlet feed conversion and carbon oxidation, which is about 115%. 

![Graph showing yield and conversion at different temperatures](image-url)
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).

Carbon deposition and its oxidation to CO₂ were confirmed in a separate set of experiments by comparing the variation in carbon balance at 550 °C as shown in Figure 4. A reaction mixture (N₂O/CH₄) having a molar feed ratio of 4:1 and with a same volume of diluent (95% in reactant feed) and catalyst was reacted. However in these experiments, instead of starting reaction from a temperature of 350 °C, the reaction was carried out at 550 °C initially, and then lowered to 350 °C. From 350 °C, the temperature was again increased to 550 °C as shown by arrows in Figure 4, where CH₄ conversion at 550 °C, 400 °C, and 350 °C is 100%, 30%, and 10% respectively. By starting the reaction studies at 550 °C, instead of lower temperatures, the stoichiometry of reaction is CH₄ + 4 N₂O → CO₂ + 2H₂O + 4N₂ and resulted in a 100% yield of CO₂ in product stream. When the reaction temperature is
decreased to 400 °C or 350 °C, then in addition to CO\textsubscript{x} formation, carbon is also deposited on the Co-ZSM-5 catalyst. The incomplete CH\textsubscript{4} combustion with N\textsubscript{2}O over active sites of Co-ZSM-5 catalyst also deposits carbon. Recently our research group observed the carbon deposition from CH\textsubscript{4} decomposition at reaction temperatures as low as 180 °C even in the presence of high oxygen concentrations [50]. The temperature rise from 350 °C to 550 °C increases the apparent CO\textsubscript{2} yield to 137% (step 3). The absence of CO in the product stream indicates that the deposited carbon reacts with N\textsubscript{2}O (C + 2N\textsubscript{2}O → CO\textsubscript{2} + 2N\textsubscript{2}) and forms CO\textsubscript{2}. At 550 °C, the apparent yield of CO\textsubscript{2} decreases with time on stream and after 15 min it drops to 109% as shown in Figure 4. (step 4).

![Figure 4. Reaction of CH\textsubscript{4} with N\textsubscript{2}O (N\textsubscript{2}O/CH\textsubscript{4} = 4); effect of temperature on yield of CO\textsubscript{2} over Co-ZSM-5.](image-url)
In order to understand the driving force for the reaction $\text{C} + 2\text{N}_2\text{O} \rightarrow \text{CO}_2 + 2\text{N}_2$, thermodynamic calculations of carbon oxidation with $\text{N}_2\text{O}$ at a feed ratio of $(\text{N}_2\text{O}/\text{C})$ 1 and 2 were studied. The pressure was fixed at 1 atm, and the temperature was 500 °C. The reaction with a feed ratio $(\text{N}_2\text{O}/\text{C})$ of 1 mainly results in $\text{CO}$, whereas for a ratio $(\text{N}_2\text{O}/\text{C})$ of 2, $\text{CO}_2$ formation is favoured.

There is an observable difference in the rate of $\text{N}_2\text{O}$ conversion at any fix temperature over Co-ZSM-5 catalyst as can be seen in Figure 1.(b), Figure (b), and Figure (b). For example, for feed $(\text{N}_2\text{O}/\text{CH}_4)$ ratio of 1, 3, and 5, and at a temperature of 425 °C, the $\text{N}_2\text{O}$ conversion is 25%, 29%, and 50%, respectively. The rate of reaction is dependent on oxidant concentrations, total feedflow rate, temperature, pressure, and catalyst [51]. Literature suggests a fairly complex mechanism for $\text{N}_2\text{O}$ decomposition reaction [52–54].

The overall quantification of the gaseous products was performed for a diluted $\text{N}_2\text{O}$ (about 7% in feed balanced with helium) feed over the same Co-ZSM-5 catalyst in a continuous fixed bed flow reactor (total feed rate = 230 mL/min) in a temperature range of 300 °C – 500 °C. The mass balance (as shown in Table 1.) of $\text{N}_2$ suggests that $\text{N}_2$ and $\text{O}_2$ are the major species formed from the $\text{N}_2\text{O}$ decomposition reaction ($\text{N}_2\text{O} \rightarrow \text{N}_2 + \frac{1}{2} \text{O}_2$). The dissociation of $\text{N}_2\text{O}$ over Co-ZSM-5 into $\text{N}_2$ and $\text{O}_2$, in a temperature range of Figure 1., Figure , and Figure , points toward a possibility of reaction of $\text{CH}_4$ with $\text{O}_2$ formed in the decomposition of $\text{N}_2\text{O}$. The oxidation of $\text{CH}_4$ with $\text{O}_2$ over Co-ZSM-5, under similar reaction conditions, is, however very limited. This will be discussed in later section of this paper.
Table 1. Nitrogen balance over Co-ZSM-5 catalyst; reaction condition: N₂O= 7%, approx. 93% helium in feed mixture; weight of catalyst 0.250 g.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>N₂O concentration in feed (%)</th>
<th>Unconverted N₂O concentration (%)</th>
<th>Produced gas concentration (%)</th>
<th>N₂O out + N₂</th>
<th>Balance (%)</th>
<th>Conversion (%)</th>
</tr>
</thead>
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</table>

In our previous work, it was proposed that, cobalt when loaded on ZSM-5, support forms active sites for the formation of synthesis gas [35]. The decomposition of pure N₂O over H-ZSM-5, instead of Co-ZSM-5 has a different rate of reaction as shown in Figure. The H-ZSM-5 support is almost inactive below 500 °C, whereas the N₂O conversion above 500 °C can be attributed to the existence of small concentration of transition metals admixtures [36]. The 50% conversion of N₂O over Co-ZSM-5 and H-ZSM-5 occurs at about 400 °C and 550 °C respectively. However in absence of catalyst, even at 600 °C, N₂O was found to be unconverted. This result (Figure ) suggests that, cobalt on ZSM-5 plays a vital role in the N₂O conversion reaction.
A mixture of $\text{N}_2/\text{O}_2/\text{CH}_4$ reacted under conditions similar to those given for Figure (b) yields product distribution listed in Table 1. In these experiments, we maintained the elemental feed the same as over Co-ZSM-5 catalyst. The concentration of diluent (helium) in a feed mixture was kept constant to a value of about 95%, whereas a feed ($\text{O}_2/\text{CH}_4$) ratio of 2.5 was reacted within a temperature range of 300–600 °C. The activity of the catalyst was quite low under similar reaction condition as shown in Table 1, while $\text{CH}_4$ and $\text{O}_2$ react and mainly form $\text{CO}_2$ and $\text{H}_2\text{O}$ as inferred from the carbon balance. Therefore, this result confirms that
CH₄ conversion over Co-ZSM-5 catalyst is due to its reaction with N₂O and not with O₂ formed from N₂O decomposition.

Table 1. Activity data of CH₄ and carbon balance.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>CH₄ conversion (%)</th>
<th>O₂ consumption (%)</th>
<th>CH₄ in feed (ppm)</th>
<th>Unconverted CH₄ (ppm)</th>
<th>Produced CO₂ (ppm)</th>
<th>CH₄ out + CO₂ out</th>
<th>Balance (%)</th>
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<td>13936.9</td>
<td>10423.4</td>
<td>3605.5</td>
<td>14028.9</td>
<td>99</td>
</tr>
</tbody>
</table>

4. Conclusions

The reaction of CH₄ with N₂O was analyzed thermodynamically and experimentally with varying molar feed (N₂O/CH₄) ratios within a temperature range of 300–550 °C. The conversion of CH₄ over Co-ZSM-5 is dependent on the oxidant concentration (N₂O). An increase in the feed (N₂O/CH₄) molar ratio from 1/1 to 3/1 increases the H₂ yield and CH₄ conversions. Based on thermodynamic simulations, the maximum H₂ yield of 38% was observed for a feed (N₂O/CH₄) ratio of 3/1 at 550 °C. N₂O used as a limiting reactant in the
reactant feed oxidizes CH$_4$ to synthesis gas. Excess ratio of N$_2$O (N$_2$O/CH$_4$ =5/1), produces CO$_2$. Molecular oxygen as a reactant forms CO$_2$ and water only under all conditions. The deposited carbon reacts with N$_2$O at higher temperature and forms CO$_2$. The N$_2$O conversion approaches to thermodynamic prediction at about 500–550 °C.

References


Graphical Abstract