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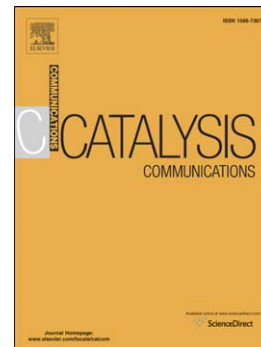
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**Partial oxidation of methane with nitrous oxide forms synthesis gas over
cobalt exchanged ZSM-5.**

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Abstract

Synthesis gas ($\text{CO} + \text{H}_2$) is a versatile and significant resource. In this communication we show that cobalt loaded on ZSM-5 (Co-ZSM-5) catalyses the formation of synthesis gas from CH_4 , under partial oxidation conditions using N_2O as oxidant. With O_2 as oxidant over the same Co-ZSM-5 catalyst, cobalt on alumina and Fe-ZSM-5, only CO_x and H_2O are formed. Isolated Co^{2+} sites in the ZSM-5 support are proposed as the active sites for H_2 (synthesis gas) formation.

1. Introduction

Industrial activities have increased N_2O (greenhouse gas) emissions significantly [1-4]. N_2O gas has negative impact on the stratospheric ozone layer and has been identified in the Kyoto protocol as a target molecule for greenhouse gas (GHG) emission reduction [5, 6]. Projects for N_2O mitigation can effectively reduce emissions from stationary sources (nitric and adipic acid plants) [7].

Panov and coworkers used N_2O as an oxidant for selective oxidations of various hydrocarbons [8]. Earlier, Wood et al studied CH_4 oxidation with N_2O over Fe/Al-MFI forming surface methoxy groups, which eventually decomposed into H_2 and CO at elevated temperature [9]. The concentration of N_2O in exhaust stream of adipic acid plants is quite high (20 – 60 %) [10]. The use of waste N_2O stream for partial oxidation of CH_4 to synthesis gas is proficient solution for clean environment and energy generation.

The catalytic partial oxidation of CH_4 was first reported in 1929 [11], with continuing interest from industry and academia in its development and commercial deployment [12]. Ideally, the catalytic partial oxidation of CH_4 is described by reaction; $\text{CH}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2$. However, the reaction mechanism is very complex and has been studied extensively using various transition and noble metal catalysts with different supports [13]. Thermodynamically, the higher selectivity of synthesis gas (produced from CH_4 partial oxidation) is favoured at higher temperatures (>1000 °C) [14]. The production of synthesis gas at relatively moderate temperatures was recently reported where the researchers used multiple catalysts with different metal promoters and cobalt loadings [13, 15].

In this paper, the catalytic partial oxidation of CH_4 to synthesis gas was investigated using N_2O as oxidant. The dissociation of N_2O during catalytic reaction is a complex process and is expected to influence the partial oxidation mechanism of CH_4 [16, 17]. We identified catalyst preparation

procedures and speculate on active sites in the catalyst that facilitate the conversion of CH₄ to synthesis gas by partial oxidation with N₂O over Co-ZSM-5 catalysts.

2. Experimental

2.1 Catalyst preparation

Cobalt (II) nitrate hexahydrate (Co (NO₃)₂·6H₂O, Sigma Aldrich) was used for cobalt loading of a NH₄-ZSM-5 (Si/Al = 15, Zeolyst). Three different methods were used for cobalt loading.

a) Using a wet ion exchange method [18], 2.47 g of cobalt salt was dissolved in 82 ml of demineralised water and was stirred for an hour at 50 °C. NH₄-ZSM-5 (9.5g) was introduced into cobalt nitrate solution and left stirring for 24 hours. The solution was then filtered and the solid catalyst collected. A freshly prepared cobalt solution of the same concentration was again mixed with dried Co-ZSM-5 catalyst (repeated 3 times). The prepared catalysts will be now defined as Co-ZSM-5_(I.E.).

b) Utilising a wet deposition method, over-exchange of cobalt was achieved. Ammonium hydroxide (37 % by wt. in aqueous solution) was added to a Co-ZSM-5 solution (quantities of Co(NO₃)₂·6H₂O and NH₄-ZSM-5 was same as given in ion exchange method) and the pH was maintained at 8 [19]. The process of cobalt loading (at pH of 8) was repeated 3 times (Co-ZSM-5_(S.P.)).

c) Incipient wetness impregnation was also used for loading cobalt onto a ZSM-5 support [20, 19]. A mass of 2.50 g of cobalt (II) nitrate hexahydrate was dissolved in 1 ml of demineralized water. The cobalt solution was added drop wise to 9.5 g NH₄-ZSM-5 in order to obtain a paste. The prepared catalyst is identified as Co-ZSM-5_(I.W.).

All catalysts were dried at 110 °C.

2.2 Catalytic measurements

All prepared catalysts were collected in ceramic boats and placed in a furnace and subsequently calcined at 550 °C (with ramp rate of 3 °C/min) for 3 hours and then were cooled to room temperature.

The catalytic reaction of CH₄ with N₂O was carried out in a fixed bed tube reactor. The catalyst was mounted between silica wool plugs in a stainless steel tube of ¼" diameter. The catalyst was activated

in helium at 550 °C in a carbolite tube furnace. The catalytic activity of the catalyst was measured on the basis of conversion of CH₄ and N₂O. Reactions were conducted at 1.01 bar and within the temperature range of 300 °C to 550 °C. All experiments were repeated at least once to verify the repeatability of experimental data. Total reactant feed flow rate over the catalyst was 230 cm³/min.

Feed compositions of 66 % He, 27 % CH₄, 7 % N₂O and 67 % He, 12 % CH₄, 21 % N₂O were reacted over Co-ZSM-5_(S.P.) catalyst. In addition a more dilute reactant feed stream (95 % helium, 1 % CH₄, and 4 % N₂O) was also studied over various catalysts. Analysis of the gaseous products was carried out on an online Varian 490-GC. A molecular sieve 5 A column quantified He, H₂, O₂, N₂, CH₄, and CO, whereas Poraplot Q column was used for analysis of CO₂ and N₂O.

2.3 Catalyst characterization

A Varian 715 ES unit was used for elemental analysis. The ex-situ X-ray photoelectron spectroscopy (XPS) of the prepared cobalt zeolite samples was carried in a ESCALAB250Xi unit (Thermo Scientific). Background vacuum was better than 2×10^{-9} mbar. Spectra were collected using monochromatic Al K α radiation (energy 1486.68 eV) with a spot size of 500 μ m. A JEOL 2100La86 unit was used for energy dispersive X-ray spectrometer (EDS) analysis.

3. Results and discussion

Figure 1 shows the partial oxidation of CH₄ with N₂O (CH₄/N₂O=4) over Co-ZSM-5_(S.P.). The concentration of CO₂, CO, and H₂ is plotted together with CH₄ and N₂O conversion, and N₂ production. We found that the reactivity of CH₄ is closely linked with N₂O. No further CH₄ conversion was observed once N₂O consumption reached 100 %. The maximum transformation of CH₄ at 100 % N₂O utilization was 10 %. The lowest temperature for measureable H₂ formation is 400 °C with its concentration steadily increasing with temperature and coincident with increasing CH₄ conversion. Note that we observed a significant increase in CO concentration at temperatures higher than 500 °C. The molar ratio of H₂/CO was approximately 2 at temperatures above 500 °C.

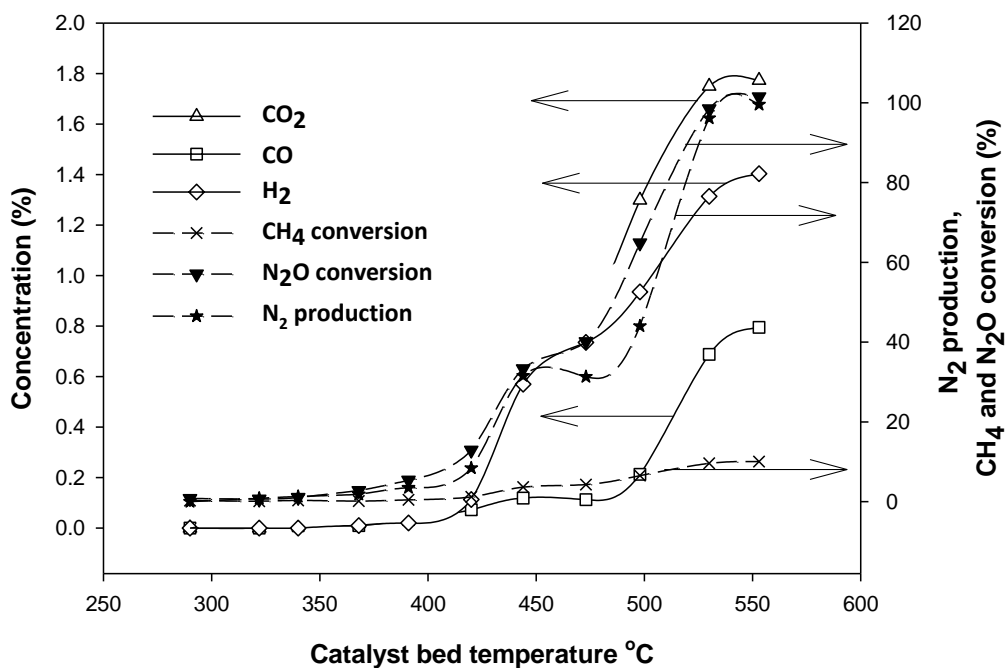


Figure 1: Effect of temperature on CH₄ and N₂O conversion; N₂ production; product distribution of CO₂, CO, and H₂ over Co-ZSM-5_(S.P.). Feed flow rate: 230 cm³/min (CH₄/N₂O=4, approx. 66% helium in feed mixture); weight of catalyst: 250 mg.

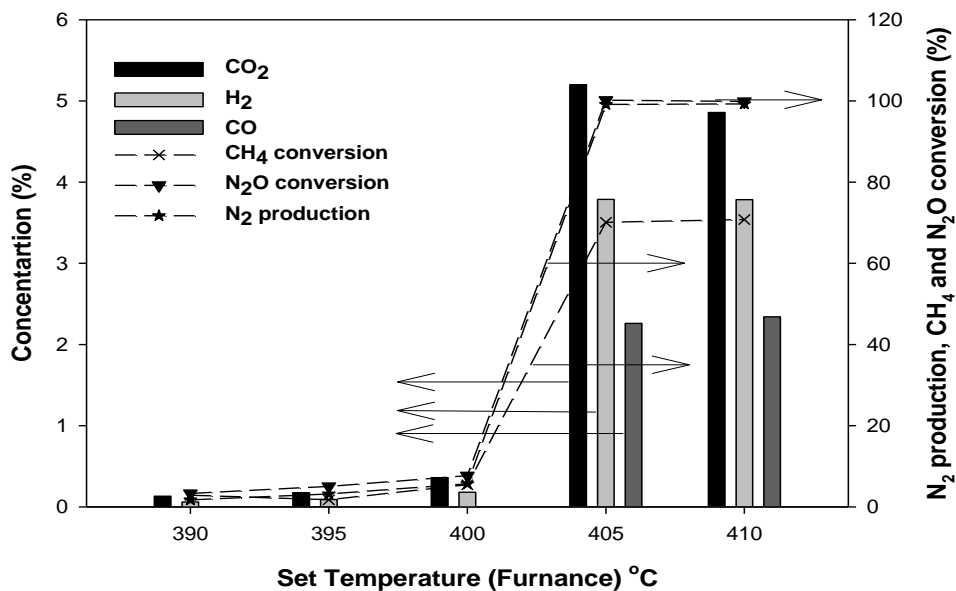


Figure 2: Effect of temperature on CH₄ and N₂O conversion, N₂ production, product distribution of CO₂, CO, and H₂ over Co-ZSM-5_(S.P.). Feed flow rate: 230 cm³/min (CH₄/N₂O=1/2, approx. 67% helium in feed mixture); weight of catalyst: 250 mg.

Figure 2 shows the CH_4 and N_2O ($\text{CH}_4/\text{N}_2\text{O}=1/2$) reaction over a narrow temperature range of $390\text{ }^\circ\text{C}$ - $410\text{ }^\circ\text{C}$. The concentration of the diluent was maintained at constant level. The increase in N_2O concentration (21%) in the reactant feed lead to a subsequent increase in the CH_4 (70 %) conversion, resulting in a higher concentration of synthesis gas in the product stream. The molar ratio of H_2/CO in the product stream remained at about 2. A “light off” conversion was observed at temperature range of $400\text{ }^\circ\text{C}$ - $405\text{ }^\circ\text{C}$. This sharp increase in catalytic activity is due to the high concentration of N_2O (21 %) in reactant feed. It is suggested that surface NO species are formed, which drastically increases the rate of reaction due to autocatalytic effects [21]. Indeed, the associated activation energy determined at low conversions (53 kJ/mol) is typical of heterogeneous catalysis. The apparent sluggish change in conversion prior to $400\text{ }^\circ\text{C}$ is symptomatic of the absence of required thermally activated sites for the CH_4 oxidation. Negligible conversion of reactant feed was observed below $400\text{ }^\circ\text{C}$. Inside the reactor, the temperature of the catalyst jumped from $400\text{ }^\circ\text{C}$ to $780\text{ }^\circ\text{C}$, when the furnace temperature was increased from $400\text{ }^\circ\text{C}$ to $405\text{ }^\circ\text{C}$.

The sudden increase of temperature prompted us to investigate the stability of the catalyst (Co-ZSM-5_(S.P.)). The reaction was analysed at $410\text{ }^\circ\text{C}$ (reactor furnace temperature) for 5 hours of continuous operation. The catalyst bed temperature was around $780\text{ }^\circ\text{C}$. After an initial drop in H_2 and CO_2 yield and an increase in CO concentration, the activity was stable for 5 hours as shown in Figure 3.

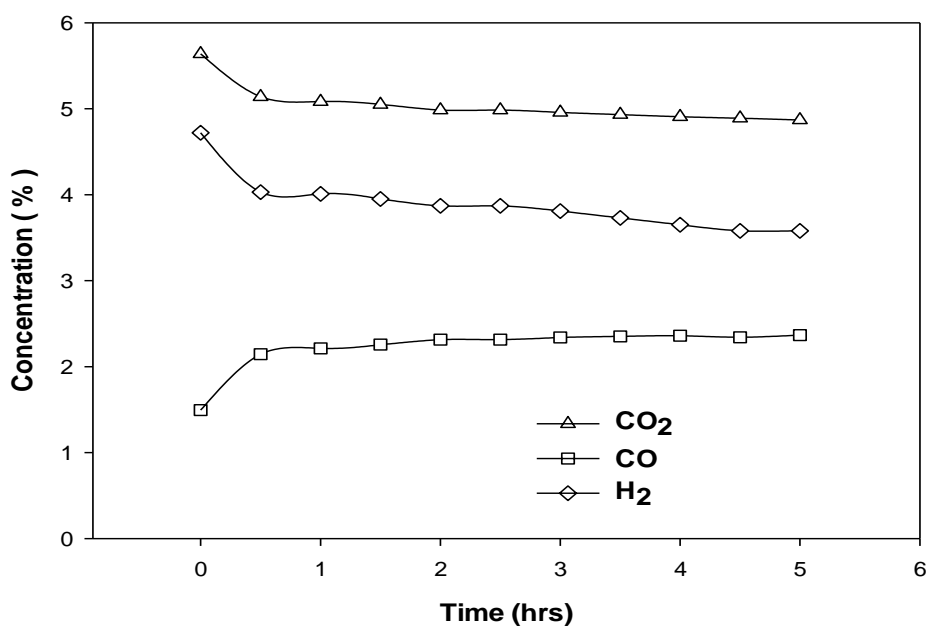


Figure 3: The product distribution of CO₂, CO, and H₂ over Co-ZSM-5_(S,P) at time range of 0 - 5hrs. Feed flow rate: 230 cm³/min (CH₄/N₂O=1/2, approx. 67% helium in feed mixture); weight of catalyst: 250 mg.

In order to study the effect of catalyst support and oxidant type, a feed composition of 1% CH₄, 4 % N₂O, and 95% He (total reactant feed flow 230 cm³/min) was reacted over different catalyst as shown in Table 1. We found that only cobalt modified ZSM-5 was selective to H₂ production. The increase of Si/Al ratio of ZSM-5 zeolite proportionally increases β sites [22]. We suggest that the cobalt β sites are more suitable for H₂ formation due to significant variation in bond strength between the cobalt and exchange sites (α , β , and γ) [22]. At higher Si/Al ratio, the percent exchange of cations increases and is expected to improve selectivity [23, 24]. Under similar experimental conditions as shown in Table 1, the conversion of CH₄ over Co-ZSM-5 (Si/Al = 140) catalyst was lower as compared to Co-ZSM-5_(S,P), while giving a higher H₂ selectivity. For iron loaded at exchange sites of ZSM-5 support (different from wood et al Fe/Al-MFI catalyst), under the same conditions, the conversion was high but H₂ was not detected. The Co-Al₂O₃ was non selective to CO and H₂ either. The activity of Co-ZSM-5_(S,P) decreased with using O₂ instead of N₂O and again no H₂ could be detected.

Table 1: Activity data of CH₄ and H₂ selectivity

CH ₄ conversion with N ₂ O, and H ₂ selectivity (CH ₄ /N ₂ O=1/4, approx. 95% helium in feed mixture; weight of catalyst 250 mg)								
	425°C		450°C		475°C		500°C	
Catalysts	X (%)	H ₂ sel. (%)	X (%)	H ₂ sel. (%)	X (%)	H ₂ sel. (%)	X (%)	H ₂ sel. (%)
Co-Al ₂ O ₃	0.96	0	3.99	0	8.91	0	12.4	0
CoO	5.69	0	16.93	0	32.51	0	50.30	0
H-ZSM-5	18.03	0	19.21	0	32.30	0	76.56	0
Co-ZSM-5 (Si/Al=140)	11.86	23	39.62	17	58.35	22	100	16
Co-ZSM-5 (I.E.)	49.73	1	69.78	4	100	4	100	0
Co-ZSM-5 (S.P.)	78.91	13	100	0	100	0	100	0
Co-ZSM-5 (I.W.)	69.0	14	100	2	100	0	100	0
	300 °C		325 °C		400 °C		425 °C	
Fe-ZSM-5	14	0	37	0	100	0	100	0
CH ₄ conversion with O ₂ , and H ₂ selectivity (CH ₄ /O ₂ =1/3, approx. 95% helium in feed mixture)								
	425°C		450°C		475°C		500°C	
Co-ZSM-5 (S.P.)	0.37	0	0.23	0	1.38	0	1.70	0

$$\text{H}_2 \text{ selectivity} = \frac{\text{ppm of H}_2/2}{\text{ppm of CH}_4 \text{ converted}} \times 100 ; \text{ ppm of CH}_4 \text{ converted} = \text{ppm CH}_4 \text{ in} - \text{ppm CH}_4 \text{ out}$$

In Table 2, we compiled the physical, chemical characterisation and activity data for the cobalt catalysts. The micropore volume and external surface area of the support (H-ZSM-5; after calcination) decreased and increased respectively with cobalt loading. Ion exchange (I.E.) increased the external surface area as compared to cobalt deposition by precipitation (S.P.) and incipient wetness (I.W.). The external specific surface area was increased during the exchange process, suggesting a reduction in the particle size.

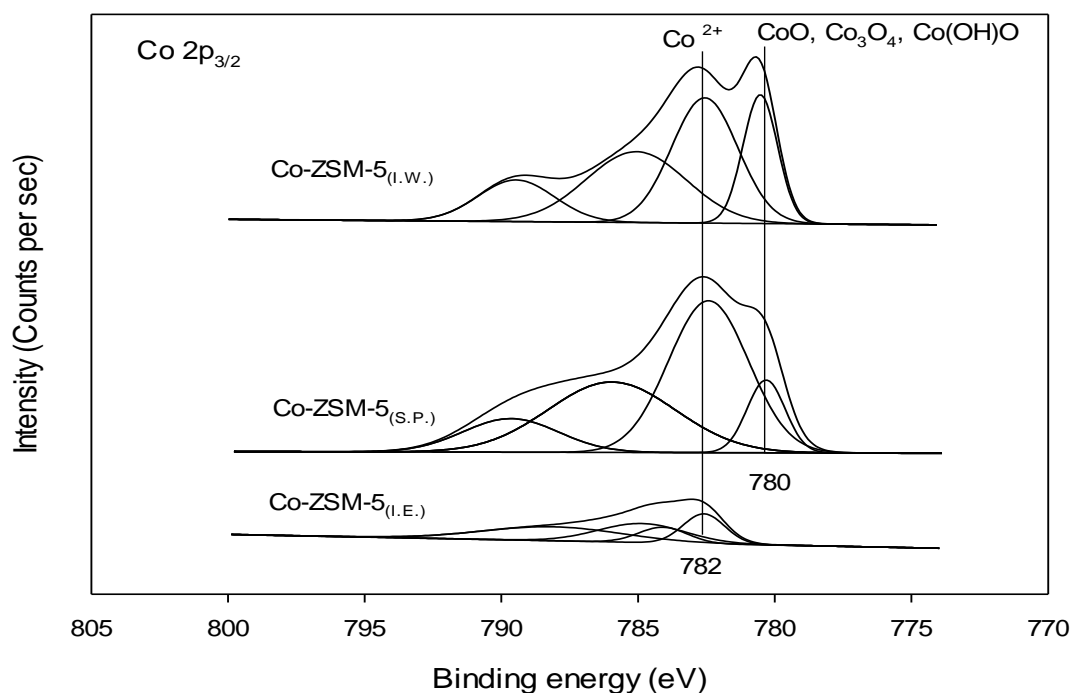


Figure 4: XPS spectra of Co2p region for the Co-ZSM-5_(I.W.), Co-ZSM-5_(S.P.), and Co-ZSM-5_(I.E.) catalysts.

X-ray photo electron spectroscopy (XPS) analysis confirmed the presence of different cobalt species (Figure 4). In accordance with published literature, the binding energy at 782.0 eV is assigned to Co^{2+} at charge compensation sites, whereas binding energies for CoO , Co_3O_4 , and Co(OH)O are found at 780.1 eV, 779.6 eV, and 780.0 eV respectively [25-29]. Cobalt on ZSM-5 support can be paramagnetic. The peaks found at a binding energy of 785 eV and 790 eV corresponds to shakeup peaks [29]. The peaks attributed to cobalt oxide and cobalt (III) hydroxide were not observed on Co-ZSM-5_(I.E.).

At 70 % CH_4 conversion, the H_2 yield (mol/min) per mol of Co (turn over frequency) was highest for Co-ZSM-5_(I.E.) as shown in Table 2 (experimental conditions; molar ratio of $\text{CH}_4/\text{N}_2\text{O} = 1/2$, 67% helium diluent), suggesting Co^{2+} as preferred active sites for H_2 formation. Cobalt in ZSM-5_(I.E.) catalyst occurs in the form of ion exchanged Co^{2+} , while over exchange of cobalt in Co-ZSM-5_(S.P.) and Co-ZSM-5_(I.W.) results in the formation of additional cobalt oxide species. Cobalt oxide species on the surface of Co-ZSM-5_(S.P.) and Co-ZSM-5_(I.W.) are suggested to be inactive for H_2 production and

thus H₂ (mol/min) formation per mol of cobalt sites is lower as compared to Co-ZSM-5_(I.E.). The inactivity of the extended cobalt oxides species for H₂ formation is inferred from the inactivity of cobalt oxide (CoO) and cobalt on γ -Al₂O₃ as shown in Table 1. The Co-ZSM-5_(I.W.) has the lowest H₂ to cobalt ratio due to presence of larger concentration of cobalt oxide species as inferred from XPS analysis. Overall, the number of mol of isolated Co²⁺ exchanged sites is higher in both over exchanged catalysts and therefore a higher H₂ yield was observed as compared to Co-ZSM-5_(I.E.). Spot analysis (EDS) of cobalt and aluminium at different locations of Co-ZSM-5_(S.P.) had different ratios of cobalt to aluminium and was in range of 0.95 – 22, suggesting the presence of different cobalt species.

Table 2: Characteristics of different cobalt catalysts on H-ZSM-5 support

Catalysts	Co (wt. %)	Methane Conversion (%)	Co/Al (molar ratio)	micro pore volume (cm ³ /g)	external surface area (cm ² /g)	H ₂ /Cobalt min ⁻¹ (mol/mol·min)	H ₂ yield
Co-ZSM-5 _(S.P.)	4.2	70	0.8	0.108	100	2.20	18
Co-ZSM-5 _(I.W.)	4.5	70	0.9	0.107	96.5	1.95	15
Co-ZSM-5 _(I.E.)	0.78	70	0.2	0.108	112	7.41	11
H-ZSM-5 _(support)	-	-	-	0.135	65.5	-	-
Carbon balance of Figure 1 at 450 °C							
CH ₄ in	CH ₄ out	CO ₂	CO	Sum of CH ₄ out, CO ₂ , and CO			Balance
26.15 %	25.97 %	0.65 %	0.11 %	26.08 %			99 %
Carbon balance of Figure 2 at 405 °C							
11.51 %	3.37 %	5.19 %	2.30 %	10.87%			94 %

4. Conclusion

In this study we report that, synthesis gas can be produced via the catalytic partial oxidation of CH₄ over Co-ZSM-5 using N₂O as oxidant. Based on laboratory reactor data and corresponding XPS analysis, it can be inferred that only cobalt-modified ZSM-5 catalyse the direct conversion of CH₄ to H₂ (synthesis gas). The temperature required for H₂ production is at least 400 °C. The concentration of H₂ can be enhanced by reducing the ratio of CH₄ to N₂O. Cobalt cations located in ion exchange sites are suggested to be the sites active in synthesis gas production.

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Figure 1: Effect of temperature on CH₄ and N₂O conversion; N₂ production; product distribution of CO₂, CO, and H₂ over Co-ZSM-5_(S.P.). Feed flow rate: 230 cm³/min (CH₄/N₂O=4, approx. 66% helium in feed mixture); weight of catalyst: 0.250 g.

Figure 2: Effect of temperature on CH₄ and N₂O conversion, N₂ production, product distribution of CO₂, CO, and H₂ over Co-ZSM-5_(S.P.). Feed flow rate: 230 cm³/min (CH₄/N₂O=1/2, approx. 67% helium in feed mixture); weight of catalyst: 0.250 g.

Figure 3: The product distribution of CO₂, CO, and H₂ over Co-ZSM-5_(S.P.) at time range of 0 - 5hrs. Feed flow rate: 230 cm³/min (CH₄/N₂O=1/2, approx. 67% helium in feed mixture); weight of catalyst: 250 mg.

Figure 4: XPS spectra of Co2p region for the Co-ZSM-5_(I.W.), Co-ZSM-5_(S.P.), and Co-ZSM-5_(I.E.) catalysts.

Highlights

- Cobalt is loaded over ZSM-5 support.
- Reactivity of CH₄ with N₂O over Co-ZSM-5 forms synthesis gas (CO + H₂).
- Co²⁺ sites are proposed active sites for H₂ formation (synthesis gas).