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A proposed reaction mechanism for the selective oxidation of methane with nitrous oxide over Co-ZSM-5 catalyst forming synthesis gas (CO + H₂)

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ABSTRACT

Probable reaction intermediates and mechanistic steps involved for the selective oxidation of methane (CH₄) with nitrous oxide (N₂O) forming synthesis gas (CO + H₂) over Co-ZSM-5 was examined. To assess the reaction kinetics reactions were conducted within a temperature range of 300 °C–550 °C and at atmospheric pressure, and the composition of reactant feed (N₂O/CH₄) was varied between three fixed ratios (5, 3, and 1). TPD, XRD, TEM and FT-IR techniques were used for catalyst characterization and mechanistic studies. It was found, that H₂ selectivity is higher for feeds with lower N₂O concentration. Furthermore, CO formation commences at lower temperatures in comparison to H₂ gas which is a result of the formation of methanol (CH₃OH) and carbon oxides (CO and CO₂) at low CH₄ conversions.

Based on the reaction conditions, the literature proposes direct and an indirect mechanistic route for synthesis gas formation. Our catalytic study suggests a direct route for the synthesis gas formation; i.e. H₂ gas is formed by the decomposition of intermediate species (methoxy and CH₂O). This is supported by spectroscopic investigation. Under favourable reaction conditions and over the Co-ZSM-5 catalyst, N₂O first oxidizes CH₄ to CH₃OH, an active reaction intermediate, which then subsequently is converted into (formaldehyde) CH₂O and H₂. CH₂O is highly reactive and decomposes into CO and H₂.

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Introduction

The CH₄ molecule is the most stable hydrocarbon and cleavage of the first C–H bond (425 kJ/mol) is often regarded as the rate determining step in CH₄ conversion reactions [1–4].

Notwithstanding thermodynamic constraints, CH₄ can be converted into a number of useful chemicals via the synthesis gas (CO + H₂) process route. Steam reforming, partial oxidation, and autothermal reforming of hydrocarbons are commonly used technologies for synthesis gas production.

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Presently, steam reforming of CH₄ is a commercially used process for H₂ production [5–8]. However, this process is highly endothermic and carries a large energy penalty [9].

In comparison to steam reforming, partial oxidation and autothermal reforming reactions are self-sustaining in terms of their energy requirements (exothermic reactions) [10,11]. Technically, autothermal reforming is a combination of steam reforming and combustion reactions, whereas combustion is preferably carried out over catalysts having higher thermal stability [12–14]. Partial oxidation is reaction under oxidant deficient conditions and a number of catalysts have been investigated [10,15–18]. Due to the exothermic nature of oxidation reactions, hotspots are often formed, where the surface temperature of parts of the catalyst surface can exceed the average bed temperature by several hundred degrees and as a result the catalyst may lose its catalytic activity [19].

After examining the early published literature it is notable that the partial oxidation of CH₄ is studied over three categories of materials; (1) supported Ni, Co, and Fe catalysts [20–23]; (2) supported noble metal catalysts [24–26]; (3) and metal carbide catalysts [27–29]. Selectivity to H₂ is dependent on the oxidation state of the active metal, where in most cases, the reduced metal was suggested to form the active site for H₂ formation [30,31]. When compared to cobalt and iron, nickel catalysts are more selective to synthesis gas production, but nickel is also favourable for CH₄ carbonization (resulting in coke formation) and thus the selectivity of synthesis gas decreases with time on stream [27]. In addition to nickel, cobalt catalysts were found to be more selective to synthesis gas production and various Al₂O₃ supported cobalt catalysts were investigated recently [32–34].

Till now a number of different mechanisms for CH₄ partial oxidation to synthesis gas (CO + H₂) have been suggested [31], in general the literature presents two distinct generic reaction mechanisms [27,35]. Prettre et al. and Vermeiren et al. are among the pioneers to study the temperature variation along the catalyst bed and proposed an indirect mechanism for synthesis gas production [20,36]. In an indirect reaction mechanism, CH₄ reacts with O₂ in the front portion of the catalyst bed, forming CO₂ and H₂O, while downstream in the catalyst bed, H₂O and CO₂ reforms CH₄ to synthesis gas. Independently, Green and co-workers also reinforced the importance of the indirect mechanism for synthesis gas production [37], whereas in contrast to Green's work, Hickman and Schmidt observed an increase in synthesis gas selectivity with increasing reactant flow rate and suggested a direct reaction mechanism for synthesis gas formation [26,38,39]. For a direct reaction mechanism to occur, CH₄ molecules most likely dehydrogenate over the active sites, forming H₂ and depositing carbon, C_xH_y, and CH_xO, while intermediate carbon species are then oxidized to CO_x [40–43].

The conversion of CH₄ to synthesis gas has also been studied using oxidants other than O₂ (for example N₂O) [44,45]. Indeed, due to numerous environmental constraints N₂O dissociation and its selective oxidation with hydrocarbons (including CH₄) has been an active research area over the past three decades [46,47]. Interest to use N₂O as an oxidant was invigorated following Panov's work on selective oxidation of benzene to phenol over an iron based catalyst [48]. In Panov's

work, it is proposed that oxygen species formed from N₂O form a nucleophilic form of oxygen (α -oxygen) on the active site of the catalyst, and α -oxygen was shown to react with hydrocarbons in an unusual way [49]. While Panov et al. carefully examined N₂O reactivity on Fe-ZSM-5 [50], most research suggests that the mechanism of N₂O conversion is strongly dependent on the zeolite type used [51]. For example, it was found that Co-ZSM-5 is a more active catalyst than Fe-ZSM-5 for the N₂O dissociation reaction [52]. However, the type of zeolite support and method of cobalt loading also influences the catalytic performance of N₂O conversion reactions [53,54]. The active site and its position in Co-ZSM-5 catalyst is a topic of considerable discussion and debate, and different types of active cobalt species have been postulated [55].

The selective oxidation of CH₄ with N₂O to form synthesis gas is a relatively new research area, and has been studied only by few research groups. A thermodynamic analysis of the reaction was undertaken and it was concluded that there is a driving force for an appreciable yield of synthesis gas, which is strongly dependent on reaction conditions such as temperature and reactant feed ratios [56]. In comparison to several other catalysts, Co-ZSM-5 prepared by wet deposition method was found to be more active for H₂ formation [45]. To best of our knowledge, the mechanism for CH₄ oxidation with N₂O to synthesis gas over Co-ZSM-5 catalyst has not been studied, and in this study we investigated the variation of H₂ selectivity with reaction conditions and proposed a novel reaction mechanism describing the reaction chemistry of N₂O and CH₄ over the Co-ZSM-5 catalyst.

Experimental

Catalyst activity analysis

Reaction of CH₄ with N₂O over Co-ZSM-5 catalyst was studied in a packed bed tubular reactor. Co-ZSM-5 was prepared by using a novel wet deposition method as discussed in our earlier articles [45,54]. Before reaction, the catalyst was heated gradually (5 °C min⁻¹) to a temperature of 550 °C in helium. A reactant feed (N₂O: CH₄) of different molar ratio (5:1, 3:1, and 1:1) was mixed well with 95% helium before entering the reactor. A high concentration of diluent (He) was used to reduce the likelihood of hot spot formation on the catalyst surface [23]. The temperature was measured inside the catalyst bed and outside the reactor and a negligible temperature difference was observed. The catalyst bed was small compared to the total reactor volume, the surface area to volume ratio was high (80 m⁻¹) and the gas stream and active sites were highly diluted and thus it can be assumed the tubular reactor was in isothermal conditions. The mass of catalyst used in each experimental run was approximately 0.250 g, with a particle size range of 250 μm–450 μm. The total flow rate of the reactant feed mixture was maintained at about 230 ml min⁻¹ (35,000 h⁻¹). The reactions were studied between 300 °C and 550 °C, with a temperature increment of 25 °C. A stainless steel tube of ¼" diameter was used as a reactor. No significant conversion was observed in the absence of a catalyst within the studied range of

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