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Effect of ruthenium addition on molybdenum catalysts for syngas production via catalytic partial oxidation of methane in a monolithic reactor

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ABSTRACT

Hydrogen is mainly produced from hydrocarbon resources. Natural gas, mostly composed of methane, is widely used for hydrogen production. As a valuable feedstock for 'Fischer–Tropsch' (FT) process and 'Gas to Liquids' (GTL) technology, syngas production from catalytic partial oxidation of methane (CPOM) is gaining prominence especially owing to its more desirable H₂/CO ratio; relatively less energy consumption, and lower investment, compared to steam reforming processes (SMR), the leading technology.

In the present study, effect of ruthenium (Ru) addition on molybdenum (Mo) catalysts for syngas production from methane (CH₄) via partial oxidation in a monolithic reactor was investigated. Mo based catalysts supported on Nickel (Ni) and Cobalt (Co) metal oxides and Ni-Co bimetallic oxides and their Ru added versions were developed, characterized, and tested for performance in a monolithic type reactor system. Catalyst activity was investigated in terms of H₂ and CO selectivity, CH₄ conversion; and CO₂ emission and it is concluded that addition of Ru over the structure led to increase in catalytic activity and reduction in carbon deposition over the catalyst surface.

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Introduction

The growing energy demand of the world is still mostly supplied by fossil fuels with finite reserves [1] and increasing amounts of GHGs resulting from their combustion keep contributing to global warming [2].

A derivative of fossil fuels or biomass, synthesis gas (H₂ + CO; or syngas) is an energy carrier conveniently convertible to other energy forms and value added products [3]. Steam and/or CO₂ reforming, partial oxidation, or auto-thermal reforming (a combination of the former two) are the

main methods for hydrogen and syngas production from any plentiful carbon or hydrocarbon source including biomass, coal, natural gas (which is mostly methane) and petroleum naphtha [3]. Catalytic processes based on hydrogen and synthesis gas are among the basic processes in providing food, fuel and chemical resources [3].

Ammonia and methanol synthesis, hydrogenation, and Fischer–Tropsch synthesis (FTS) for production of liquid hydrocarbons from syngas were among the most significant technical developments marking the beginning of modern chemical industry early in the 20th century. Syngas based fuel production via coal gasification and FTS supply approximately

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2% of world energy demand presently [3]. However this share is projected to increase significantly. Syngas production from hydrocarbons with established infrastructure such as methane (CH₄) is still continuing to be attractive for manufacturing hydrogen and synthetic fuels. In addition to its vast natural reserves as the main constituent of natural gas, an exhaustible fossil resource, methane is among the species in industrial gas streams such as the ones resulting from coal gasification. Methane can be formed as a by product from the decay or fermentation of biomass.

Methane is also present in the 'product gas' obtained by gasification of biomass which provides an abundant renewable resource for synthesis gas and hydrogen [4] and for which the demand is expected to grow, along with coal, as feedstocks [3]. Biomass originated methane conversion to synthesis gas can be associated with the carbon-neutral energy chain, owing to the effective carbon sequestration [5] alternative it offers. In 1902, following the discovery of synthesis gas formation in the presence of steam and methane [6,7], various routes have been developed for its production.

Steam reforming, partial oxidation, and dry reforming are mostly used for large-scale catalytic processing of CH₄ and production of synthesis gas [3]. SMR (Steam methane reforming) is the leading technology presently. However, CPOM (Catalytic partial oxidation of methane), although it was considered as early as 1929 [8] its study started growing in the 1990s; and it is emerging as a promising process owing to the advantage that the H₂/CO ratio of the gas is 2 approximately, which is suitable for Fischer–Tropsch synthesis [9] for methanol and motor fuel production. Through manufacturing of FTS products from methane/natural gas, problems involving pollutants such as sulfur compounds, heavy metals and fine particles, generally associated with coal, can be reduced. Exothermic process, yielding 2 mol of H₂ and nearly 36 kJ energy per mole of CH₄ without NO_x generation, and utilization of smaller reactors are additional advantages. Moreover, nearly 30% cost reduction relative to SMR has been reported [9]. Reactions of CH₄ partial oxidation (at 25 °C and 1 atm) are given in Table 1 [10].

In Table 1, reaction 1 is the main step in producing synthesis gas, and reaction 2 is a full combustion reaction. Side reactions 3 and 4 increase selectivity of CO and H₂ respectively. Various aspects of CPOM for synthesis gas production and the catalysts involved have been reviewed [11–14] in detail. Metal containing catalysts have been developed in granular and structured forms.

Metals such as cobalt (Co) [9,10,14–18], nickel (Ni) [9,14–16,19–29], also perovskites with Co and Ni [30]; copper (Cu) [14,21,31–33], iron (Fe) [31,34–37], rhenium (Re) [38], molybdenum carbide (Mo₂C) [39,40], tungsten carbide (WC) [40]; transition metals including iridium (Ir) [41], palladium

(Pd) [41,42], platinum (Pt) [22,41,43], rhodium (Rh) [41], ruthenium (Ru) [41,44–46], have been studied as CPOM catalysts; and oxides such as alumina (Al₂O₃) [9,17,20,23], ceria (CeO₂) [26], lanthania (La₂O₃) [47,48], magnesia (MgO) [49], mayenite (CaAl₂Si₂O₈) [31], silica (SiO₂) [16], yttria (Y₂O₃) [50], zirconia (ZrO₂) [16,51–53], yttria-stabilized zirconia (YSZ) [51–55] have been used either as catalysts or as catalyst supports. Structured metal catalysts have also been investigated [10,20,28,29,41–43,56–58]. Structured catalysts, such as monoliths, render operation at higher linear gas velocities and at reduced pressure drop over the bed possible. Consequently, residence times are quite short, in the range of a few milliseconds [14].

Although nickel (Ni) is an excellent catalyst and is relatively cheap for synthesis gas production [9], its utilization may involve severe coking. In the catalyst bed, in general, coking and hot spots formation are common problems, eventually leading to catalyst deactivation when group VIII metals (Ni, Pt, Rh, Ru) are used as supported CPOM catalysts. During CPOM to syngas at CH₄/O₂:2 and 777 °C, carbon deposition rate was reported to follow the order Ni > Pd ≥ Rh > Ru > Ir ≈ Pt. For Pt and Ir deposition was at negligible level [41]. However noble metals Ru, Pt, Pd or Rh are generally added at low percentages to metal catalyst as promoters. To improve the reducibility of Co at low temperatures a promoter, with a tendency to oxidize at lower temperatures, may be required to provide active sites [59]. Ignition temperatures of Ni catalysts can be lowered upon addition of promoters [60]. Carbon formation rate can be reduced upon Co addition [15–17], sometimes at the expense of decrease in activity of catalysts, as in the case of Ni [9]. Metal loading, nature of support and calcination temperature may strongly affect Co catalysts [18]. Molybdenum (Mo) can be active and stable, displaying activities comparable to activities of noble metal catalysts [13,40,61]. In terms of activity and selectivity, the performance of Mo₂C was found to be close to that of elemental Ir or Ru [39,40] when used in SMR, POX and dry reforming of methane. A limited number of studies with powder catalysts with Mo are also available [13,23,40,61]. Studies on utilization of monolithic catalysts containing Mo for H₂ production via partial oxidation of CH₄ have not been reported yet.

In the present study, monolithic catalysts supporting oxides of Mo-Co, Mo-Ni, Mo-Co-Ni and Ru added versions were prepared and used for syngas production by CPOM, with the purpose of developing carbon and temperature resistant active structured catalysts. Tests for determining the structural properties (such as crystal phases, specific surface areas and metal loading) and chemical activity of the catalysts were carried out. Present study is one of the very few examples of Mo containing catalysts for partial oxidation of CH₄.

Experimental

Characterization of materials

Analytical grade, over 99% pure reagents were used as received in all experiments: (NH₄)₆Mo₇O₂₄ (Alfa Aesar), RuCl₂x·H₂O (Merck), Al(NO₃)₃·9·H₂O (Merck), Ni(NO₃)₂·6·H₂O

Table 1 – Reactions of partial oxidation of methane (at 25 °C and 1 atm) [10].

R1	CH ₄ + (0.5) O ₂ → CO + 2H ₂	ΔH = -35.59 kJ mol ⁻¹	(1)
R2	CH ₄ + (2.0) O ₂ → CO ₂ + 2H ₂ O	ΔH = -802.0 kJ mol ⁻¹	(2)
R3	CH ₄ + (1.5) O ₂ → CO + 2H ₂ O	ΔH = -519.33 kJ mol ⁻¹	(3)
R4	CH ₄ + (1.0) O ₂ → CO ₂ + 2H ₂	ΔH = -318.66 kJ mol ⁻¹	(4)

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