

Simultaneous Catalytic Oxidation of Methane and Carbon Monoxide: A Strategic Proficient Way to Abate CNG Emissions

Snehlata Singh, Jitendra Kumar, Deepak Yadav

Department of Chemical Engineering, Harcourt Butler Technical University, Kanpur-208002, UP, India

Abstract - The atmospheric methane problem is cumulative due to rapid growth of compressed natural gas (CNG) vehicles in past two decades. It is highly conflicting to achieve the objectives of the 2015 United Nations Framework Convention on Climate Change (UNFCCC) Paris Treaty. Crucial achievement is obligatory to aim methane emission reduction especially from anthropogenic sources for example fast-growing tropical megacities, exponentially growing CNG vehicle count assisted with technical advances to reduce methane and carbon monoxide emissions. Rapid technical advances in oxidation catalysts varieties proposed lucrative and are capable to cut short vehicular emissions. The emission control strategies could significantly alter the global methane (2nd most abundant Greenhouse Gas) burden toward consistent pathways with the intentions of the Paris Agreement goals.

Key Words: CNG, greenhouse gas, CO and CH₄, Paris Agreement, oxidation catalyst.

1. INTRODUCTION

Compressed natural gas (CNG) vehicles are deliberately the most favorable substitutes to diesel, and gasoline fuelled vehicles because of rise in fuel prices and their growing severe discharge parameters [1]. CNG fuel comprises 90.6% methane (CH₄), 5.9% ethane (C₂H₆), 2.1% CO₂ and rest other gases [2]. Consequently, CNG vehicles emissions are less lethal due to less hydrocarbon (HC), carbon monoxide (CO), nitrogen oxides (NO_x) and very little particulate matter (PM) emissions in comparison to the traditional fuelled vehicles [3]. Sources of methane emissions include leaks from mechanical fittings at production wells, filling stations, unburnt methane, vents from storage tanks, supply chain, compressors, vehicles, and fuelling systems, etc.

The main challenge in CNG vehicles are unburned CH₄ and CO emission and slip in the exhaust [4]. Methane is 2nd utmost essential anthropogenic greenhouse gas (GHG) and weirdly striking objective for decreasing special greenhouse warming. It partakes a 100-years global warming potential (GWP) of 21 times compared to CO₂, rise in tropospheric ozone, and a key greenhouse gas [5]. CO is a noxious gas, also recognized as the 21st century's silent killer and hazardous for living beings [6]. The real impact confronts average tropospheric lifetime ~9-10 years, effective changes to diminish methane and carbon monoxide emissions can have quick efficacy [7, 8]. Subsequently in the year 2007, this anthropogenic methane load has grown abruptly, it began rising by around 6 ppb/yr and progression percentage enhanced in 2014 and presently it has crossed 10 ppb/yr [9]. As a consequence of which the government imposed strict emission standards such as the Euro-VI (European emission standards) limit (0.5 g/kWh) tightened the CH₄ emission by >55% as compared to Euro V limit (1.1 g/kWh) for CNG vehicles [10].

1.1 Catalytic abatement technology

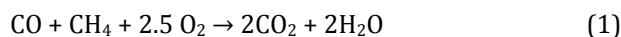
In recent times, further 1.5 Million vehicles plus all sorts of automobiles from auto rickshaw to HDV (heavy-duty vehicle, e. g. ships, trains and trucks) are fuelled with CNG. In most polluted cities like New Delhi, a drive of diesel-fuelled vehicles has been regulated, while CNG vehicles (CNGVs) have elated because of lesser emissions of toxic contaminants. Furthermore, underneath lean burn situations the fuel productivity of CNGV upsurges linked with stoichiometric state [11]. Consequently, CH₄ and CO release control over CNGV deplete is vital to keep social well-being, environment besides to sustain emission ethics. Though, removal of CH₄ is not an easy job, because it ignites above 540°C [12] in air, whereas the temperature of CNGVs exhaust gases lies between 150-450 °C. Hence, with the intention to lower the necessary combustion exhausts, catalytic oxidation appears to be most viable ways to reduce such pollutants and substitute expertise to the thermal combustion [13].

1.2 Legislations

According to the US EPA legislation, CH₄ can be structured at 0.1 g /hp/h for HDV and 0.05 g/mile for LDV (light-duty vehicles). Presently, Euro-6 and Euro-VI for CNG fuelled LDV and HDV are obligatory to meet both hydrocarbon (HC) or CH₄ emissions constraints as mentioned in Table 1.

2. Reactions and oxidation mechanism

It can be distinguished from Table 1 that the reduction in CH₄ emission is around 55% for HDV. To meet the stringent regulatory limits of CO and CH₄ emissions, catalytic oxidation of the engine exhaust of CNGVs has been proposed best and eco-friendly. The catalyst oxidizes CO and CH₄ to less toxic products, CO₂ and H₂O (see reaction 1).



CO₂ and water vapor or moisture are found in the atmosphere and are used for photosynthesis by the plants and vegetation. Numerous types of catalysts have been investigated for the combustion of CH₄ and CO for example platinum group metals (PGM), perovskite-oxides, spinel oxides, and miscellaneous transition metal oxides. The noble metal catalysts (Pd, Pt, and Rh) are recognized as most superior for vehicular exhaust control. The intermittent readiness and high cost of noble metals may restrict its broad applications over the long term use. In modern years, some earth-abundant supplies for example cobalt-based spinels with general formula; AB₂O₄ wherever A and B are divalent and trivalent cations distinctly, have been widely inspected as the utmost prominent catalyst for total oxidation of CH₄ and CO. Figure 1 shows that the divalent and trivalent cations A and B reside as tetrahedral and octahedral sites separately in a standard spinel structure.

Table -1: European Emission Standards for LDV and HDV [14,15]

Vehicles Emissions	LDV (g/km)		HDV (g kW/h)	
	Euro 5	Euro 6	Euro V	Euro VI
CO	1	1	4.0	4.0
NMHC (Non-Methane Hydrocarbons)	-	-	0.55	0.16
CH ₄	-	-	1.1	0.60
NO _x	-	-	2.0	0.46
HC + NO _x	0.18	0.18	-	-

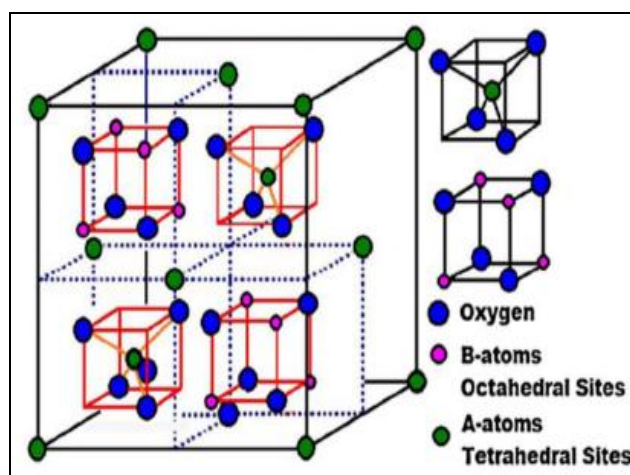


Figure-1: The General Structural Arrangement of Spinel. [Figure cited from wileyonlinelibrary.com]

CH₄ and CO oxidation reactions are structure-sensitive reactions. The catalytic activity and stability of the spinel structure are highly dependent on the precise ratio of Co³⁺/Co²⁺, morphology, texture, and oxygen position of the catalyst. Pretreatment process in the several situations has frequently been recycled for morphological revolution in the catalyst assembly. The Co₃O₄ and NiCo₂O₄ catalysts were calcined in the stagnant air and varied environments has been proposed in the literature for complete oxidation of CO and CH₄ [16].

3. Catalysts selection and preparation strategies

Among the noble metal catalysts, Pd and Pt revealed encouraging action for the oxidation of CH₄ and CO gaseous mixtures. Though, the complications accompanying with noble metal catalysts are its erratic readiness, luxury, high sintering rate, and poisoning in the presence of distressing elements. Transition metal oxides for example perovskite and spinels have been reflected as a smart substitute to the noble metals catalysts for catalytic oxidation of CO as well as CH₄ owing to their high activity and low cost. Among transition metals, the cobalt spinels have been exposed to be the proficient dynamic catalysts for simultaneous oxidation of CO and CH₄.

The total catalytic oxidation performance of CH₄ at low temperatures has been enhanced by doping a suitable promoter for variation in textural and morphological features of the catalyst. In recent years, highly active nickel cobaltite (NiCo₂O₄) spinel catalyst in the temperature range of 350–400°C has been designated for oxidation of CH₄ (maximum conversion is restricted to 90%). A single agent considered the complete concurrent oxidation of CO-CH₄ over nano-sized Fe₂O₃ catalyst at 650°C, which is away from the range of CNG vehicular exhausts (150–450°C).[17]

It is eminent that in the formulation of catalyst the precipitating agents and calcination temperature of the precursor have prominent impact on the catalyst's performance. Moreover, the calcined catalysts are lastly stimulated by in situ pretreatment in cautiously organized under controlled environments (inert/oxidizing/reducing), temperature, flow rate, etc. to stretch extreme activity. Yu et al. (2009) exhibited that the pretreatment of Co₃O₄ in dry air, N₂ or CO/air at 150°C, directed to total CO oxidation at –80°C. The pretreatment of the catalysts, modification of the surface active sites are responsible to enhance the catalytic activity such as improvement in reactivity of surface oxygen, growth of surface oxygen vacancies, surface enhancement of active component, etc. The performance of the catalysts is influenced by the calcination conditions and the subsequent pretreatment of the precursors and catalysts. The higher calcination temperatures in varied environments cause sintering of the active crystallites with a subsequent loss of active surface area, which reduces the catalyst's performance. Consequently, to minimize the above stated disadvantages of the two step pretreatment followed by calcination, a novel route of single step thermal treatment of the precursors in a reactive 4.5% CO–air mixture at low temperature (160°C) has been recently proposed in the literature to design highly active catalysts. Such single step thermal treatment of the precursor was so-called as "Reactive Calcination (RC) method". It was suggested that during RC method, the concurrent diverse phenomena of CH₄ and CO oxidation and precursor decomposition, cause a synergistic influence in the development of the oxygen deficient catalyst surface at low temperature. So, there should be periodic up gradation in the research methodologies to ensure environment intact. On the other hand, if methane is not taken below control, the penalties will be severe [18]. Further, the emissions of CH₄ will lead to the global warming and will hinder in meeting the objectives of Paris conclave.

Conclusion

The utmost fast growth in population and upgraded living ethics claim technical opportunities argued GHGs growth. On the other hand, if methane emission is not taken under control, then the penalties will be extreme in terms of global warming. Methane emission control is significant, not extremely expensive, and can be finished speedily. If the Paris Agreement is to thrive, then methane emission control should be considered seriously. The anthropogenic methane emissions load is increasing drastically due to CNG exhausts. This advancement is a communal threat to the Paris Agreement of the UNFCCC. Emissions can be amended by cutting biomass burning, improving landfills, particularly ending fossil fuel emissions and using high performance economical catalytic convertors practices.

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