

Catalytic Abatement of CO-CH₄ Emissions from CNG Vehicles

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Abstract—Cheap and highly efficient spinel catalysts; NiCo₂O₄, K-NiCo₂O₄, Pd-NiCo₂O₄ and K-Pd-NiCo₂O₄ were developed for total oxidation of CO-CH₄ emissions from CNG vehicles within the temperature window of exhaust (150-450°C). The catalysts were prepared by co-precipitation of basic carbonates of Ni and Co followed by doping of the promoters and reactive calcination in 4.5%CO-air mixture. The catalysts were characterized by XRD, TPR, XPS, BET and SEM-EDX. The air oxidation of CO-CH₄ mixture was performed in a fixed-bed-tubular-reactor under following conditions: 1.5%CO, 1.5%CH₄, rest air, 100ml/min total gas flow-rate, 500mg catalyst and at atmospheric pressure. The inlet and outlet of the reactor were analysed by GC. The optimum promoters doping found was 2wt% K and 0.1wt% Pd. The catalyst K-Pd-NiCo₂O₄ showed the best performance for oxidation of CO-CH₄ mixture at ~320°C. The activity order of the catalysts was as follows: K-Pd-NiCo₂O₄ > Pd-NiCo₂O₄ > K-NiCo₂O₄ > NiCo₂O₄. The unusual performance of the promoted catalyst was due to its unusual texture and reducibility.

1. INTRODUCTION

CNG is an attractive alternative fuel to gasoline or diesel for automobiles. An increased adoption of CNG for transportation will assist in lowering carbon dioxide (CO₂) emission due to highest H:C ratio. Additionally, CNG engine has several merits such as high efficiency, low nitrogen oxides (NO_x), negligible particulate matter (PM) emissions, and homogeneous combustion [1]. However, the problem of CNG vehicles are CO emission and methane (CH₄) slip, i.e., the release of a small amount of unburned methane in the exhaust [2]. CO is a poisonous gas, known as the 21st century silent killer and dangerous for living beings [3]. CH₄ is a direct greenhouse gas having the global warming potential of 21 times more than CO₂ [4]. Therefore, the government has stricter emission standards such as the Euro-VI limit (0.5 g/kWh) tightened the CH₄ emission by >55% in comparison to Euro V limit (1.1 g/kWh) for CNG vehicles [5].

The catalytic oxidation is proved to be the best technique to control both CO as well as CH₄ emissions from automobiles. Among various catalysts, noble metal catalysts exhibit high activity for the combustion of a lean mixture at low temperature. Several articles have been published for the separate oxidation of CO [6] and CH₄ [2, 7, 8] over noble

metal catalysts. On account of the inadequacy and high-cost of noble metals, worldwide efforts are being made to substitute noble metal by non-noble metal catalysts. In this regard transition-metal oxides offer a range of real-world and marketable advantages that make them attractive. Several non-noble metal catalysts such as perovskite, spinel, hydroxalite and mixed oxides [9-14] have been studied to oxidize CO and CH₄ individually into CO₂ and H₂O. Only a few studies are reported for complete oxidation of CO-CH₄ mixture over transition metal oxides [4, 15-17]. Among them, nickel cobaltite (NiCo₂O₄) spinel appears as the most attractive catalyst for total oxidation of CO as well as CH₄. Recently, Tao et al. [12] reported limited CH₄ conversion of 90% over NiCo₂O₄ beyond 340°C. Some studies confirmed that the conversion of CH₄ could be enhanced by increasing the structural defects and amount of nonstoichiometric oxygen and its mobility in the catalyst [18, 19]. Such defects and oxygen mobility in the catalysts can be developed by doping a small amount of alkali or noble metals. Alkaline metal especially, potassium (K) metals, have been widely studied for the catalyst surface alteration due to its better activity for the oxidation reaction [20, 21]. Chen et al. [22] testified the performance order of alkaline metals as K > Na > Li for the coal catalytic gasification with CO₂ and H₂O. Further, Chen et al. [23] studied the effect of K and Al in NiCo₂O₄ catalyst for VOCs oxidation. They established that the K as a promoter improves NiCo₂O₄ catalyst for the oxidation reaction due to a decrease in particle size and TPR temperature as well as an increase in surface area.

Likewise, Pd also improves the catalytic performance for CO and CH₄ oxidation. In earlier studies Pd supported on Al₂O₃ has been reflected as one of the important catalysts for the methane combustion [24]. Doping of small amount of Pd on the transition metal catalysts was used to save cost and enhance the catalytic activity. When a spinel oxide interacted with Pd metal, it can exchange the oxygen with the active component of Pd, then exchanged oxygen was bonded to Pd, finally used in the reaction [25]. Further, calcination of the precursors in a reactive gas mixture of CO in air, so called reactive calcination (RC) at low temperature produced highly

active oxidation catalysts [26]. Thus, in the present treatise, the gap in the literature about the effect of dopants such as K-Pd to modify NiCo₂O₄ catalysts produced by RC route for the oxidation of CO-CH₄ mixture is described. The amounts of individual dopants and their subsequent combination were optimized for the oxidation reaction. The results of investigation were discussed in light of the catalysts characterization by XRD, XPS, BET, TPR, SEM, and SEM-EDX.

2. EXPERIMENTAL

2.1 Material and Methods

The K-Pd promoted NiCo₂O₄ catalysts were prepared by reactive calcination (RC) of co-precipitated basic carbonates precursor doped with promoters. First, NiCo₂O₄ precursor was synthesized by co-precipitation method as described in details elsewhere [17] followed by sprayed doping of KNO₃ and PdCl₂ Solutions separately as well as together. Second, the promoter doped precursors were reactively calcined *in-situ* in flowing mixture of 4.5%CO in air. Details of RC method investigated in our laboratory are described in reference [26]. Brief procedures of catalysts preparation are described below: The nitrates of Ni and Co in their stoichiometric ratio were precipitated by Na₂CO₃. The precipitates were filtered using a vacuum filtration system and washed with hot distilled water to remove all the nitrate ions. The precipitated cake was dried at 100°C for 24 h. All the chemicals used in the synthesis of the catalyst were of analytical grade (AR).

Further, for doping, the precursors by K (1, 2, 3, 4wt. %) and Pd (0.05, 1, 2, 3%) their nitrates were dissolved in distilled water. The salt solution of K and Pd were sprayed onto dried NiCo₂O₄ precursor and thoroughly mixed. Both promoters in their required amount of aqueous solutions were added in the same precursor in sequence by spraying to see the coincidence effect of dopants on properties of the catalyst. The doped and un-doped catalysts precursors were dried at 100°C overnight in an oven. The dried precursor was thermally treated *in situ* in two steps, first at 160°C by reactive calcination (RC) in 4.5%CO-air mixture, second, the sample was then annealed at 400°C in the same atmosphere; detailed procedures are given in reference [26]. The nomenclatures of the prepared catalysts are specified in Table 1.

Table 1: Nomenclature Of Catalysts

Catalyst	Nomenclature
NiCo ₂ O ₄	Cat-Ni
2%K-NiCo ₂ O ₄	Cat-NiK2
0.1%Pd-NiCo ₂ O ₄	Cat-NiPd0.1
0.1%Pd-2%K-NiCo ₂ O ₄	Cat-NiK2Pd0.1

2.2 Catalysts Characterization

XRD patterns of the catalysts were studied on Rigaku Ultima IV X-ray diffractometer (Germany) using nickel-filtered Cu K α radiation. The diffractogram were recorded at 40 kV and

40 mA in a continuous mode in the 2 θ range from 20 to 80°. The mean crystallite size (d) of the phase was calculated from the line broadening of the most intense reflection using the Scherrer equation (1).

$$d = \frac{0.89\lambda}{\beta \cos\theta} \quad (1)$$

Where d is the mean crystallite diameter, 0.89 is the Scherrer constant, λ is the X-ray wave length (1.54056 Å), and β the effective line width of the observed X-ray reflection, calculated by the expression $\beta^2 = B^2 - b^2$ (where B is the full width at half maximum (FWHM), b is the instrumental broadening determined through the FWHM of the X-ray reflection at 2 θ of crystalline SiO₂ for the instrument used (b = 0.00274).

H₂-Temperature programmed reduction (TPR) analysis was carried out in a fixed bed flow reactor. TPR measurements were done under the following conditions: reducing gas 10% H₂-Ar mixture, 0.2-0.25g sample weight, 40 mLmin⁻¹ flow rate, 10 °C min⁻¹ heating rate, and temperature range from 150-450 °C. The hydrogen content in the effluent gas from the reactor was measured by a TCD detector and molecular sieve column of a Nucon series 5765 gas chromatograph.

2.3 Activity Measurement

The catalytic activity tests for oxidation of CO-CH₄ mixture were performed under the following reaction conditions: 500mg of catalyst with feed consisting of a lean mixture of 1.5% CO and 1.5% CH₄ in air at a total flow rate of 100 mL/min., using a fixed bed tubular down flow reactor with an equivalent diameter 5.0 mm. The catalyst was diluted to 1 mL with α -alumina so that isothermicity of the bed could be realized. The gases CO and CH₄ as well as air were fed from pressurised cylinders. The reactor was placed in a split open furnace. The reaction temperature ranged from ambient to 500°C. The temperature of the catalyst-bed was monitored with the help of K-type thermocouple with an accuracy of $\pm 0.2^\circ\text{C}$, controlled by a microprocessor based temperature controller. The experimental measurements were performed under steady state conditions. Air fed was made free of moisture and CO₂ by passing it through CaO and KOH drying towers. The flow rates of CO, CH₄ and air were monitored with the help of digital gas flow meters.

The gaseous reactants and products were analysed by an on-line gas chromatograph (Nucon series 5765) equipped with Porapack q-column, Methaniser and FID detector for the concentration of CH₄, CO and CO₂. The catalytic activity for the simultaneous oxidation was expressed in term of the conversion of limiting reactants such as; CO, CH₄ and overall CO-CH₄. The conversion of CO at any instant was calculated on the basis of values of the concentration of CO in the feed and product stream by the following equation (2):

$$\begin{aligned} (X_{\text{CO}}) &= [(C_{\text{CO}})_{\text{in}} - (C_{\text{CO}})_{\text{out}}] / (C_{\text{CO}})_{\text{in}} \\ &= [(A_{\text{CO}})_{\text{in}} - (A_{\text{CO}})_{\text{out}}] / (A_{\text{CO}})_{\text{in}} \end{aligned} \quad (2)$$

Where, concentration of CO is proportional to the area of chromatogram A_{CO} . Similarly, the conversion of CH_4 was calculated using the following equation (3):

$$(X_{CH_4}) = [(A_{CH_4})_{in} - (A_{CH_4})_{out}] / [(A_{CH_4})_{in}] \quad (3)$$

Overall conversion of CO- CH_4 was calculated on the basis of values of the concentration of CO_2 in the product stream by the following equation (4).

$$(X_{CO+CH_4}) = (C_{CO_2})_{out} / [(C_{CH_4})_{in} + (C_{CO})_{in}] \\ = (A_{CO_2})_{out} / [A_{CO_2}]_f \quad (4)$$

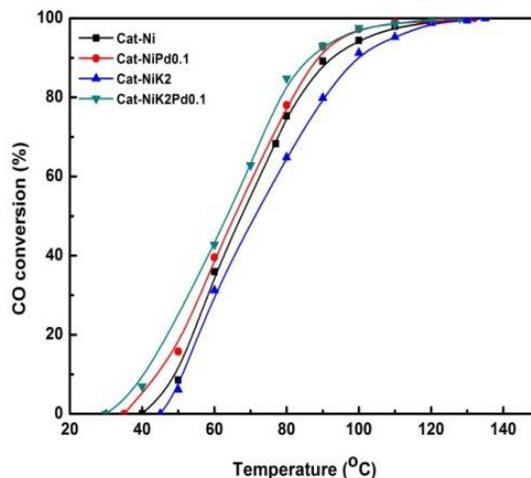
Where, change in the overall concentration of CO- CH_4 due to simultaneous oxidation at any instant is proportional to the area of chromatogram of CO_2 formed $[A_{CO_2}]$, and overall concentration of CO- CH_4 in the inlet stream is proportional to the area of CO_2 chromatogram $[A_{CO_2}]_f$ resulting at 100% conversion of CO- CH_4 together, i.e. single peak of CO_2 in GC chromatogram.

3. RESULTS AND DISCUSSIONS

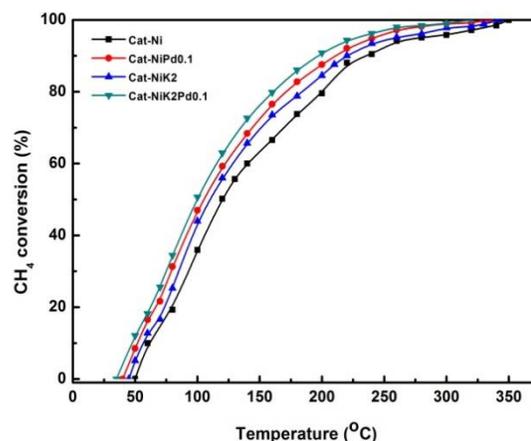
3.1 Activity comparison of catalysts

The activity of un-doped and K-Pd doped $NiCo_2O_4$ catalysts for oxidation of CO- CH_4 mixture was tested and the results are shown in figure 1. The light off characteristics of the catalysts for oxidation of CO and CH_4 in CO- CH_4 mixture is given in Table 2. The activity of the catalyst was measured in terms of conversion of reactants as a function of temperature. It is very clear from the figure that the conversion of CO and CH_4 in the mixture over Cat-Ni was completed below $350^\circ C$, which was in the temperature range of vehicular exhaust. While, the temperatures of total conversion of CO- CH_4 mixture was started to decrease by the addition of dopant in the catalyst. Cat-NiK2 achieved 100% conversion at $342^\circ C$, though; Cat-NiPd0.1 attained the same conversion at still lower temperature $335^\circ C$. The lowest temperature achieved for oxidation of CO- CH_4 mixture over Cat-NiK2Pd0.1 was $320^\circ C$. It might be due to fact that the combined promoters, K-Pd and $NiCo_2O_4$ made a strong interaction which influences the catalytic activity for the oxidation reaction.

One of the remarkable observations is that the temperature for complete conversion of CO in the mixture was almost same for Cat-NiPd0.1 and Cat-NiK2. The activity of Cat-NiK2 was little bit better than Cat-NiPd0.1. It seems that dopants individually did not much affect the performance of the catalysts for CO oxidation. While, in case of CH_4 oxidation activity plots was changed as compare to CO over Cat-NiPd0.1 and Cat-NiK2 catalysts. The main effect of dopants individual and in combined form was observed in CH_4 oxidation. Achievement of even small decrease in the temperature for complete combustion of strongly bonded CH_4 is appreciable. Therefore, the overall performance order of the catalysts according to their activity is as follows: Cat-NiK2Pd0.1 > Cat-NiPd0.1 > Cat-NiK2 > Cat-Ni.



1a



1b

Figure 1. Catalytic activity for oxidation of (a) CO and (b) CH_4 in CO- CH_4 mixture over doped and un-doped catalysts.

Table 2. Light off characteristics of catalysts

CO oxidation			
Catalyst	T10 (oC)	T50 (oC)	T100(oC)
Cat-Ni	52	77	130
Cat-NiK2	47	71	132
Cat-NiPd0.1	44	65	135
Cat-NiK2Pd0.1	45	64	128
CH4 oxidation			
Cat-Ni	65	120	350
Cat-NiK2	58	110	342
Cat-NiPd0.1	50	105	335
Cat-NiK2Pd0.1	45	100	320

3.2 Characterization Results

3.2.1. Phase and purity of the catalysts by XRD

The phase and purity of the catalysts are characterized by XRD and patterns are shown in figure 1. The common peaks (220), (311), (400), (511), (400) are indexed to NiCo₂O₄ have cubic crystal structure (JCPDS: 20-0781). Distinctive lines of NiCo₂O₄ spinel in XRD patterns was observed in all catalysts. There was no K and Pd species observed for any sample, which indicated that the dopants were highly dispersed on NiCo₂O₄ sample or in microcrystalline state in the spinel phase. In addition, there was no other crystalline line in Cat-NiK₂Pd_{0.1} due to Pd or K addition in the catalyst. XRD results may be described on the basis of interaction between dopants and main spinel.

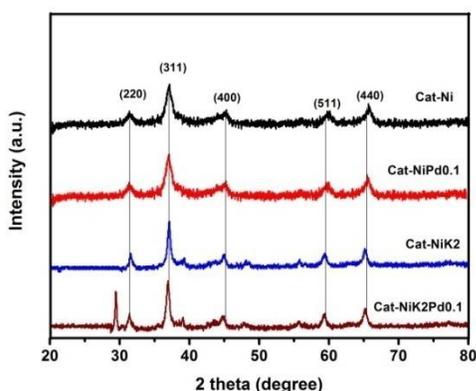


Figure 2. XRD patterns of NiCo₂O₄ and K-Pd doped NiCo₂O₄ catalysts

3.2.2. Temperature programme reduction (TPR)

In order to investigate the reduction temperature or reducibility of the doped and un-doped catalysts, H₂-TPR experiments were carried out and results are shown in figure 5. TPR profile of Cat-Ni was shown by three peaks

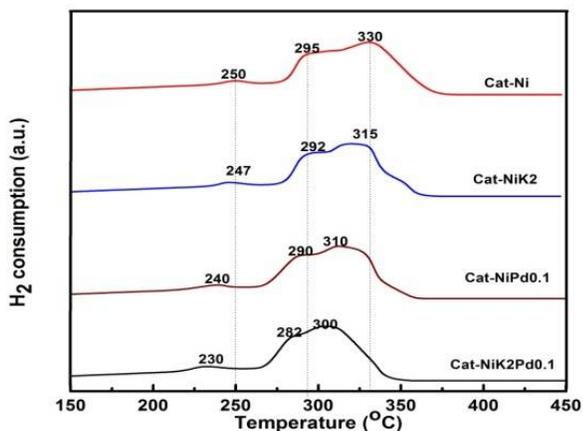


Figure 3. TPR profile of doped and undoped NiCo₂O₄ catalysts

α , β and γ in the experimental temperature range of 150-450°C. Among them, α peak (250°C) was ascribed to the reduction of the dispersed and small particle size of Cat-Ni and they were reduced at lower temperature. While, γ peak at 330°C was attributed to the reduction of the big or agglomerated particles size of Cat-Ni and they were reduced at higher temperature. The change in the profile of the catalysts with addition of dopants, Cat-NiK₂, Cat-NiPd_{0.1} and Cat-NiPd_{0.1}K₂ are shown in figure 3. The largest peak area and lowest reduction temperature was indicating that the sample NiCo₂O₄ can be easily reduced by adding both K-Pd dopant in sufficient amount. The reducibility order of the catalysts which supports the activity results is as follows: Cat-NiPd_{0.1}K₂ > Cat-NiPd_{0.1} > Cat-NiK₂ > Cat-Ni.

4. CONCLUSIONS

In this study, K and Pd as additives considerably improve the activity of NiCo₂O₄ catalyst for oxidation of CO-CH₄ mixture. Physical characterization of the catalysts reveals that the beneficial effect of dopants on NiCo₂O₄ can be linked to the good intimate contact between dopants with spinel catalyst, high surface area and small particle size. It can be concluded that addition of K-Pd decreases the reduction temperature of the catalyst which is also favourable for its activity. The reducibility order of the catalysts is found to be Cat-NiK₂Pd_{0.1} > Cat-NiPd_{0.1} > Cat-NiK₂ > Cat-Ni, which is consistent with the activity order of the catalyst.

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