Development of nano-NiCo₂O₄ spinel for abatement of CO-CH₄ emissions from CNG vehicles

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Compressed natural gas (CNG) is an alternative fuel for automotive applications with significant advantages such as it is cheaper and causes lower emissions of higher hydrocarbons with practically no soot than gasoline or diesel. However, the concentration of CO and unburned CH₄ are much higher in the exhaust of the CNG-vehicles than other fuelled vehicles. CH₄ emission is 40% more in CNG fuelled engines compared to gasoline and diesel [1]. CO is a poisonous gas and CH₄ is a greenhouse gas having 21 times more global warming potential than CO₂. Catalytic oxidation of the emissions is the best end of the pipe treatment technology. The development of low cost, highly active, selective and robust catalysts workable within the temperature window of the exhaust (150-450°C) is the measure challenge. The present investigation was devoted in the same direction for total oxidation of lean-mixture of CO-CH₄ at low temperature.

NiCo₂O₄ spinel consisting of earth-abundant elements exhibits higher catalytic activity than noble-metal-based catalysts [2]. In the present work, nano NiO, Co₃O₄ and NiCo₂O₄ catalysts were prepared by precipitation/co-precipitation methods followed by calcinations under CO-air reactive mixture. The catalysts were characterized by XRD, N₂-physisorption, XPS and FTIR. Their catalytic performances were evaluated in a fixed-bed-tubular-flow-reactor under the following conditions: catalyst=500mg, flow rates of CO and CH₄=1.5ml/min each air flow rate=97ml/min and at a heating rate of 1°C/min. Reactants and products were analyzed by an online GC equipped with porapack q-column, methanizer and FID detector for CO, CH₄ and CO₂. The XRD/FTIR analyses showed the formation of nano-Co₃O₄ and NiCo₂O₄ spinel structures.

Figure 1: XRD Pattern of the catalysts

Table 1: Crystallite size of the catalysts

Catalyst	Crystallite size (nm)
NiO	19.03
Co ₃ O ₄	12.28
NiCo ₂ O ₄	7.97

XRD pattern of the catalysts are shown in figure 1. Compared to NiO, Co₃O₄ the XRD patterns of the

NiCo₂O₄ is very different. The intensity of peaks is very less in NiCo₂O₄, show its amorphous nature. The crystallite sizes of the various cobaltite catalysts were calculated using the Debye-Scherrer, as given in Table 1. It is very clear from figure and table all catalysts are in nano-range. The crystallite size of NiCo₂O₄ (7.97 nm) is very less compare to Co₃O₄ (12.28 nm) and NiO (19.03 nm).

Figure 2: Comparison of catalytic activity for (a) CO and (b) CH₄ oxidation in simultaneous CO-CH₄ oxidation

Table 2: Light off temperature characteristics

Catalyst	Reactants					
	CO			CH ₄		
	T ₁₀	T ₅₀	T ₁₀₀	T ₁₀	T ₅₀	T ₁₀₀
NiO	93	108	190	128	318	470
Co ₃ O ₄	67	94	170	93	278	450
NiCo ₂ O ₄	52	77	150	63	125	350

Nano particle of NiCo₂O₄ showed total oxidation of lean CO-CH₄ mixture at the lowest temperature (350°C) in comparison to Co₃O₄ (450°C) and NiO (470°C) as mentioned in Table 2. The remarkable activity of NiCo₂O₄ nano-catalyst at relatively low temperature results from integration of Ni- and Co-cations and surface lattice oxygen vacancies. The benefits of Ni-incorporation in Co₃O₄ could be attributed to highly active sites created by Ni-cation. Thus, NiCo₂O₄ showed significant improved catalytic performance and could be recommended for control of CO-CH₄ emissions from CNG vehicles (Figure 2).

References

1. M. Kumar, G. Rattan, R. Prasad, Canadian Chemical Transactions 3 (2015) 381-409.
2. H. Zhang, H. Qiao, H. Wang, N. Zhou, J. Chen, Y. Tang, J. Li, C. Huang, Nanoscale 6 (2014): 10235-10242.