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Short Communication

Catalytic Removal of Methane Over Cobalt Chromite ($CoCr_2O_4$) Nanospinels for CNG Vehicles

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Abstract

Cobalt chromite ($CoCr_2O_4$) with normal spinel structure, shows catalytic activity for oxidation of unburned methane in the natural gas vehilcles (NGV). In this study, $CoCr_2O_4$ nanoparticles were synthesized through a conventional co-precipitation technique and investigated for the catalytic combustion of methane. Cobalt nitrate hexahydrate, chromium nitrate nonahydrate and ammonia solution (25%) were used as the starting materials. The obtained results show that the $CoCr_2O_4$ nanospinels were produced as single phase with an average diameter between 25-50 nm. Characterization studies by X- ray diffraction (XRD), N_2 adsorption/desorption (BET), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), temperature program oxidation (TPO) and O_2- temperature programmed desorption (O_2-TPD) were carried out. The specific surface area (S_{BET}) of the synthesized nanoparticles was measured using multiple point Brunauer–Emmett–Teller (BET) method.40 $m^2.g^{-1}$ was obtained for $CoCr_2O_4$ nanoparticles. The results revealed that cobalt chromite nanoparticles have significant capability for methane conversion at 435^oC.

Keywords*: Cobalt chromite; Co-precipitation; Methane conversion; Nanoparticles.*

1. INRODUCTION

Natural gas engines have noticeable advantages over gasoline and diesel engines. Since compressed-natural-gas (CNG) is widely recognized as the cleanest hydrocarbon fuel, CNG engines could lead to very low pollutant emissions. However, unburned methane is much harder to oxidize than gasoline-derived unconverted hydrocarbons. Methane as one of the greenhouse gases is recognized to contribute in the global atmospheric warming potential (Li, 2009). The strong greenhouse effect of methane forces to abate these emissions from CNG engines. Nevertheless catalysts based on transition metal oxides, such as Co, Mn, Cu, Cr and Fe oxides, become appealing due to lower cost and relative abundant resources. Amongst these catalysts, spinel-type oxides have attracted much attention for many years and the spinel-type-oxides catalysts, Cr_2CoO_4 was found to be very active for the oxidation of hydrocarbons (Chen, 2011).

NG exhibits reduced emissions during cold start and its low carbon to hydrogen ratio results in lower CO_2 emission compared to gasoline. However, CO and unburned methane, which is a major greenhouse gas, are present in the exhaust stream. Therefore, catalytic treatment is necessary for the abatement of pollutants emitted from the natural gas fueled vehicles (NGFVs).

Conventional automotive exhaust catalysts that contain precious metals (Pt,

Pd and Rh) were used for the treatment of pollutants like CO, unburned hydrocarbons and NOx. Among the precious metals, Pd in its oxidized form (PdO) is believed to be the most active catalyst for methane oxidation (Ziaei-azad, 2011).

Cobalt chromite ($CoCr_2O_4$), one of the spinel family (AB_2O_4), is ferrimagnetic in nature in which magnetic Co^{2+} ions occupy A site and magnetic Cr^{3+} ions occupy B site. As well as, cobalt chromite is a multiferroic material, it has been widely used as dye, substrate for film growth and catalyst (Rath, 2011).

Four spinel-type-oxide ($CoCr_2O_4$, $MnCr_2O_4$, $MgFe_2O_4$ and $CoFe_2O_4$) were studied as catalysts for methane removal in compressed natural gas (CNG) vehicles. Among them, $CoCr_2O_4$ was found to be very active for the oxidation of hydrocarbons, as well as for catalytic removal of NOx and diesel soot (Fino, 2006)

In another study, cerium modified cobalt chromite catalyst with different cerium content was prepared by co-precipitation method and the catalytic activities were evaluated toward methane (Chen, 2011).

Up to now, various techniques have been reported for cobalt chromite nanoparticles synthesis. For example cobalt chromite was synthesized by hydrothermal method with mean crystallite size 112 ± 1.4 nm (Durrani, 2012). Cr_2CoO_4 was prepared by solution combustion synthesis (SCS) method (Fino, 2006), the most of the obtained spinel crystals nanoparticles were between 20 - 50 nm in size range (Fino, 2007). In other study, cobalt chromite nanostructure was prepared by thermolysis of the co- polymer- metal complex at high temperature (Li, 2006).

The present study concerns the development of nanostructured spinel-type catalysts for the oxidation of methane. For this purpose $CoCr_2O_4$ nanoparticles were synthesized via co-precipitation method that it is a technique with desirable efficiency and mild condition.

2. EXPERIMENTAL

2.1. Materials

Cobalt nitrate hexa hydrate ($Co(NO_3)_2.6H_2O$), chromium nitrate nona hydrate ($Cr(NO_3)_3.9H_2O$) and ammonia solution (25%) were used as the starting materials. All of them were purchased from Merck Company and used without further purification.

2.2. Catalyst preparation

Conventional co-precipitation method was used to synthesize cobalt chromite nanoparticles. Solutions of cobalt nitrate (0.5M), chromium nitrate (1M) and ammonia solution (25%) were prepared in 25 ml volumetric flasks separately by dissolving appropriate amount of them in distilled water, respectively. Desired quantity of cobalt nitrate solution was taken in a 100 ml beaker and then chromium nitrate solution was added slowly to it under continuous stirring.

The mixed solution was stirred at room temperature for 2h. Then, aqueous ammonia solution (25%) was added dropwise to the mixed solution till the pH of 9 was attained. The hydroxide precipitate was filtered and washed several times with distilled water till the filtrate attained a pH value of about 7. The obtained precipitate was dried in an oven at 120^{o}C for 16h and calcined at 600^{o}C for 4h to get well jasper green powder.

2.3. Catalytic activity measurement

A mixture of 2500 ppm CH_4, oxygene (0.5 and 2.0vol%) and Ar were ensured via mass flow controllers. Flow rates of methane and Ar were 30 and 60 mL/min, respectively. Flow rates of this gas mixture and air were set by mass flow controllers in order to obtain a synthetic exhaust gas.

Oxidation of methane was studied in a fixed bed microreactor at atmospheric pressure. The Spinel samples were pelleted, crushed and sieved to particle size of 0.125-0.297 mm (60–100 mesh size). 100 mg of each sample, supported on a

small amount of quartz wool, was used to measure the oxidation activity of the catalyst. A thermocouple, placed inside the catalyst bed, was used for both monitoring and controlling temperature of the reactor. Samples were heated from ambient temperature up to 700°C under the reaction atmosphere and after the steady state condition was achieved at the desired temperature, concentration of the effluents was analyzed by a Shimadzu GC-8A gas chromatographe quipped with a methanizer and an FID. Also a set of valves allowed by passing the reactor feed directly into the gas chromatograph, which provided a direct measurement of the methane concentrations in the feed.

2.4. Characterization

Structural information of the calcined powders was obtained by X-ray diffraction. XRD pattern of sample was recorded on PW-1800 Philips operated at 40 [KV] voltage and 30 [mA] current with monochromatic CuKα (λ=1.54 [A°]) radiation in the scan range of 2θ between 4 to 74 (2θ/S) with a step size of 0.04. A Hittachi S-4160 field emission scanning electron microscope (FESEM) and Philips CM- 30 transmission electron microscope (TEM) were used for characterization of the morphology and measure the size of nanoparticles. The specific surface area was conducted at liquid nitrogen temperature (77K) using BELSORP-mini II. O_2-temperature programmed desorption (O_2-TPD) and temperature programmed oxidation (TPO) experiments were carried out using a Quantachrome CHEMBET-3000 apparatus. The O_2-TPD experiments were performed with 250 mg of samples enclosed in a U-shaped quartz reactor. Prior to each TPD run, the catalyst was heated under an O_2 flow (20 ml/min) up to 600°C. After a 30 min exposure to O_2 flow at this temperature as a common pretreatment, the reactor temperature was lowered down to room temperature by keeping the same flow rate of oxygen, thereby allowing a fully oxidized catalyst with adsorbed oxygen over its surface. Helium was then fed to the reactor at 10 ml/min flow rate and kept for 0.5h at room temperature in order to purge any excess oxygen molecules out of the catalyst surface. The catalyst was then heated to 1000°C under a flow of 10 ml/min of helium at a constant heating rate of 10°C/min. The O_2 desorbed during the heating was detected by a TCD detector.

3. RESULT AND DISCUSSION

The XRD pattern of $CoCr_2O_4$, that calcined at 600°C for 4h, is shown in Figure 1. The well defined peaks are corresponding to the miller indices (111), (220), (311), (400), (422), (511) and (440). The only peak observed is related to $CoCr_2O_4$ (JCPDS card: 22-1084). The obtained results demonstrate that cobalt chromite nanoparticle were synthesized as single phase and pure.

The FESEM and TEM images are indicated in Figure 2. As it can be observed, the $CoCr_2O_4$ nanoparticles have a mean diameter between 25-50 nm. The obtained particles are mostly agglomerated.

The specific surface area (S_{BET}) of the synthesized nanoparticles was measured using multiple point Brunauer–Emmett–Teller (BET) method. Surface area of $CoCr_2O_4$ nanoparticles is equal to 40 $m^2.g^{-1}$ for.

The mobility of oxygen was investigated by O_2-TPD experiments as illustrated in Figure 3. As it was reported by others [3], two types of oxygen species are distinguished in a TPD profile: a low temperature specie, named α-type oxygen or suprafacial, desorbed in the 300-600°C range, which is ascribed to the adsorbed oxygen bound to the surface anion vacancies, and high temperature one, named β-type oxygen or intrafacial, desorbed at above 600°C.

The same behavior was observed for perovskite. It is observed that the α-type oxygen peaks are plateau-like and

relatively weak, while the β-oxygen peaks are sharp and more intense (see Figure3).

The amount and the temperature in which α-type oxygen is desorbed seem to be the key factors for the catalytic activity of pure spinels.

Figure4. shows the activity results of chobalt chromite nanocatalyst for oxidation of CH_4. This nanocatalyst shows a mild S-shape profile for CH_4 conversion. T_{50} and T_{90} values indicated temperature for 50% and 90% methane oxidation. T_{50}°C (CH_4-0.5% O_2) and T_{50}°C (CH_4-2% O_2) is 405 °C and 365 °C, respectively. Also T_{90}°C (CH_4-0.5% O_2) and T_{90} (CH_4-2% O_2) is 480°C and 435°C, respectively.

CH_4 oxidation at low temperatures is proposed to be a suprafacial reaction, which occurs via the Eley–Rideal mechanism, where adsorbed oxygen in the vacancies is assumed to react with the methane in the gas phase. However, at elevated temperatures methane oxidation is suggested to be an intrafacial reaction dominantly involving lattice oxygen [3].

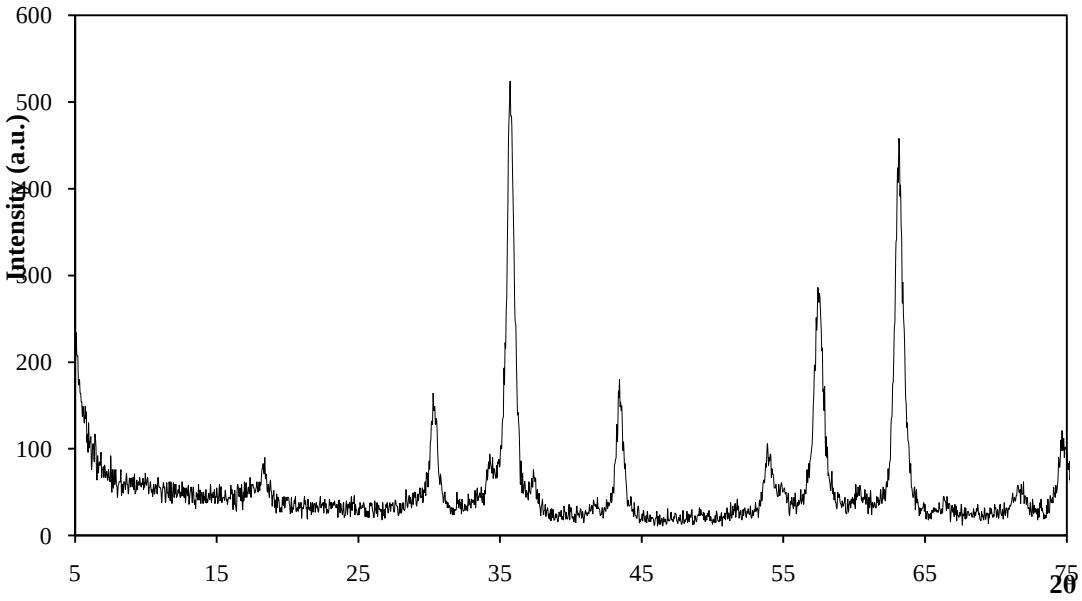
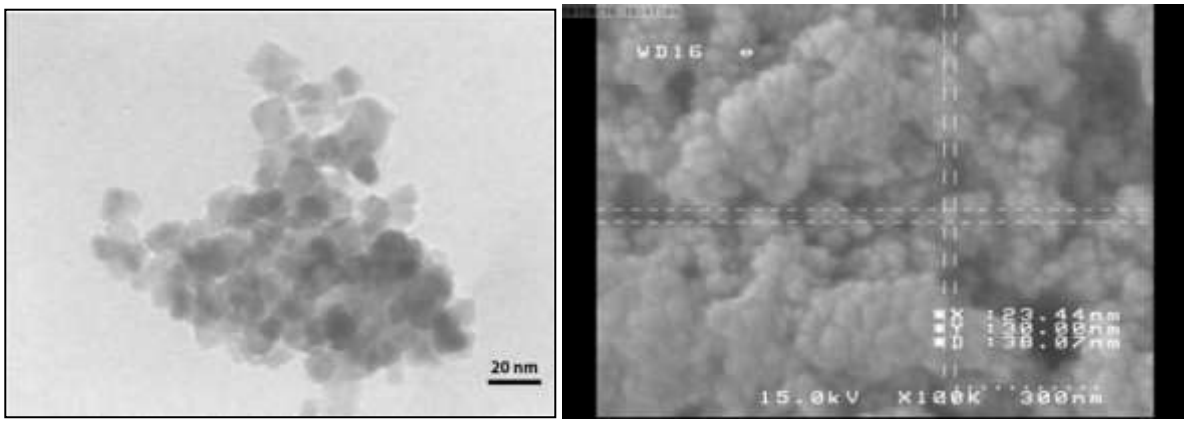


Figure1. *XRD pattern of calcined $CoCr_2O_4$ nanoparticles*



(a) **(b)**

Figure2. *(a) FESEM and (b) TEM images of $CoCr_2O_4$ nanoparticles*

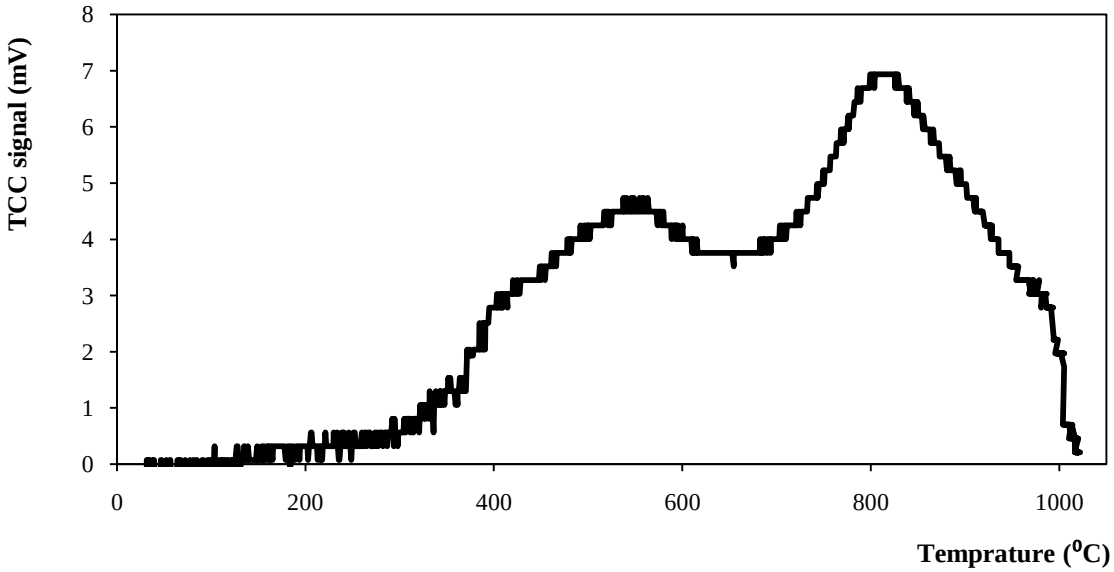


***Figure3**. O_2-TPD of fresh $CoCr_2O_4$ nanoparticles, 10 sccm He, 10 ˚C/min from100 to 1000˚C.*

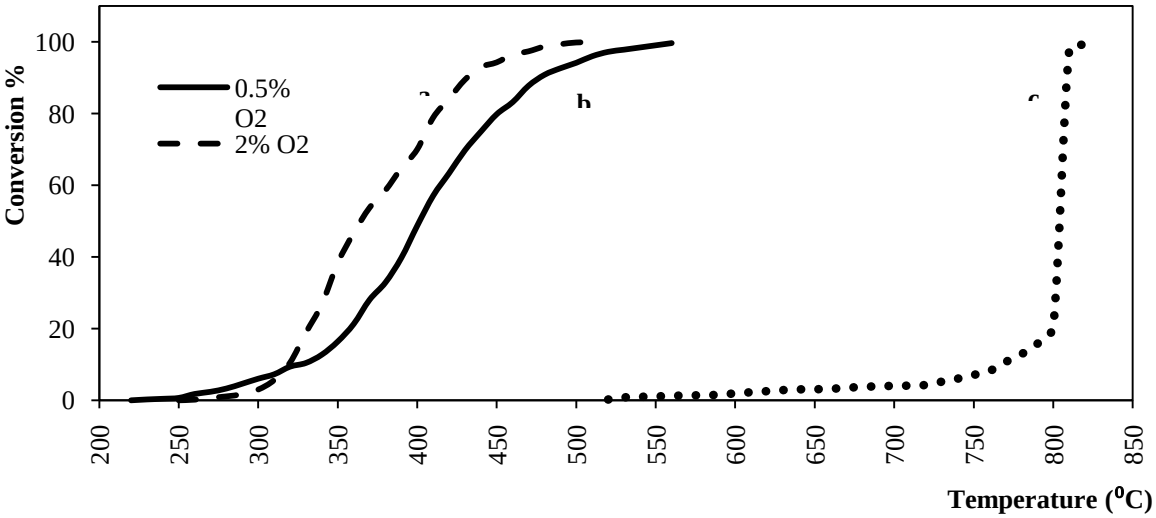


***Figure4.** Methane conversion vs. temperature plots: comparison of the catalyst considered with the non-catalytic blank. Amount of nanoparticles =100 mg (a) 0.5% O_2 (b) 2% O_2 (c) blank*

Therefore, the very high activities of $CoCr_2O_4$ for CH_4 oxidation can be related to its highest amount of β-oxygen desorption.

4. CONCLUSION

Cobalt chromite nanoparticles were synthesized through conventional co-precipitation technique as a mild synthesis method with high efficiency. The characterization of the prepared sample was done by XRD, N_2 adsorption/desorption, FESEM and TEM. The obtained results show that the $CoCr_2O_4$ nanospinels were produced as single phase with an average diameter between 25-50 nm. The specific surface area of the synthesized nanoparticles was 40 $m^2.g^{-1}$. Half conversion temperature (T_{50}˚C) was lowered to 365˚C from 805˚C in default of catalyst and also T_{90}˚C was 435˚C. It can be seen cobalt chromite nanospinels were found to be very efficient in methan combustion. Therefore $CoCr_2O_4$ nanospinel is proposed to be used in catalytic converter in CNG vehicles.

According to advice of experts, methane catalytic combustion in NGVs is a promising technology that can convert methane into carbon dioxide at relatively low temperature; catalysts based on transition metal oxides can exhibit noticeable catalytic behavior at low temperatures. Amongst these catalysts, spinel-type oxides such as $CoCr_2O_4$, have attracted much attention for many years [2].

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