

CALCIUM-BORO-PHOSPHATES SUPPORTED NiO CATALYST FOR ENHANCED OXIDATION OF CARBON MONOXIDE AND HYDROCARBONS

B. Gajalakshmi¹, S. Induja^{1*}, V. Vigneshwaran², A.L. Sriram Sudhan²
and P.S. Raghavan¹

¹Department of Chemistry, Hindustan Institute of Technology and Science,
Chennai-603103, (Tamil Nadu) India

²Department of Mechanical Engineering, Hindustan Institute of Technology and Science,
Chennai-603103, (Tamil Nadu) India

*E-mail : sinduja@hindustanuniv.ac.in

ABSTRACT

Noble metal catalysts are used for oxidation of carbon monoxide and hydrocarbons, and sincere efforts are being made worldwide to replace with non-noble metals. Conventional catalyst supports used for precious metals were not found to be suitable for base metals. The present paper investigates on the synthesis of nickel oxide supported on a non-conventional catalyst support namely, calcium phosphate-borophosphate for the oxidation of both carbon monoxide and hydrocarbons. The catalyst was synthesized with varying borate molar ratio and NiO contents. The physicochemical characterization of the catalysts was carried out using XRD, FTIR, FE-SEM and UV-Visible spectroscopic techniques which revealed the presence of required phosphate phase in the support for enhancing the oxidation process. The present catalytic system showed 83% conversion of carbon monoxide and 75% conversion of hydrocarbons.

Keywords: NiO catalyst, SCaP-B, calcium phosphate-borophosphate support, CO-HC oxidation.

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INTRODUCTION

Oxidation of carbon monoxide and hydrocarbons are generally carried out using precious metals, deposited on alumina support^{1,2}. Exploration for suitable non-metal substitutes yet remains a challenge. Literature review on the oxidation of carbon monoxide, employing the base metals such as Cu, Mn, Cr, Co, Ni, Fe, etc., are reported and their relative activities were found to be in the order Pd>Pt>Co₃O₄>CuO>MnO₂>NiO^{3,4}. Among the base metals, cobalt oxide was found to be more active than CuO for the oxidation of CO, but deactivates at a faster rate⁵. Though, the NiO catalysts are thermally stable, few reports are available towards oxidation of both CO and hydrocarbons. Nickel cuprate was evaluated for the oxidation of CO by depositing around 20% of CuO-NiO on the cordierite which exhibited 59.2% conversion⁶. NiO-ZrO₂ based catalyst prepared with 10.1 mole % of NiO for oxidation of methane showed T⁵⁰ (temperature for 50% conversion) >470°C⁷. NiO composite exhibited 100% activity towards CO oxidation at ambient temperature with 15,000 GHSV, but 6 mole % of precious metals were used as a dopant⁸. The catalyst support also plays a vital role in influencing the activity of the catalyst and the same was studied by depositing cobalt oxide on conventional supports for oxidation of carbon monoxide⁹. It was found that catalysts with γ -alumina and titania as supports were active but, deactivate at higher temperatures forming respective aluminates and titanates, whereas the silica support showed poor activity due to weak interaction. Thus, using conventional catalyst support, appreciable activity could not be achieved with base metals as active species. The present investigation aims to prepare NiO supported on a non-conventional catalyst support, namely, calcium phosphates-borophosphate and its expected advantage being strong interaction with active species due to the presence of terminal -P-O

groups and good thermal stability^{10,11}. The catalyst was found to be active towards oxidation of carbon monoxide and hydrocarbons and the results are compared with that of the unsupported catalyst.

EXPERIMENTAL

Preparation of Catalyst Support

Sintered calcium phosphate (SCaP)¹² containing borates was used as the catalyst support coated over cordierite substrate in the form of beads with 5 mm diameter. The preparation involves mixing appropriate quantities of calcium carbonate (99.9%) and phosphoric acid (85%) in the mole ratio CaO:P₂O₅ of 1.0:0.9 with 25 mL of distilled water. After effervescence subsides, calculated quantities of boric acid (99.5%) (CaO:B₂O₃= 0.1 – 0.75) was added under vigorous agitation to form a slurry and was coated on the ceramic beads by the wash-coat method. The coated beads were dried at 120°C for 12 h, sintered at between 500°C and 850°C for 90 minutes and labeled as SCaP-B. The typical coating of SCaP-B support over the ceramic beads was 10% by weight.

Preparation of Catalyst

The catalyst was prepared by dissolving calculated quantities of nickel nitrate hexahydrate (98%) in a minimum quantity of distilled water and added to the coated beads (SCaP-B) under mild agitation. Around 20 mL of ammonia solution (25%) was added drop wise on the surface of the beads, uniformly. The contents were dried at 120°C for 4 h and calcined at 400°C for 90 minutes to form fine particles of nickel oxide and labeled as Ni(a)SCaP-B(b), (where, 'a' represents weight % of NiO and 'b' represents mole ratio of B₂O₃). As a control sample, nickel nitrate was deposited on uncoated blank beads followed by addition of ammonia and calcination at 400°C (labeled as Ni-Beads-Imp).

Characterization Techniques

Powder X-ray diffraction patterns were recorded on a GE3003TT equipped with CuK α radiation as the X-ray source of 1.5406Å between 2 θ range 10-60° at a rate of 0.1°/min. FTIR was recorded using Perkin Elmer (Model: Spectrum RXi) in diffuse reflectance mode by making pellets with potassium bromide. Optical absorption properties of the samples were determined by UV-Visible diffuse reflectance recorded on a Perkin Elmer (Model: Lambda 19) instrument in the wavelength ranging from 200 to 800 nm. FE-SEM images obtained with FEI Quanta 200.

Catalytic Oxidation Reactions

The oxidation of carbon monoxide (CO) and hydrocarbons (HC) from the exhaust of 4-Stroke gasoline engine over the catalyst was carried out in a tubular-flow reactor made of alumina (1 m length, ID 3 cm), fitted with perforated alumina disc (4 mm dia holes) in the middle, to hold the catalyst beads (150 ml). The tube was clad with spiral KanthalTM wire heater externally, controlled by a thermocouple placed at catalyst bed. The gaseous products from the reactor were analyzed for its composition using AVL Digas analyzer. The conversion of the CO and HC were calculated by recording the initial values without any catalyst beads and decrease in concentration of the same when passed through the catalyst-bed as the final value. Under the present conditions of the study, the exhaust gases did not show the presence of NO_x to an appreciable amount. Prior to each experiment, the catalyst was equilibrated/activated by passing air for 10 minutes under the conditions to be studied, and the engine is equilibrated under idling conditions for 15 minutes.

RESULTS AND DISCUSSION

Influence of Sintering Temperature

The phase formation of the catalyst support with borate molar content of 0.5 (represented as SCaP-B(0.5)) was studied at different temperatures, using X-ray diffraction analysis and the patterns are given in Fig.-1. At 500°C, calcium metaphosphate (δ -Ca(PO₃)₂; JCPDS:09-0363), calcium pyrophosphate (γ -Ca₂P₂O₇; JCPDS:17-0499) and borophosphate (BPO₄; JCPDS:34-0132) phases were formed (Fig.-1A). On increasing the temperature to 750°C, the crystallinity increased (Fig.-1B,1C) and on further increase in temperature to 850°C, the formation of thermodynamically controlled borophosphate was favored, suppressing both the calcium phosphates (Fig.-1D). FTIR for SCaP-B(0.5) sample recorded at different

temperatures is presented in Fig.-2. Vibrations corresponding to phosphate units and P-O-B were distinctly seen in the sample¹³.

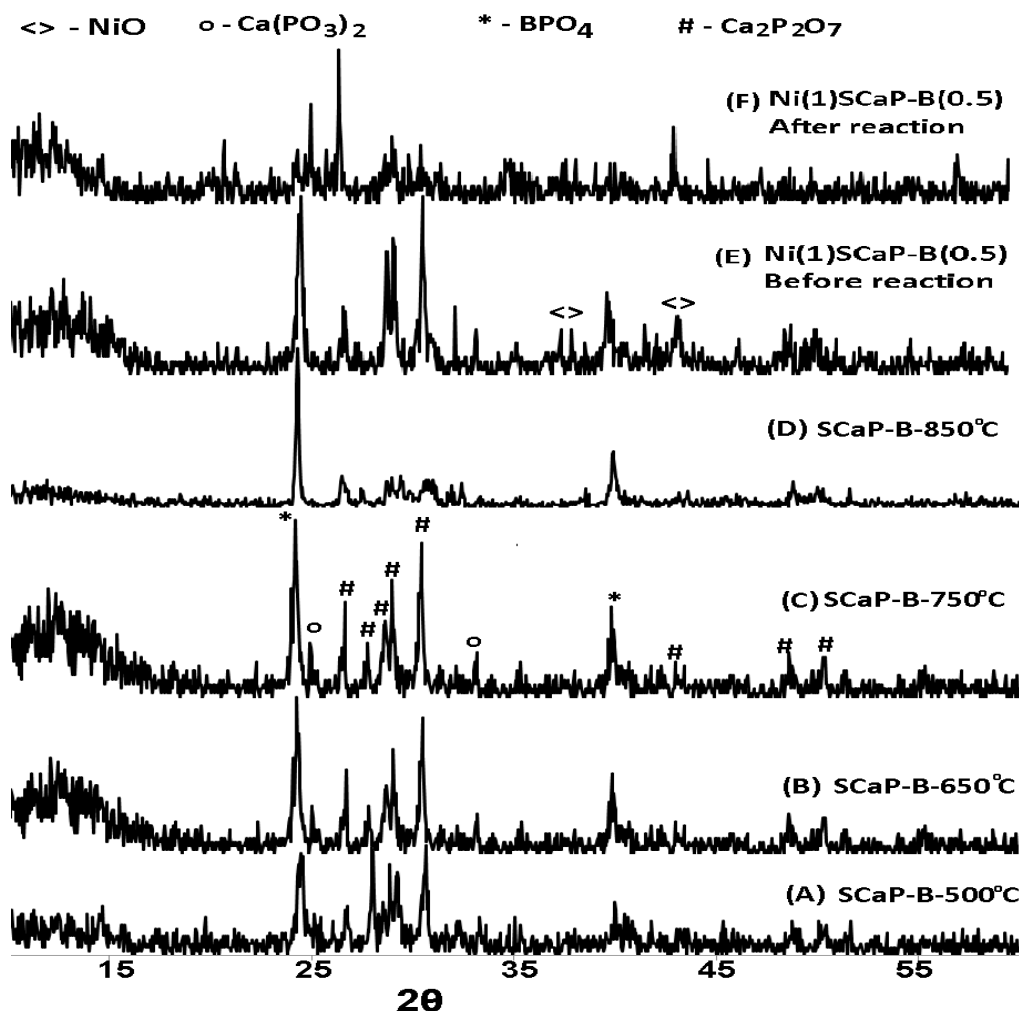


Fig.-1: XRD patterns of SCaP-B: Effect of temperature on phase formation in SCaP-B(0.5) support (A) 500°C (B) 650°C (C) 750°C and (D) 850°C (E) Ni(1)SCaP-B(0.5)-Fresh catalyst (F) Ni(1)SCaP-B(0.5)-Used catalyst

The sample calcined at 650°C showed vibration corresponding to carbonate species¹⁴ which disappeared on increasing the calcination temperature to 750°C. Thus, from XRD and FTIR analyses, the sintering temperature of 750°C was selected for the preparation of the catalyst support throughout the investigation. The FTIR of Ni(1)SCaP-B(0.5) showed vibrations corresponding to NiO (Figure 2D)¹⁵.

Influence of Borate Content in the Catalyst Support

The XRD phase formation of SCaP-B with different borate molar content, sintered at 750°C was studied and presented in Figure-3. The sample with borate molar content of 0.1 showed calcium metaphosphate as major phase and borophosphate, calcium pyrophosphate as a minor phase. With the increase in borate mole ratio to 0.2, γ -Ca₂P₂O₇ was formed as major phase and δ -Ca(PO₃)₂ & BPO₄ as minor phase (Figure-3B). When the borate mole ratio was increased to 0.5, BPO₄ and γ -Ca₂P₂O₇ were formed in the equimolar ratio (Figure-3C). Further increase in borate molar content (0.75), favored the formation of borophosphate and γ -Ca₂P₂O₇ phase, whereas the δ -Ca(PO₃)₂ phase disappeared completely (Figure-3D). Additional peaks corresponding to unreacted calcium carbonate (JCPDS: 87-1863) and excess B₂O (JCPDS: 88-2485) was observed.

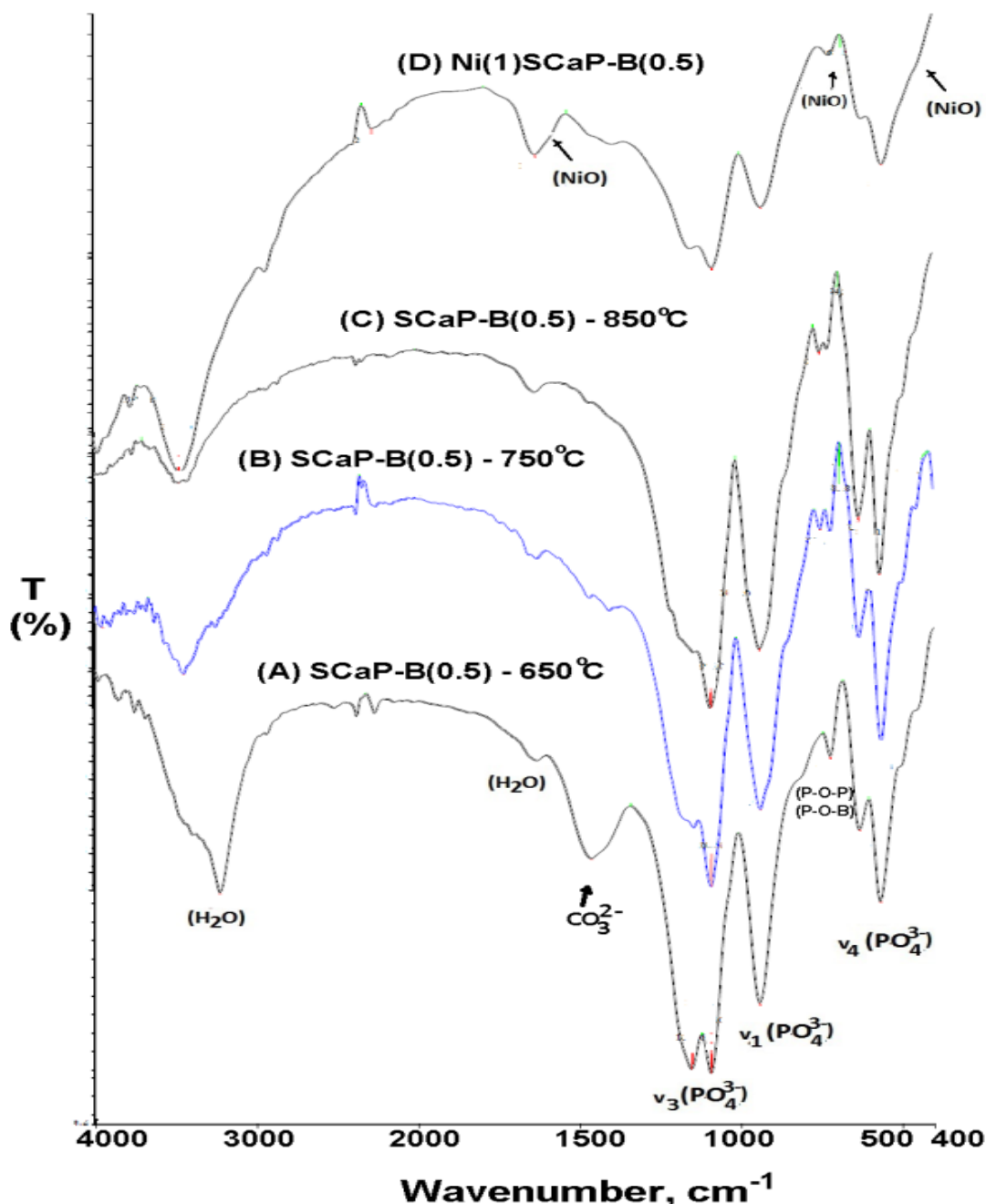


Fig.-2: FTIR spectra of SCaP-B(0.5) at (A) 650°C (B) 750°C (C) 850°C and (D) Ni(1)SCaP-B(0.5) catalyst

Influence of Nickel Oxide Content on the Catalyst

The FE-SEM image of the Ni(1)SCaP-B(0.5) catalyst consisting of 1% nickel oxide loading showed the particle size of 40 – 50 nm deposited on the support (Fig.-4), further increase in NiO content leads to agglomeration of particles. The UV spectra of the Ni(1)SCaP-B(0.5) catalyst in diffuse reflectance mode is presented in Fig.-5. The absorptions of NiO were observed at 291nm, 365nm and 423nm, which correspond to d-d transitions of Ni²⁺ ions in octahedral coordination and assigned to NiO nanostructures from the ground state ³A_{2g} to ³T_{2g}(G), ³T_{1g}(P) and ³T_{1g}(F) states¹⁶. The XRD of Ni(1)SCaP-B(0.5), calcined at 400°C confirms the formation of NiO phase (Fig.-1E; JCPDS:89-5881).

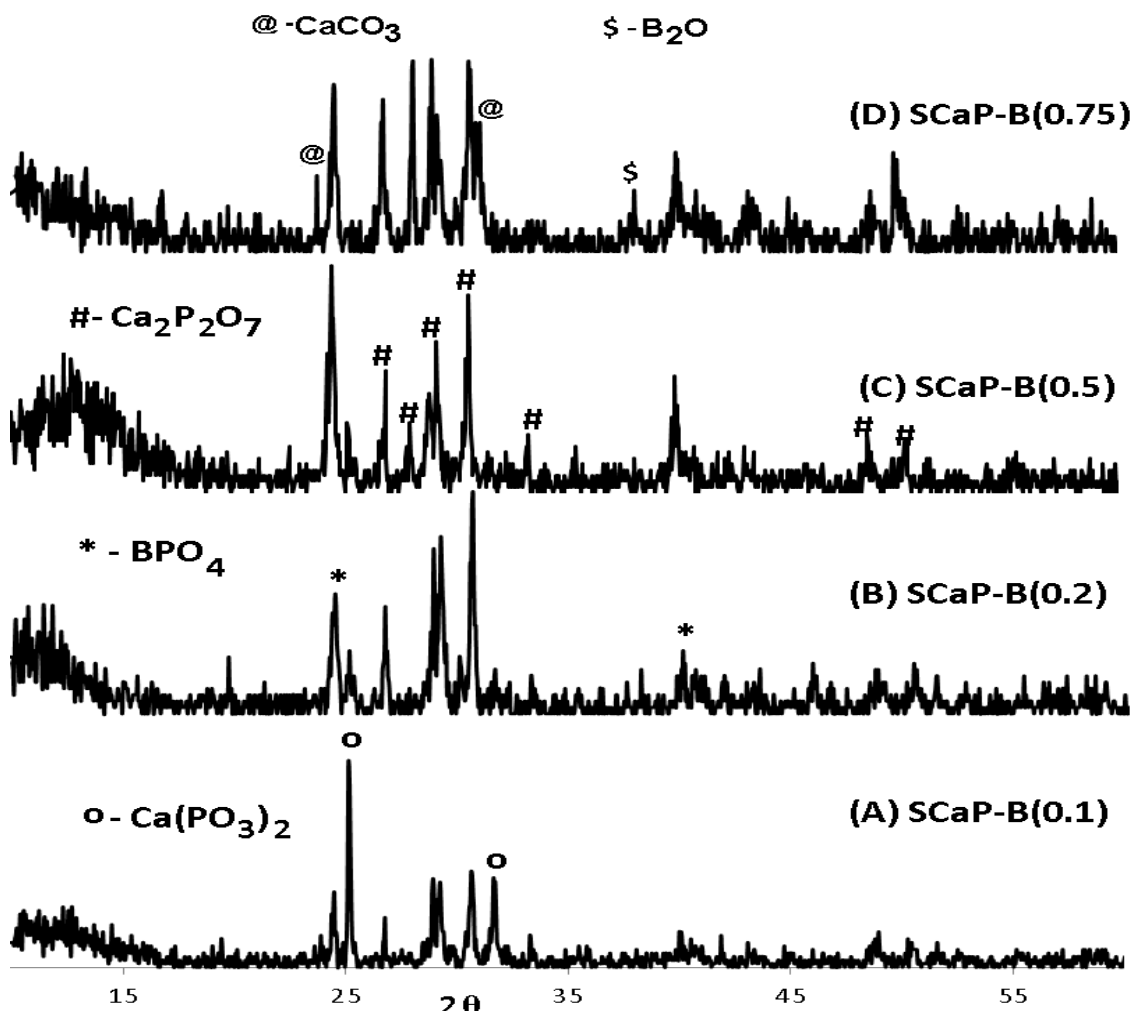


Fig.-3: XRD patterns of SCaP-B: Effect of borate molar content on phase formation in SCaP-B (A) B₂O₃-0.1 mole (B) B₂O₃-0.2 mole (C) B₂O₃-0.5 mole (D) B₂O₃-0.75 mole.

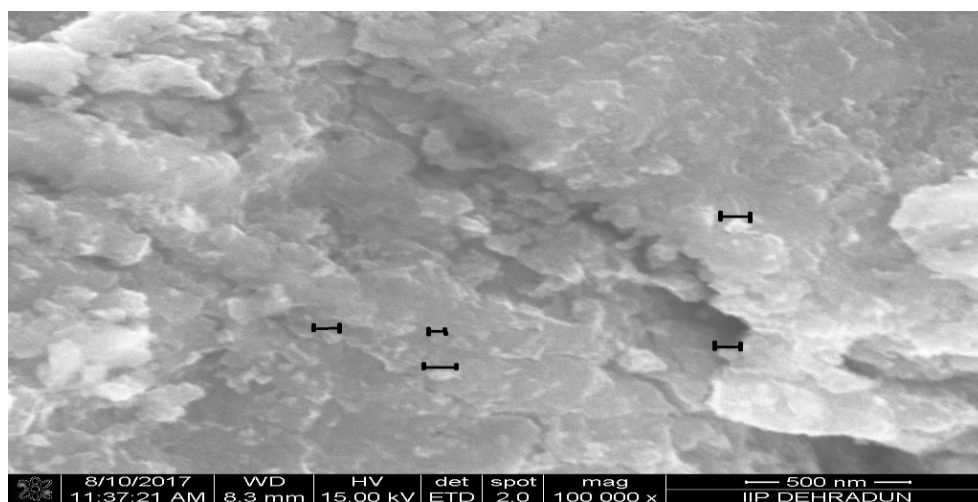


Fig.-4: SEM image of Ni(1)SCaP-B(0.5)

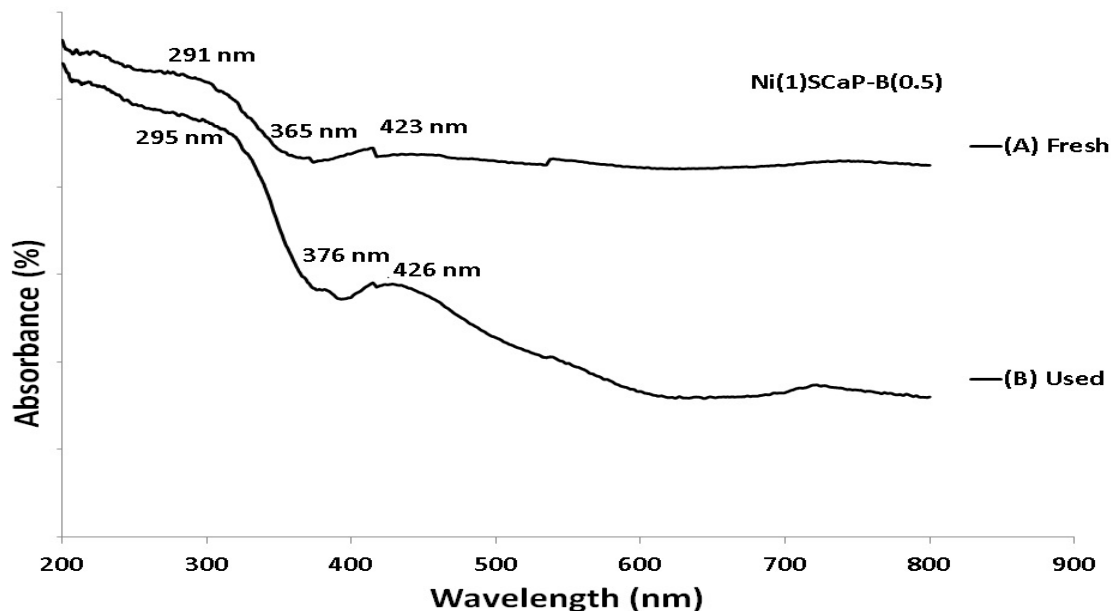


Fig.-5: UV-DRS of Ni(1)SCaP-B(0.5) (A) Fresh catalyst (B) Used catalyst

Catalytic Activity Studies

In the present investigation cylindrical ceramic beads (cordierite) of dimension 5 mm dia X 5 mm height, with 3 mm hole in the middle, was selected, whose open frontal area was measured to be 62%, which ensures effective gas-solid surface contact without back-pressure⁹. The exhaust from a gasoline engine was used as the feed for the reaction, whose composition is given as carbon monoxide (CO) – 0.94±0.04 vol.%; hydrocarbons (HC) – 800±15 ppm; carbon dioxide – 10±0.2 vol.%; oxygen – 0.6±0.1%; NO_x - 2±2ppm. The catalytic activities of the catalysts were tested at the temperature ranging between 75°C - 550°C and the space velocity was maintained at 24,000 GHSV. The time on stream studies for the catalyst Ni(1)SCaP-B(0.5) at different temperatures are given in Fig.-6. The oxidation of CO reached equilibrium within 5 minutes at temperatures >350°C, while the same at lower temperatures was achieved in 15 minutes (Fig.-6A). The oxidation of hydrocarbons was observed after 10 minutes and reached equilibrium beyond 15 minutes (Fig.-6B). Thus, from TOS studies the further measurements were made after 15 minutes of reaction time.

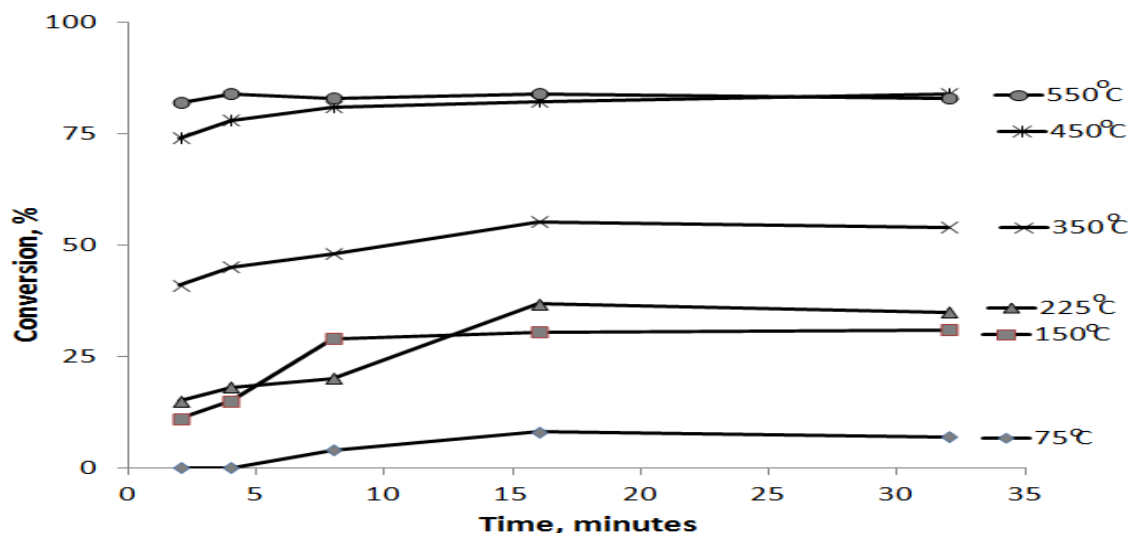


Fig.-6A: TOS studies for Ni(1)SCaP-B(0.5) at different temperatures for CO oxidation

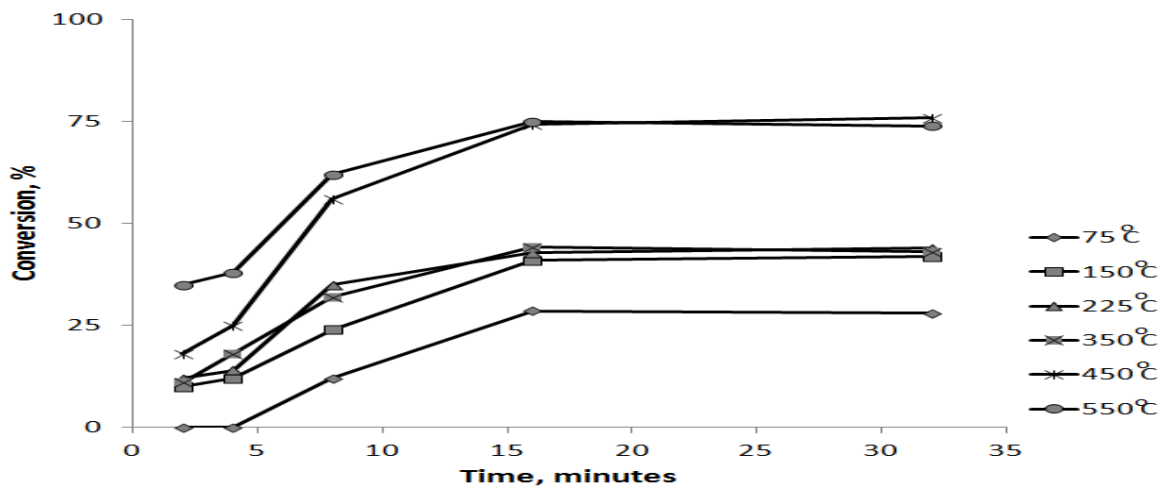


Fig.-6B: TOS studies for Ni(1)SCaP-B(0.5) at different temperatures for HC oxidation

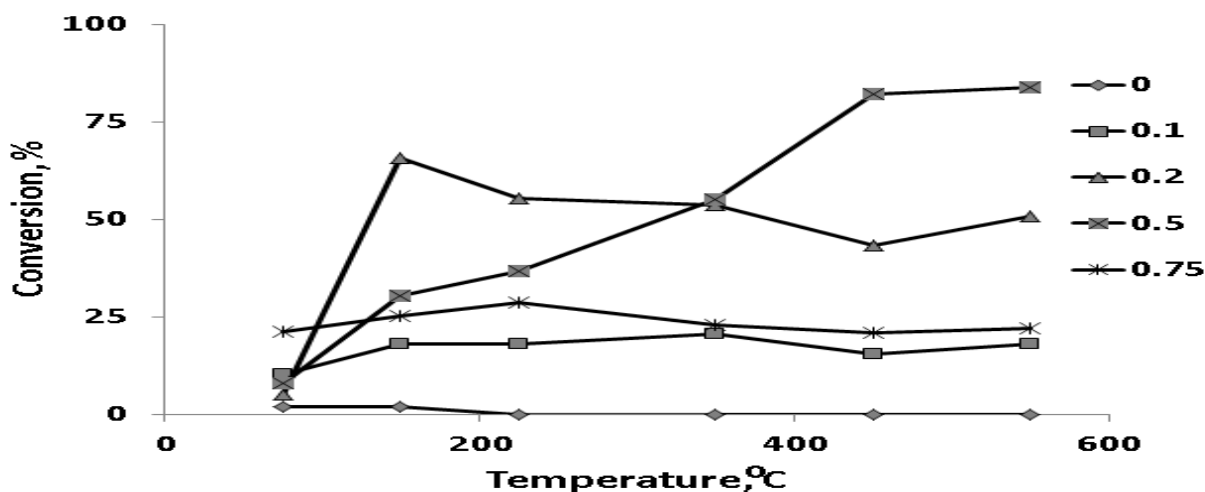


Fig.-7A: Effect of temperature on CO conversion over Ni(1)SCaP-B catalyst with different borate molar content (A) $B_2O_3=0$ (B) $B_2O_3=0.1$ (C) $B_2O_3=0.2$ (D) $B_2O_3=0.5$ (E) $B_2O_3=0.75$

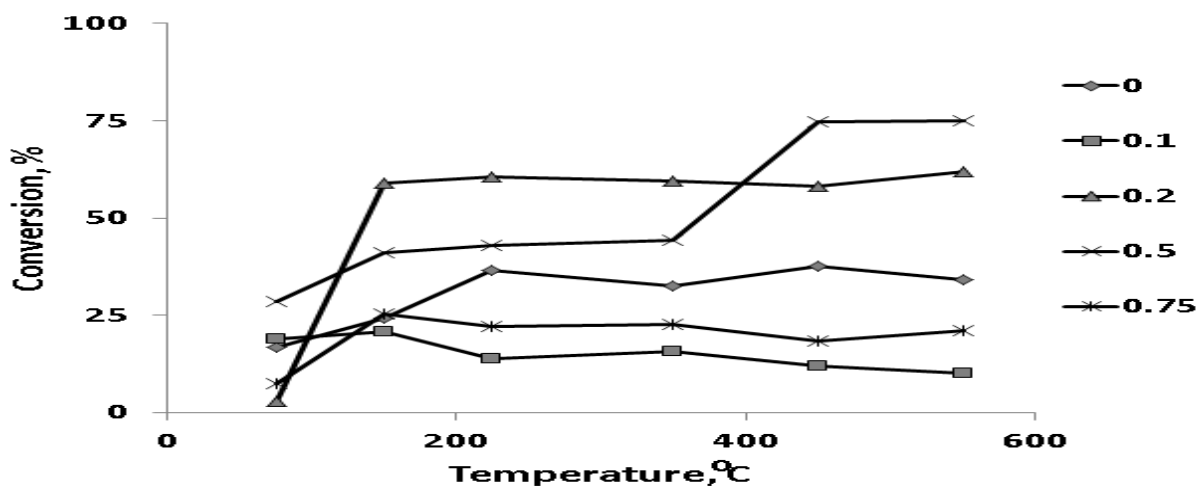


Fig.-7B: Effect of temperature on HC conversion over Ni(1)SCaP-B catalyst with different borate molar content (A) $B_2O_3=0$ (B) $B_2O_3=0.1$ (C) $B_2O_3=0.2$ (D) $B_2O_3=0.5$ (E) $B_2O_3=0.75$

The blank support, namely, SCaP-B (without NiO) did not show any appreciable oxidation of CO and HC. The influence of borate molar content in the catalyst support for the oxidation of CO & HC was studied by varying the same in the molar ratio of CaO:B₂O₃ in the range 1:0.1 to 1: 0.75 (Fig.-7). The catalysts without borate (Ni-Beads-imp - control sample) did not show appreciable activity towards CO oxidation but exhibited mild oxidation of hydrocarbons, while the catalyst with borate content of 0.1 & 0.75 showed relatively less activity. The catalyst with borate content of 0.2 showed high activity at around 150°C for both CO and HC oxidation, which, marginally reduced with a further increase in temperature (Fig.- 7A and 7B). On the other hand, the catalyst with borate content of 0.5 showed less conversion at low temperature, which increased with increase in temperature and a conversion of CO to an extent of 83% and 75% for HC was observed at 450°C. T⁵⁰ for a catalyst with borate content of 0.2 was 150°C and that of 0.5 was 350°C.

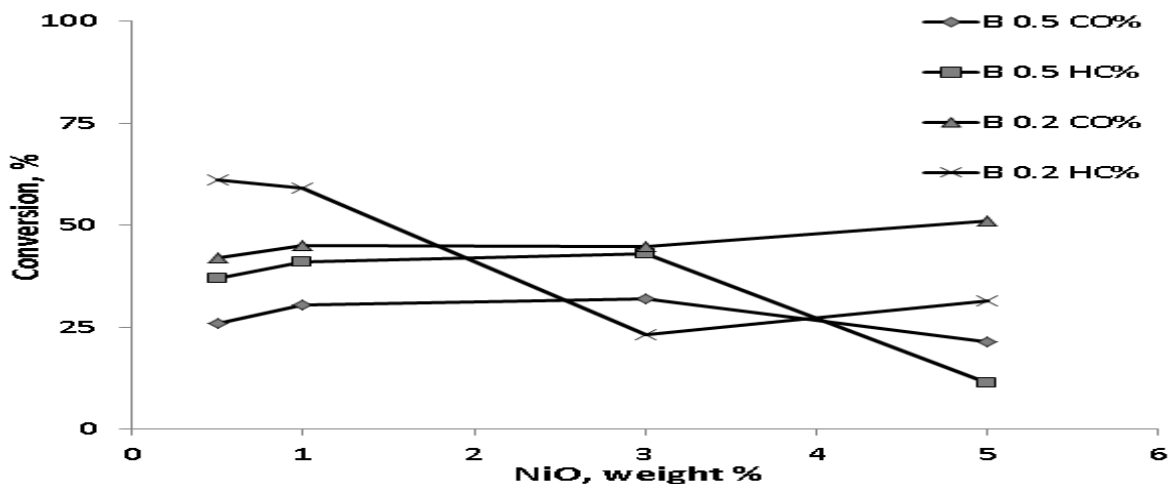


Fig.-8A: Influence of NiO content in SCaP-B(0.5) for oxidation of CO& HC at 150°C

The borate content in the catalyst support was found to play a vital role in the influencing the catalytic activity. This was attributed to the introduction of P-O⁻ species which interacts with the nickel species, thus participating in catalytic oxidation. The catalyst with borate molar content of 0.1 shows poor activity due to the presence of calcium metaphosphate as the major phase which lacks P-O⁻. On the other hand, the reduced activity of the catalyst with higher borate molar content (0.75) can be explained due to the presence of B₂O and unreacted calcium carbonate on the surface that masks the P-O⁻, thus affecting the interaction of the active species on the catalyst support. The catalyst with borate molar content of 0.2 showed higher activity at 150°C, due to the presence of pyrophosphate and borophosphate phases. But, the presence of thermally unstable calcium metaphosphate deactivates with further increase in temperature. The catalyst with borate molar content of 0.5 showed the highest activity, which can be attributed to the equimolar mixture γ -Ca₂P₂O₇ and BPO₄. In addition, the presence of BPO₄ imparts thermal stability to the catalyst. The influence of NiO content supported on the catalysts for oxidation of CO & HC was studied and the results are presented in Figure-8A & 8B. The temperatures selected for comparison was 150°C & 450°C. The highest conversion was observed for the catalyst with NiO content of 1%, which decreased when increased to 5%. This is due to the increase in particle size due to agglomeration.

Influence of space velocity on the activity of the catalyst was studied in the range 24,000 to 60,000 GHSV. Without disturbing the flow rate and composition of the source feed gas, the GHSV was increased by reducing the catalyst volume accordingly. On increasing the space velocity both CO and HC conversion decreased. But, the decrease in CO conversion was marginal while that of hydrocarbon conversion was more. The stability of the catalyst was determined by analyzing the used Ni(1)SCaP-B(0.5) catalyst for 5 hours at 550°C. The XRD of the used catalyst (Figure-1F) showed retention of

phases including that of NiO, and the UV-Visible spectra of used catalyst (Fig.5B) showed absorptions at 295nm, 376 and 426 nm which corresponds to that of NiO.

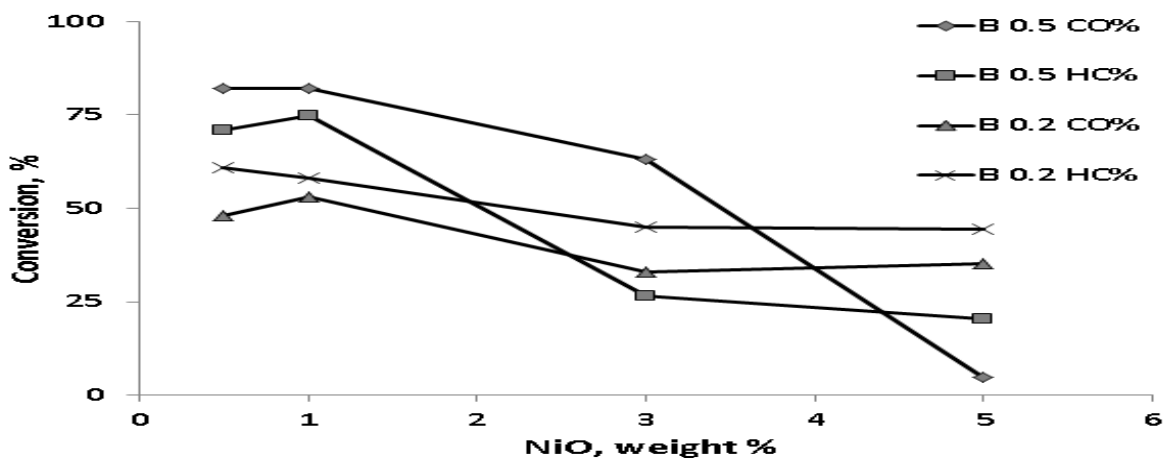


Fig.-8B: Influence of NiO content in SCaP-B(0.5) for oxidation of CO & HC at 450°C

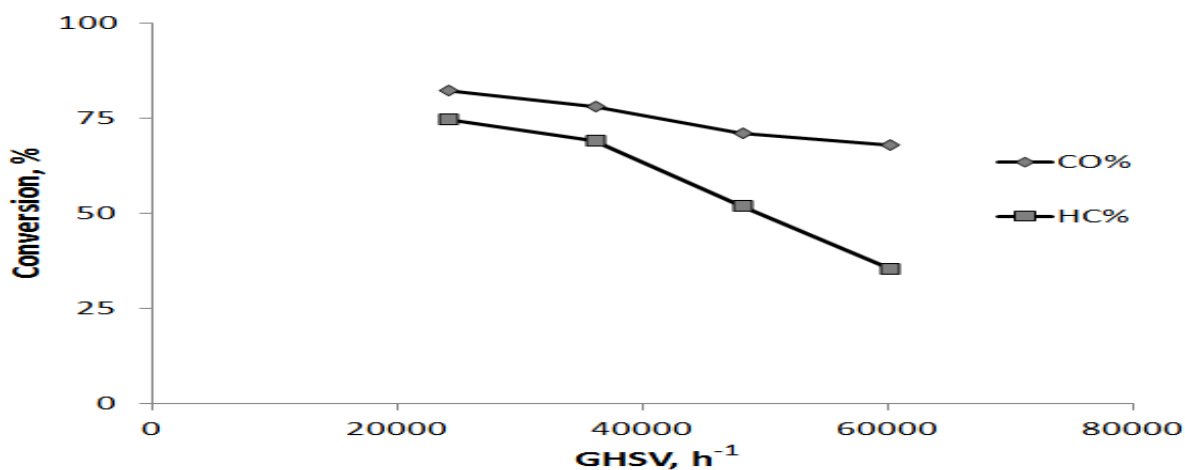


Fig.-9: Influence of space velocity over Ni(1)SCaP-B(0.5) at 450°C for CO & HC oxidation

CONCLUSION

In conclusion, the present investigation attempts to design and evaluate a non-noble metal catalyst (NiO) using a non-conventional support (SCaP-B) for oxidation of CO and HC. The catalyst support contained δ -Ca(PO₃)₂, γ -Ca₂P₂O₇ and BPO₄ phases. The conversions of CO and HC over the catalysts were studied by varying the borate molar ratio at different temperatures and different NiO content. The catalyst containing an equimolar ratio of γ -Ca₂P₂O₇ and BPO₄ exhibited CO & HC conversion of 83% & 75%, respectively. The observed catalytic activity was attributed to the introduction of $-P-O^-$ groups by γ -Ca₂P₂O₇ and thermal stability imparted by the BPO₄ phase. Presence of δ -Ca(PO₃)₂, in the catalyst, shows reduced activity (absence of $-P-O^-$ groups). The percentage of NiO deposited over support has been optimized as 1%, which showed particle size of 40 – 50 nm, beyond which, agglomeration takes place resulting in reduced activity. The XRD and UV-Visible absorption of used catalyst proved its stability.

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[RJC-2046/2018]