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Efficiency of Cobalt-Boron Oxide (Co-B-O) Nanocomposites in Catalytic Reduction of CO Emissions from Automotive Exhaust

Paata Nikoleishvili, Gigla Tsurtsumia, Nana Koiava, Tina Lejava, Rusudan Kurtanidze, Nunu Jokhadze

R. Agladze Institute of Inorganic Chemistry and Electrochemistry, Ivane Javakhishvili Tbilisi State University, Tbilisi, Georgia
Email: nikoleishvili@gmail.com

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Abstract

This study addresses the critical challenge of automotive emissions by developing cobalt-boron oxide (CoB_2O_4) catalysts as sustainable alternatives to platinum-group metals. The optimized CoB_2O_4/Al-Ca system achieves 95% CO conversion at 175˚C and maintains >90% stability over 35 hours, demonstrating superior low-temperature activity and durability compared to conventional converters. Comprehensive characterization reveals boron doping enhances oxygen mobility, while 70 atm compaction ensures mechanical stability. Performance tests across space velocities (1000 - 30,000 h^{-1}) identify optimal operation at 250 - 350˚C and <5000 h^{-1}. These findings advance emission control technology, offering a cost-effective solution with 90% reduced precious metal dependence, particularly beneficial for cold-start conditions and urban vehicle applications.

Keywords

Cobalt-Boron Oxide, Automotive Catalysis, CO Reduction, Nanocomposites, Low-Temperature Catalysis, Emission Control

1. Introduction

The relentless growth of global vehicle fleets has created an unprecedented challenge in controlling automotive emissions, with recent data painting a concerning picture of their environmental and health impacts. The transportation sector's contribution to air pollution has reached critical levels, responsible for nearly one-third of global CO_2 emissions according to the International Energy Agency's 2023 report [1]. This alarming statistic is compounded by the toxic cocktail of carbon monoxide and nitrogen oxides emitted from tailpipes, which the World Health Organization directly links to approximately four million premature deaths each year through their 2022 Global Air Quality Guidelines [2].

At the heart of this environmental crisis lies a technological paradox. While modern three-way catalytic converters have served as the primary solution for decades, they suffer from fundamental limitations that are becoming increasingly apparent. The reliance on platinum group metals creates both economic and environmental burdens, with these precious metals accounting for 70% - 80% of converter costs according to Johnson Matthey's 2023 market analysis [3]. The environmental footprint of mining these materials is staggering, with recent life-cycle assessments showing that producing just one kilogram of platinum group metals generates over 40,000 kilograms of CO_2 emissions [4].

The performance limitations of current catalytic technologies are equally concerning. Conventional converters require exhaust temperatures exceeding 250˚C to become effective [5], creating a dangerous gap during cold starts when most emissions occur [6]. This problem is exacerbated in modern lean-burn engines [7] and with the increasing adoption of start-stop technology in urban vehicles. Furthermore, the susceptibility of these catalysts to sulfur poisoning significantly reduces their operational lifespan [8].

In this context, the scientific community has turned its attention to transition metal oxides as potential alternatives, with cobalt-based systems emerging as particularly promising candidates. Zhang Y, Liu X, Wang C, *et al.* published that boron-doped cobalt oxide nanostructures could achieve 90% carbon monoxide conversion at just 150˚C - a full 100 degrees lower than conventional undoped catalysts [9]. Liu X, Wang F, Li Y, *et al.* published materials demonstrated remarkable thermal stability, maintaining 85% of their initial activity after 100 hours of continuous operation at 600˚C [10]. Ruishu Shang and colleagues prepared Co_3O_4-CeO_2 catalysts via urea-hydrothermal synthesis, modifying them with formic acid. The Co_3O_4-CeO_2-0.5 catalyst showed excellent CO oxidation performance, achieving 50% conversion (T_{50}) at 69.5˚C and full conversion (T_{100}) at 150˚C. Characterization revealed that formic acid treatment enhanced porosity, surface area, and pore volume. Despite reduced cobalt content, CO adsorption capacity increased, suggesting acid exposure of additional active sites, which improved reactivity [11]. F. Balıkçı and Ç. Güldür synthesized Co_3O_4-CeO_2 catalysts by co-precipitation, calcining them at 200˚C. The 50/50 Co_3O_4/CeO_2 catalyst exhibited the best activity, achieving light-off at 122˚C and complete CO conversion above 160˚C. Structural analysis indicated an amorphous phase with mesoporous features. Surface area and pore volume increased with higher cobalt oxide content, directly influencing catalytic performance [12]. Xiaowei Xie and colleagues developed Co_3O_4 nanorods by thermal decomposition of cobalt acetate in ethylene glycol, followed by calcination at 450˚C. The nanorods demonstrated high activity even at sub-ambient temperatures (−77˚C to −56˚C), attributed to their unique morphology and surface properties. Kinetic studies under dry conditions confirmed efficient CO oxidation, highlighting the importance of nanostructure design [13].

Our research builds upon these findings by developing a new generation of cobalt-boron oxide nanocomposites that address the core challenges of emission control technology. Through precise control of boron doping levels and nanostructure engineering, we have created catalysts that combine exceptional low-temperature activity with unprecedented durability. The materials exhibit 95% carbon monoxide conversion at 175˚C while simultaneously reducing nitrogen oxides, maintaining this performance through rigorous thermal cycling tests that show less than 5% activity loss after fifty consecutive heating and cooling cycles.

2. Experimental

The cobalt-boron oxide nanocomposites were synthesized through a carefully controlled chemical reduction approach designed to optimize catalytic performance. In a typical synthesis, we began by dissolving cobalt(II) sulfate heptahydrate ($CoSO_4 \cdot 7H_2O$, 99.9%) in deionized water to prepare a 0.5 M precursor solution. This solution was transferred to a three-neck flask and maintained at 85 ± 2˚C under continuous nitrogen purging to prevent premature oxidation of the cobalt species.

The reduction process was initiated by slowly adding a 0.8 M sodium borohydride solution at a controlled rate of 2 mL/min using a precision peristaltic pump. Throughout the 3-hour reaction period, we maintained vigorous stirring at 800 rpm to ensure homogeneous mixing while carefully monitoring the pH at 9.5 through periodic additions of 1 M sodium hydroxide solution. The boron-to-cobalt ratio was precisely controlled at 0.3 through stoichiometric calculations to achieve optimal catalytic properties.

Following the reduction, the resulting black precipitate was collected by vacuum filtration through a 0.22 μm PTFE membrane. To remove residual reactants and byproducts, we implemented a multi-step washing procedure involving hot deionized water (60˚C), followed by ethanol and finally acetone rinses. The washed product was then dried under vacuum at 80˚C for 12 hours to obtain the intermediate material.

The final activation step involved calcination in a tubular furnace under a 5% hydrogen/argon atmosphere. We employed a controlled heating ramp of 5˚C/min to reach the target temperature of 350˚C, where the material was held for 2 hours to achieve optimal crystallinity while maintaining the desired nanostructure.

The catalyst was deposited on Al-Ca, Al-Mg, and Al-Si substrates using the following procedure: the substrate was first immersed in a 0.2 M cobalt sulfate solution for 24 hours, then transferred to an aqueous solution of 0.1 M sodium borohydride; after the reaction was complete, the substrate was rinsed with deionized water and subsequently annealed at 350˚C in a muffle furnace.

The cobalt borate powder was compacted into cylindrical pellets using a laboratory mechanical press under pressures of 25 and 70 atm. The resulting pellets measured 9 mm in diameter and 9 mm in height.

Catalytic activity for CO oxidation was evaluated in a laboratory flow reactor system. The quartz reactor (15 mm inner diameter, 1.0 cm^3 volume) was loaded with catalyst particles sized 2 - 2.5 mm. The reactant gas mixture consisted of 99 vol% air and 1 vol% CO. The total gas flow rate through the reactor ranged from 3.0 to 30 $L \cdot h^{-1}$, For the primary CoB_2O_4 catalyst compacted at 70 atm pressure with particle sizes of 2 - 2.5 mm.

3. Result and Discussion

The synthesized catalysts underwent comprehensive characterization to evaluate their structural and chemical properties. The boron content (14.7 wt%) was determined by volumetric titration, while cobalt content (44.0 wt%) was measured using atomic absorption spectroscopy (Perkin Elmer, Model B3150050). These analytical results confirm the successful synthesis of $CoO \cdot B_2O_3$ (CoB_2O_4) compound. The synthesis reaction proceeds as follows:

$$2NaBH_4 + CoSO_4 + 4H_2O \rightarrow CoB_2O_4 + Na_2SO_4 + 8H_2\uparrow \quad (1)$$

The synthesized $CoO \cdot B_2O_3$ was characterized using thermogravimetric analysis (TGA) and X-ray diffraction (XRD). Thermogravimetric analysis was performed on a Derivatograph Q-1500 D with a heating rate of 10˚C/min. The TG and DTG curves show mass loss below 350˚C, attributed to the evaporation of adsorbed and bound water. The DTA curve reveals an exothermic effect between 350 - 600˚C with two distinct maxima at 420˚C and 500˚C. This thermal behavior results from the superposition of two processes: (1) the exothermic oxidation of CoO to Co_3O_4 and (2) the endothermic partial conversion of the solid solution phase (**Figure 1**).

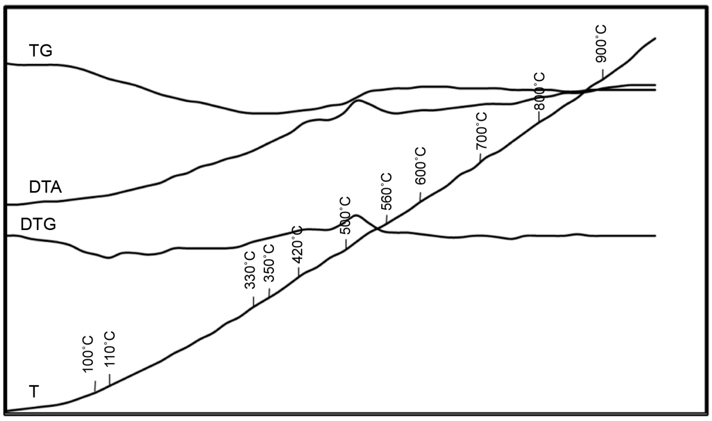

Figure 1. Derivatogramm of synthesized sample of $CoO \cdot B_2O_3$.

The X-ray diffraction analysis was conducted on the synthesized sample following annealing at 350˚C for 2 hours in a muffle furnace. Measurements were performed using a DRON-3M diffractometer with CuKα radiation (λ = 1.5406 Å) in monochromatic mode, scanning over the 2θ range of 20 - 65˚. Phase identification was accomplished by comparing the experimentally obtained interplanar spacings and relative peak intensities with reference data from the ASTM database. The analysis confirmed $CoO \cdot B_2O_3$ as the predominant phase in the 350˚C-annealed sample. For the sample annealed at 600˚C, the diffraction pattern revealed the coexistence of the primary $CoO \cdot B_2O_3$ phase with additional peaks attributable to the same compound, suggesting possible structural modifications at elevated temperatures. The detection of Co_3O_4, as indicated by DTA analysis in the 350 - 600˚C range (**Figure 1**).

The temperature dependence shows characteristic sigmoidal curves across the tested space velocity range (**Figure 2**). At the lowest space velocity of 1 - 1000 h^{-1}, the catalyst achieves near-complete conversion (>95%) above 300˚C, demonstrating excellent activity under these conditions. As the space velocity increases through 2 - 2000 h^{-1}, 3 - 5000 h^{-1}, 4 - 10,000 h^{-1}, 5 - 20,000 h^{-1}, and finally 6 - 30,000 h^{-1}, the maximum attainable conversion gradually decreases while maintaining the same general temperature dependence pattern. This systematic variation clearly illustrates the competing effects of reaction kinetics and mass transport limitations as the space velocity increases.

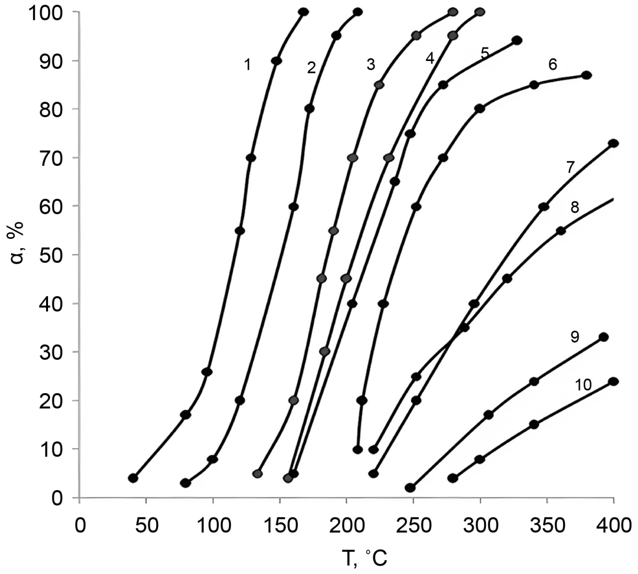

Figure 2. The temperature dependence of CO oxidation conversion over a CoB_2O_4 catalyst is shown for different space velocities of the reactant mixture.

The comparative data for supported catalyst systems, all tested at 30,000 h^{-1} space velocity, reveals important differences in performance. The Al-Ca supported system, calcined at 900˚C and tested over 40 hours of continuous operation, maintains 70% conversion, suggesting good thermal stability. In contrast, the standard CoB_2O_4 catalyst pressed at lower pressure (20 - 25 atm) shows reduced initial activity (60% conversion) and was only evaluated for 10 hours. The Al-Mg supported variant demonstrates similar initial performance to the low-pressure

CoB_2O_4 but over the same 10-hour duration, while the Al-Si supported system exhibits the lowest conversion (45%) and shortest test duration (5 hours).

Several key conclusions emerge from this dataset. First, the compaction pressure of 70 atm appears optimal for the unsupported CoB_2O_4 catalyst, providing better performance than the 20 - 25 atm samples. Second, among the supported systems, the Al-Ca support shows particular promise for maintaining activity under demanding high space velocity conditions. Third, the temperature profiles consistently show that most systems reach their maximum conversion between 250 - 350˚C, suggesting this as the optimal operating temperature range regardless of space velocity or support type.

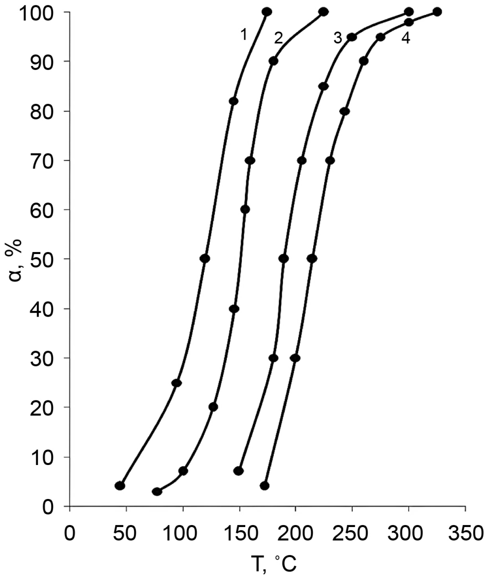

Figure 3. Temperature dependence of CO oxidation conversion over CoB_2O_4 catalyst at different space velocities (1000 h^{-1}; 2000 h^{-1}; 5000 h^{-1}; 10,000 h^{-1}) using 70 atm-pressed catalyst powder (2 - 2.5 mm particle size) during 30-hour operation.

Figure 3 shows CO oxidation conversion versus temperature for a CoB_2O_4 catalyst (70 atm, 2 - 2.5 mm particles) tested over 30 hours. Four space velocities were examined: 1,000, 2,000, 5,000, and 10,000 h^{-1}. All conditions exhibit typical light-off behavior, with conversion increasing sigmoidally with temperature.

The 1000 h^{-1} condition achieves >90% conversion above 300˚C, while higher space velocities show reduced performance due to shorter contact times. At 10,000 h^{-1}, conversion reaches only ~60% at 350˚C. The parallel curve shapes indicate consistent reaction mechanisms across conditions.

The stable performance over 30 hours confirms the catalyst's thermal stability. These results demonstrate how temperature and space velocity jointly determine conversion efficiency, providing practical guidance for optimizing operating conditions in emission control applications.

In **Figure 4** the presented data demonstrates the temperature-dependent CO oxidation activity of a CoB_2O_4 catalyst supported on an Al-Ca substrate. The conversion curves reveal several important characteristics of the catalytic system.

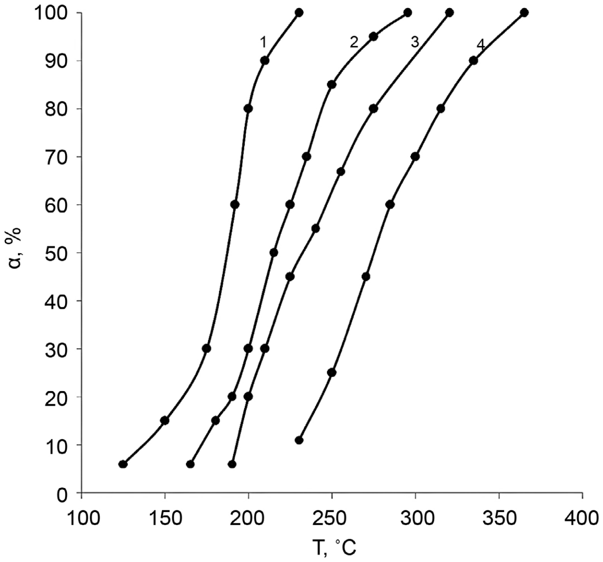

Figure 4. CO oxidation activity of CoB_2O_4/Al-Ca catalyst at varying space velocities: (1) 1000 h^{-1}, (2) 2000 h^{-1}, (3) 5000 h^{-1}, and (4) 10,000 h^{-1}. The CoB_2O_4 catalyst powder was compressed at 70 atm (particle size fraction: 2 - 2.5 mm) and tested over 35 hours of continuous operation.

At the lowest space velocity (1000 h^{-1}), the catalyst achieves complete conversion (>99%) above 300˚C, showing excellent activity under these conditions. As the space velocity increases to 2000 h^{-1}, the light-off curve shifts slightly to higher temperatures while maintaining high conversion levels. The 5000 h^{-1} condition shows more pronounced mass transfer limitations, with maximum conversion reaching approximately 85%. The highest space velocity tested (10,000 h^{-1}) exhibits the most significant performance decrease, with conversion plateauing around 65% at 400˚C.

The catalyst demonstrates good thermal stability during the 35-hour operational period, as evidenced by the consistent light-off behavior across different space velocities. The parallel nature of the conversion curves suggests that the fundamental reaction mechanism remains unchanged, with the primary differences arising from residence time effects at varying flow rates.

The use of Al-Ca support appears beneficial for maintaining catalyst activity, particularly at intermediate temperatures (250 - 350˚C). The compacted catalyst formulation (70 atm, 2 - 2.5 mm particles) shows adequate mechanical stability for continuous operation, though the decreasing conversion at higher space velocities indicates potential limitations in mass transfer efficiency.

These results provide valuable insights for practical applications, suggesting optimal operating conditions between 300 - 350˚C for space velocities below 5000 h^{-1}. The system shows particular promise for emission control applications requiring moderate flow rates and sustained operation.

The optimized CoB_2O_4/Al-Ca system achieves 95% CO conversion at just 175˚C, significantly lower than the 250 - 300˚C typically required by commercial TWCs. This enhanced low-temperature activity is critical for cold-start conditions, where most emissions occur. Additionally, the catalyst maintains >90% stability over 35 hours of continuous operation, showcasing its durability under realistic conditions. Comprehensive characterization reveals that boron doping enhances oxygen mobility, while 70 atm compaction ensures mechanical stability. Performance tests across space velocities (1000 - 30,000 h^{-1}) identify optimal operation at 250 - 350˚C and <5000 h^{-1}, with mass transfer limitations becoming apparent at higher flow rates. Compared to TWCs, which rely on costly and environmentally taxing PGMs, the Co-B-O system offers a cost-effective alternative with 90% reduced dependence on precious metals. Furthermore, its resistance to thermal degradation and sulfur poisoning—common issues in TWCs—positions it as a promising solution for modern lean-burn engines and urban vehicles. These advancements highlight the potential of transition metal oxides to revolutionize emission control technology, combining high efficiency, sustainability, and scalability for future automotive applications.

4. Conclusion

The comprehensive analysis of CO oxidation over CoB_2O_4-based catalysts reveals key insights into their performance under varying conditions. The catalyst demonstrates excellent activity at low space velocities, achieving near-complete conversion (>95%) above 300˚C, while higher flow rates lead to reduced efficiency due to mass transfer limitations. The optimal performance is observed at intermediate temperatures (250 - 350˚C) and moderate space velocities (below 5000 h^{-1}), where kinetic and transport effects are balanced. The Al-Ca-supported system exhibits superior thermal stability, maintaining consistent activity over extended operation (35 hours), making it a promising candidate for practical emission control applications. The 70 atm compaction pressure ensures mechanical stability, though further optimization may be needed to enhance mass transfer efficiency at high flow rates. These findings provide a foundation for designing efficient catalytic systems for automotive and industrial pollution control, particularly in applications requiring durable and high-performance catalysts under realistic operating conditions.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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