CO Oxidation

Deutsche Ausgabe: DOI: 10.1002/ange.201506093
Internationale Ausgabe: DOI: 10.1002/anie.201506093

Low-Temperature CO Oxidation over a Ternary Oxide Catalyst with High Resistance to Hydrocarbon Inhibition

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Abstract: *Platinum group metal (PGM) catalysts are the current standard for control of pollutants in automotive exhaust streams. Aside from their high cost, PGM catalysts struggle with CO oxidation at low temperatures (< 200 °C) due to inhibition by hydrocarbons in exhaust streams. Here we present a ternary mixed oxide catalyst composed of copper oxide, cobalt oxide, and ceria (dubbed CCC) that outperforms synthesized and commercial PGM catalysts for CO oxidation in simulated exhaust streams while showing no signs of inhibition by propene. Diffuse reflectance IR (DRIFTS) and light-off data both indicate low interaction between propene and the CO oxidation active site on this catalyst, and a separation of adsorption sites is proposed as the cause of this inhibition resistance. This catalyst shows great potential as a low-cost component for low temperature exhaust streams that are expected to be a characteristic of future automotive systems.*

In order to reduce greenhouse gas emissions and petroleum consumption, new fuel economy standards for passenger cars and light trucks have been implemented by the National Highway Traffic Safety Administration (NHTSA) and the Environmental Protection Agency (EPA) in the U.S.[1] As fuel economy improvements occur to meet these standards, the automotive industry will also need to reduce pollutant tailpipe emissions that affect air quality and human health. Specifically, emission levels of the criteria gaseous pollutants NO_x (oxides of nitrogen), CO, and non-methane hydrocarbons are all being further reduced from present day levels with the introduction of new U.S. EPA Tier 3 emission standards.[2] The combination of improving fuel economy while reducing tailpipe pollutant emissions presents a significant challenge for the automotive industry.

Vehicles with internal combustion engines will likely remain a dominant fraction of the light-duty fleet in both hybrid and non-hybrid drivetrains,[3] and new combustion techniques are showing greater fuel efficiency for these engines. Obviously, improved engine efficiencies help meet the fuel economy goals, but lower exhaust temperatures resulting from the improved extraction of work inside the engine cylinders can be problematic for catalytic emissions control. Furthermore, a promising class of fuel-efficient advanced combustion techniques, while demonstrating less NO_x and particulate emissions, produces higher levels of CO and hydrocarbons.[4,5] The combination of lower exhaust temperatures and higher CO and hydrocarbon levels challenges existing catalyst technologies; thus, new catalysts are being needed.

The vast majority of commercial catalysts employed in automotive exhaust streams make use of supported platinum group metal (PGM) nanoparticles. There are a number of examples of PGM-based catalysts showing exceptional activity for CO oxidation[6–8] but upon introduction of hydrocarbons these catalysts experience severe inhibition due to competition for PGM active sites[9] which limits their use for low temperature catalysis in practical applications. PGM catalysts are also susceptible to sintering at high temperature, which can also reduce crucial pollutant conversion at low temperature. These critical weaknesses, as well as the high cost of precious metal materials, have spurred considerable interest in the development of low cost, highly stable catalysts that are capable of meeting the demands of complex exhaust streams.

Non-PGM catalysts are always of great interest in reducing the costs of the emissions control systems.[10] Recent studies of binary oxides composed of CuO, Co_2O_3, and CeO_2 have all previously highlighted high activity for both CO[11,12] and hydrocarbon[13,14] oxidation. Furthermore, in a report by Luo et al.[15] oxidation of CO and C_3H_8 were proposed to occur over different active sites. The ability to separate the active sites of CO and hydrocarbons may drastically reduce the inhibition effects that plague current PGM catalysts. Unfortunately, as with previous binary oxide studies, the oxidation reactions were studied separately and at space velocities far below those necessary for automotive viability. Encouraged by an earlier study on $CuO–Co_3O_4–CeO_2$ in a simple gas stream by Liu and co-workers[16] which showed room temperature activity for CO oxidation ($T_{50} <$ 70 °C) even after exposure at temperatures as high as 800 °C, we studied this ternary oxide system in hopes of overcoming the weaknesses of current PGM catalysts.

Here we present a ternary oxide catalyst composed of CuO, Co_3O_4, and CeO_2 (dubbed CCC), which shows high activity for CO oxidation in simulated exhaust conditions relevant to lean-burning diesel engine emissions. The stream

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201506093.

includes common inhibitors such as propene, water, and NO_x. This non-PGM catalyst demonstrates higher activity for CO oxidation than both a commercial diesel oxidation catalyst (DOC) and a synthesized $Pd/ZrO_2/SiO_2$ catalyst (PdZrSi). Moreover, the CO oxidation activity of CCC is unaffected by the presence or removal of propene from the exhaust stream indicating a resistance to propene inhibition, which is a major problem found in PGM catalysts. Diffuse reflectance IR spectroscopy (DRIFTS) and comparative binary oxide catalyst studies further indicate a lack of interaction between the propene and CO species, due to a weak adsorption of propene over CCC and/or a separation of active sites.

To gain a better understanding of the catalyst surface, aberration-corrected STEM imaging, EELS, and EDX analysis was conducted on the CCC catalyst to determine the structure, morphology, and distribution of phases. STEM imaging (Figure SI1; SI = Supporting Information) shows the catalyst is primarily composed of interfacing regions of crystalline Co_3O_4 and CeO_2 but no Cu or CuO species could be found. To determine the elemental distribution of Cu within the Co_3O_4 and CeO_2, EDX elemental mapping was performed. An ADF STEM image of the CCC catalyst is shown in Figure 1a along with corresponding elemental EDX maps in Figure 1b–e. Figure 1b is the EDX map of Cu that shows how Cu is uniformly dispersed throughout the Co_3O_4 (Figure 1c) and CeO_2 (Figure 1d) regions. The STEM images (Figure SI1) combined with XRD (Figure SI2), which shows no evidence of Cu or CuO phases, suggest the Cu species is highly dispersed and/or exists as a solid solution in the CeO_2 and Co_3O_4 phases. This result agrees well with previous studies on the CCC catalyst as well as $CuO–CeO_2$ binary catalysts.[17,18]

Figure 2 presents CO and C_3H_6 conversion activities for CCC, PdZrSi, and the commercial DOC catalyst in simulated exhaust. The PGM-free CCC is active at lower temperatures than the commercial catalyst for CO oxidation in simulated exhaust conditions; however, the propene oxidation activity is significantly worse with the CCC. For further comparison, we synthesized another high performing PGM catalyst, PdZrSi,

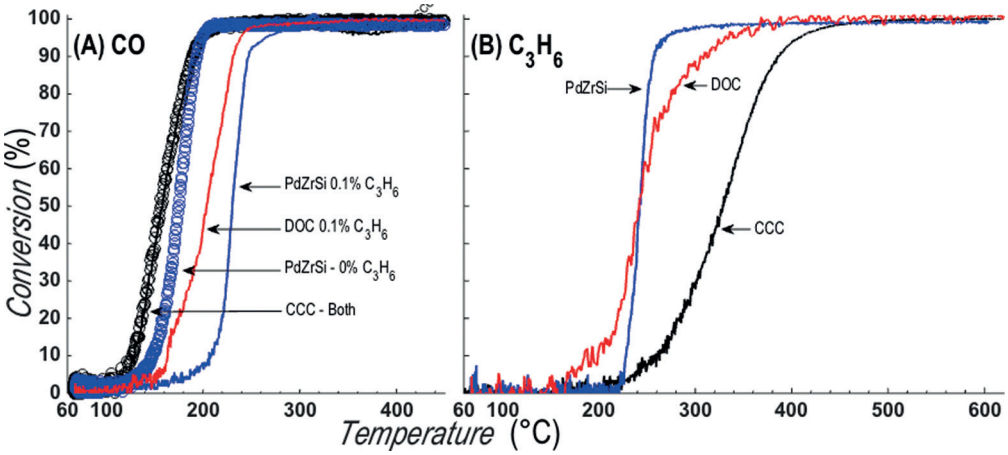

Figure 2. Light-off curves under simulated exhaust conditions for CCC (black), PdZrSi (blue), and DOC (red). A) CO Oxidation with and without $[C_3H_6] = 0.1\%$ (solid and circle, respectively). B) C_3H_6 conversion. $[O_2] = 10\%$, $[H_2O] = 5\%$, $[NO] = 0.05\%$, $[CO] = 0.4\%$ balanced with Ar at GHSV $\approx 150\,000^{-1}$.

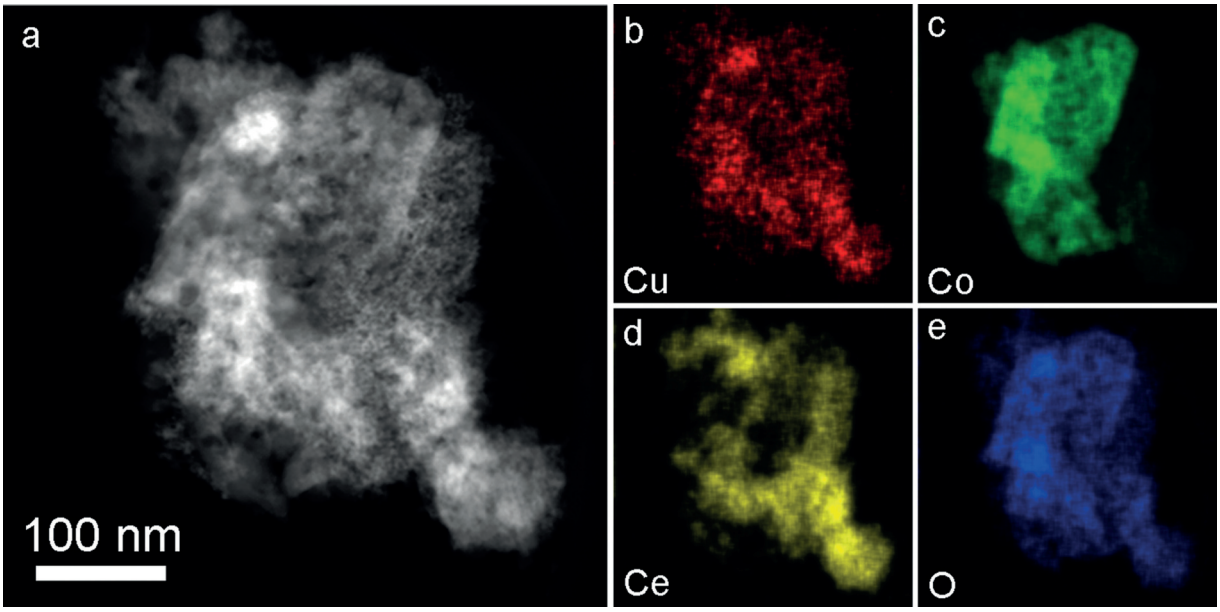

Figure 1. a) ADF STEM image of the CCC catalyst with corresponding b–e) EDX elemental maps showing the chemical distribution of b) Cu within the c) Co_3O_4 and d) CeO_2 phases.

and compared its properties with the ternary oxide. Despite far lower BET specific surface area ($SSA_{PdZrSi} = 404\ m^2 g^{-1}$, $SSA_{CCC} = 41.7\ m^2 g^{-1}$), the ternary oxide demonstrates improved CO oxidation activity over the PGM catalyst. Similar to the DOC, PdZrSi also outperformed CCC in C_3H_6 oxidation behavior. A secondary function of the DOC is to produce NO_2 to aid a downstream NO_x SCR catalyst, Figure SI4 also shows a maximum NO to NO_2 conversion to 325 ppm NO_2 (65% of input NO) at 375°C.

In order to examine the inhibitory effects of hydrocarbons on CO oxidation, propene (0.1%) was included in the evaluation as a model hydrocarbon (Figure 2a, circles). As expected, the PdZrSi catalyst showed a significant loss in activity ($\Delta T_{50} = 56$°C) due to the introduction of C_3H_6, whereas CO oxidation activity of CCC was unaffected by the addition of propene. The inhibitory effect of hydrocarbons on CO oxidation over PGM-based catalysts is well known[9,19] and has been widely attributed to competitive adsorption between reactants on PGM active sites.[9,20] Indeed, diffuse reflectance IR (DRIFTS) data (Figure 3a) shows that upon introduction of C_3H_6 to PdZrSi with pre-adsorbed CO, the Pd^{2+}–CO band immediately disappears and reappears over 30 min at a shifted position ($\Delta = -35\ cm^{-1}$) indicating a reduction of the Pd metal and a change in the CO adsorption site characteristics on the active metal.[7] On the CCC catalyst, no disappearance of the Cu^{+}–carbonyl band (Figure 3b) is observed and only a slight shift ($\Delta = -5\ cm^{-1}$) can be seen on the DRIFTS spectra of CCC, still within the region for Cu^{+}–carbonyl on CuO–CeO_2.[21] Furthermore, the C–H stretching bands that appear upon C_3H_6 adsorption are significantly weaker and broader for the CCC catalyst compared to PdZrSi, suggesting a weaker C_3H_6 adsorption on CCC at lower temperatures where CO oxidation occurs. The increased adsorption of propene at lower temperatures over PdZrSi was demonstrated by TPO of pre-adsorbed propene (Figure SI2). Weak propene adsorption and subsequently minimal interaction with active Cu sites is the likely cause of the resistance to inhibition over CCC.

Since CO inhibition by hydrocarbons over PGM catalysts is caused by competition for active sites; another explanation for the inhibition resistance seen over CCC could be a separation of active sites. The inhibition over PGM catalysts is caused by a competitive adsorption and poisoning of the precious metal (Pd, Pt, etc.) active sites by hydrocarbons such as propene.[9,22] Because the oxidation of hydrocarbons occurs at higher temperatures than CO, sites with adsorbed propene block CO adsorption and oxidation until the propene is itself oxidized and the active site is cleared. In 2008, the Guo group conducted a study of CO and propane (C_3H_8) oxidation (separately) over binary oxides CuO–CeO_2 and Co_3O_4–CeO_2.[15] Their analysis indicated that the copper–ceria and cobalt–ceria interface sites play a major role in CO oxidation by providing oxygen via a weakened metal–oxygen bond, making copper–ceria/copper–cobalt interface sites the primary active site for CO oxidation. On the other hand, they found that propane oxidation occurs over CuO or Co_3O_4 surface sites due to the requirement for an initial C–H bond-breaking step,[23] with Co_3O_4 being far more active. This presents a picture of two separate active sites for CO and hydrocarbon oxidation which could reduce or eliminate inhibitory competition. CO oxidation occurs primarily at interface sites between CuO and either Co_3O_4 or CeO_2, and hydrocarbon oxidation occurs primarily over the surface of CuO or Co_3O_4.

To this end we synthesized a series of binary oxides CuO–Co_3O_4, CuO–CeO_2, and Co_3O_4–CeO_2 to examine their activities for CO and propene oxidation under simulated exhaust conditions. Molar ratios of individual metals and structural characteristics of the calcined catalysts are given in Table SI1. Catalytic oxidation under simulated exhaust conditions was again studied to compare the ternary CCC catalyst with the synthesized binary catalysts CoCe, CuCo, and CuCe. Figure 4a shows the CO oxidation light-off for each catalyst. While all of the catalysts are active for CO oxidation, the unique synergy between all three oxides in CCC increases its activity over the binary catalysts. Of the binary catalysts CuCe is the most active at lower temperatures with the reaction initiating at lower temperatures than either CoCe or CuCo. Reports of CO oxidation over these oxide mixtures indicate a low intrinsic activity for CO oxidation by pure CeO_2;[11,18,24,25] thus, it is likely that the highly dispersed Cu sites interacting with CeO_2 are the primary active component

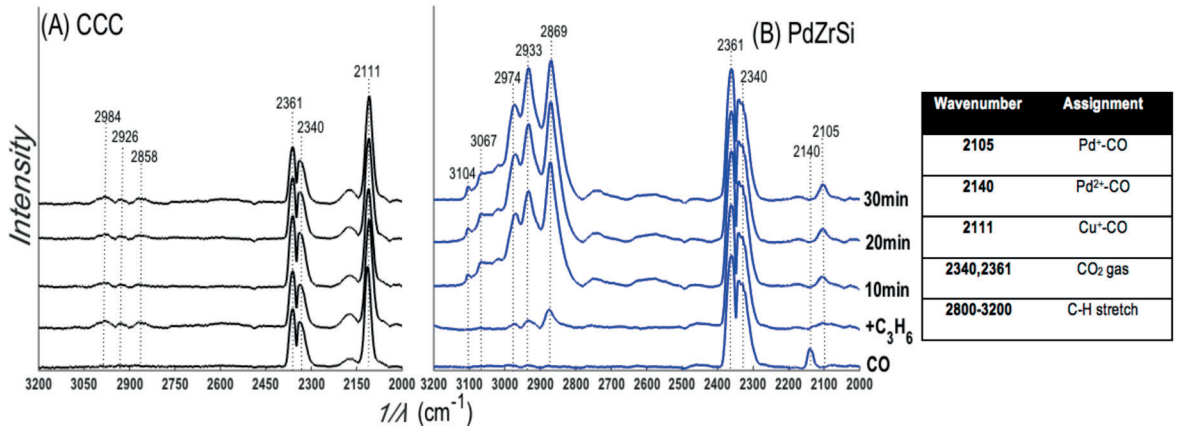

Figure 3. DRIFTS data collected for A) CCC at 120°C and B) PdZrSi at 140°C before and after introduction of $[C_3H_6] = 0.1\%$. Initial stream: $[O_2] = 10\%$, $[CO] = 0.4\%$, Ar balance.

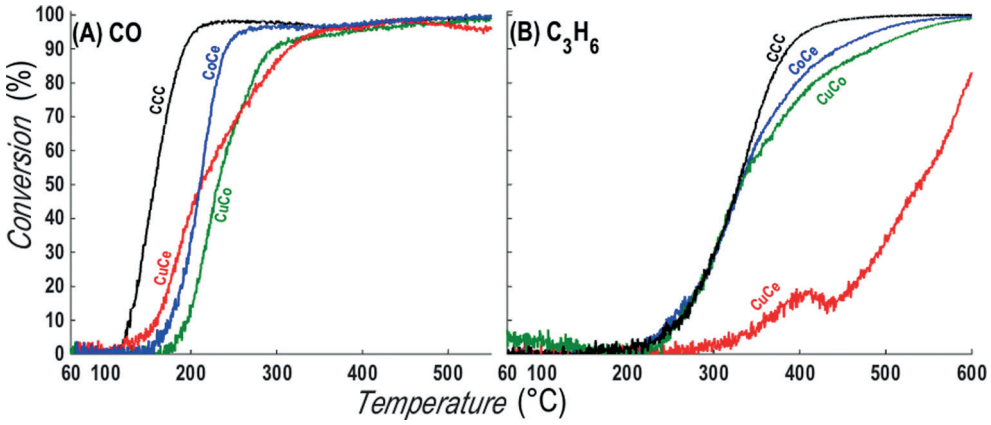

Figure 4. Light-off curves under simulated exhaust conditions for ternary CCC and binary catalysts. A) CO oxidation. B) C_3H_6 conversion. $[O_2]=10\%$, $[H_2O]=5\%$, $[NO]=0.05\%$, $[CO]=0.4\%$, $[C_3H_6]=0.1\%$, balanced with Ar at GHSV $\approx 150000^{-1}$.

in the low temperature light-off for CCC. The Co_3O_4 phase (which has far more abundance than the Cu) may be necessary for maintaining good conversion at the high flow rates studied. In particular, the interaction of CuO, or Co_3O_4, and CeO_2 has been reported to weaken the oxygen bonds at the interface increasing the availability of active oxygen at the surface.[15,24] The intrinsically higher activity of the copper sites paired with a high amount of these interface sites provided by the majority Co_3O_4 and CeO_2 phases may explain the improvement in activity for CCC over CuCe.[17] What is clear though is that the interface sites do indeed play a significant role in CO oxidation since variation of the interface composition significantly changes the catalyst activity.

For propene conversion (Figure 4b) we find that all three cobalt-containing catalysts show nearly the same light-off temperatures despite the vast difference in surface area and Co_3O_4 crystallite size between CuCo and the other catalysts; however, the temperature at which 90% conversion occurs increases as surface area decreases indicating possible mass-transfer limitations at this flow rate.[26] Evidently, the Co_3O_4 phase alone is the primary active component for propene conversion since the increased number of interface sites in CoCe and CCC do not increase the activity over CuCo, and the propene oxidation activity of CuCe is very poor. The high intrinsic activity of Co_3O_4 for volatile organic compound (VOC) oxidation is well known and pure Co_3O_4 is able to catalyze propene oxidation at equivalent or lower temperatures than Co_3O_4–MO_x binary mixtures.[14,23] The mechanism for olefin oxidation over metal oxides is believed to occur through hydrogen abstraction followed by reaction with electrophilic oxygen at the surface[23,27,28] without the need for weakened M–O bonds at interfacial sites. Here we find that the composition of the catalyst does not significantly change the C_3H_6 oxidation activities of the cobalt containing catalysts, which agrees well with cobalt oxide surface active sites for propene activation.

In summary, regulations and advances in engine combustion technology have resulted in the need to push the activity of emissions control catalysts to lower temperatures, <200 °C, and in addition the catalysts are required to convert higher levels of CO and hydrocarbons. The PGM-based catalysts in their current manifestation are unable to operate effectively in these conditions; thus, alternative solutions are necessary. The CuO–Co_3O_4–CeO_2 ternary oxide (CCC) presented here shows potential as a low cost alternative to PGM catalysts in lean-burn applications with higher capability for low temperature CO oxidation and a unique resistance to inhibition by hydrocarbons. Further study is needed to confirm the separate active site model and evaluation of model systems would prove valuable in understanding the interaction of surface reactions on this system. That said, the inhibition resistance found here is a new a promising property for this type of catalyst, which could prove very useful for emissions control in complex streams. While the necessary hydrocarbon activity is currently too low for CCC, combining these catalysts with a highly active hydrocarbon oxidation catalyst or enhancing the Co phase activity/surface area in the CCC catalyst may yield a complete solution for the CO and hydrocarbon emission control challenges.

Acknowledgements

This research was sponsored by the U.S. Department of Energy (DOE); both the Office of Energy Efficiency and Renewable Energy–Vehicle Technologies Office (A.J.B., T.J.T., and J.E.P.) and the Office of Basic Energy Sciences–Division of Chemical Sciences, Geosciences, and Biosciences (A.J.B. and S.D.) contributed to the support. Microscopy was conducted as part of a user proposal at ORNL's Center for Nanophase Materials Sciences (CNMS), which is an Office of Science User Facility. (RRU) This manuscript has been authored by UT-Battelle, LLC, under Contract No. DE-AC0500OR22725 with the U.S. Department of Energy. The United States Government retains and the publisher, by accepting the article for publication, acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for the United States Government purposes. The Department of Energy will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan (http://energy.gov/downloads/doe-public-access-plan).

Keywords: CO oxidation · emissions control · heterogeneous catalysis · IR spectroscopy · transition metals

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 13263 – 13267
Angew. Chem. **2015**, *127*, 13461 – 13465

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Received: July 2, 2015
Revised: August 6, 2015
Published online: September 11, 2015

