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Hydrophobic Polymer-Coated Metal Oxide Catalysts for Effective Low-Temperature Oxidation of CO under Moisture-Rich Conditions

Chun-Hu Chen,[†] Eric C. Njagi,[†] Shih-Po Sun,[‡]
Homer Genuino,[†] Boxun Hu,[§] and Steven L. Suib^{*,†,§}

[†]Department of Chemistry, [‡]Polymer Program, Institute of Materials Science, and [§]Institute of Materials Science, University of Connecticut, Storrs, Connecticut 06269-3060

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For the past several decades, the oxidation of carbon monoxide (CO) has become important in numerous applications, such as air/gas purification, life-support respirators, exhaust pollution reduction for automobiles/factories and Pt electrode protection in the low-temperature fuel cell system.¹ This results in a pressing need for CO oxidation catalysis; and many catalyst systems (noble metals, metal oxides, and composites) have been studied for high CO conversion at various temperatures and environments.² Among them, metal oxide catalysts with low production costs and high CO oxidation activity proved to be the most attractive.

Most CO oxidation applications involve moist environments with rapid flow rates, so highly moisture tolerant catalysts are necessary. Noble metal catalysts are known to be less susceptible to water and have been successfully applied in motor vehicles, but high production costs hinder their wider applications. Most of the inexpensive and highly active metal oxide catalysts, such as Co₃O₄, on the other hand are rapidly deactivated with trace amounts of moisture (3–10 ppm moisture level) from the feed gas. The super dry conditions (< 1 ppm moisture level), created by passing the feed gas through molecular sieve traps

at dry ice temperature (−77 °C) is required to avoid water deactivation.^{3,4} This pretreatment, however, is not applicable for most applications. Other studies show that the incorporation of CeO₂ into metal oxide catalysts can improve the water tolerance by decomposing water molecules via the water-gas shift reaction (WGSR).⁵ Nevertheless, this approach is limited to a specific material (CeO₂) and the occurrence of WGSR at temperatures higher than 110 °C.

Studies show that the surface hydrophobicity/hydrophilicity and membranous modification utilizing polymers is a promising strategy to enhance the selectivity, conversion, and recyclability of catalysts in many systems.⁶ Our previous work shows that the polydimethylsiloxane (PDMS) coated nanostructured manganese oxide materials exhibit a superhydrophobicity and highly selective adsorption of organic molecules in the presence of water.⁷ Accordingly, hydrophobic PDMS coatings on metal oxides prevent water from deactivating metal oxide catalysts. Although numerous attempts focusing on intrinsic modification of catalysts to address water deactivation at low temperatures,^{3,5} the idea of introducing a protective layer with high hydrophobicity on the catalysts has not been reported yet.

Here, we demonstrate the first example of the preparation and evaluation of a highly water-tolerant, hydrophobic polymer coated metal oxide catalyst for CO oxidation. The harsh experimental conditions, high moisture level (~3%), high space velocity (35 000 mL h^{−1} g_{cat}^{−1}) and low oxygen content (2%) in the feed gas were investigated to evaluate the catalytic performance for rapid air purification.⁸ Well-studied catalysts with various compositions, crystallinity, and surface areas, e.g. commercial product Hopcalite (HOP, CuMnO_x), amorphous manganese oxide (AMO), and crystalline cobalt oxide (COX, Co₃O₄) were selected to examine the generality of this hydrophobic surface coating approach.

In a typical polymer-coating procedure, 0.5 g of the selected catalyst was placed on the as-prepared PDMS films and then heated at 200 °C for various periods of time (2 and 4 days) to obtain the polymer-coated samples (see the Supporting Information). The vaporized PDMS was

*Corresponding author.

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- (8) Our results show that high content of oxygen (20%) and low space velocities give total conversion under many conditions. To know the catalytic performance limits of our samples, these harsh conditions found in literature are adopted in this work.

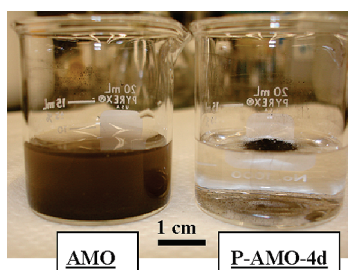


Figure 1. Hydrophobicity after the polymer coating procedure. All the other polymer-coated samples showed similar floatable behavior as **P-AMO-4d**.

deposited on the surface of the catalysts to form a hydrophobic layer.⁷ The indication of this water repellent behavior of PDMS-coated catalysts can be observed as they became floatable on the surface of the water (Figure 1). After the coating procedure, **P-AMO-4d**, the four-day polymer coated AMO sample, is highly hydrophobic and floatable on the surface of water. The surface tension is enough to support the weight of materials. On the contrary, the pure AMO is much more hydrophilic and well-suspended in water.

The catalytic activities of materials for CO oxidation are highly sensitive to their crystal structures and morphologies, particularly in the case of amorphous materials (**HOP** and **AMO**). To validate that the CO oxidation conversion change of the PDMS coated catalysts is due to the formation of a hydrophobic surface rather than the intrinsic change of morphology or crystal structure during the coating procedure, a detailed characterization study was performed. The X-ray diffraction (XRD) technique was applied to confirm that no additional phase was present after this polymer deposition procedure (Figures S1 and S2 in the Supporting Information) In Figure S3 in the Supporting Information, the results of transmission electron microscopy (TEM) show that there were no significant morphological changes or additional crystalline phases after the polymer coating process for AMO samples. No crystal structural or morphological change of this amorphous material is observed after the coating procedure. The elemental analysis of energy dispersive X-ray spectroscopy (EDXS) shows that the Si signal is only observed in the coated **P-AMO-2d** but not in the uncoated **AMO** sample, showing the existence of a PDMS hydrophobic layer after the coating procedure.

Characterization using Fourier transform infrared spectroscopy (FT-IR, Figure 2), and thermal gravimetric analysis (TGA) was carried out to identify the PDMS polymer coating on catalysts. The PDMS coated samples show bands at 1260 and 1020 cm^{-1} , corresponding to Si—O—Si stretching of PDMS, indicating the formation of PDMS coating. The TGA results in Figure S4 in the Supporting Information show two major weight losses. Because of the desorption of surface water and atmosphere gases, the first weight loss at 250 °C is 14.6% for **AMO**, 12.4% for **P-AMO-2d**, and 10.0% for **P-AMO-4d**. This result shows that the polymer-coated samples might have less water accumulation and cleaner surfaces

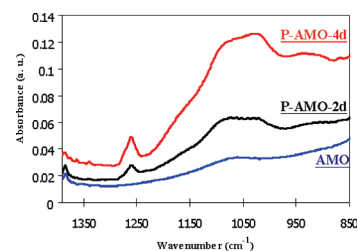


Figure 2. FTIR spectra of coated and uncoated AMO samples.

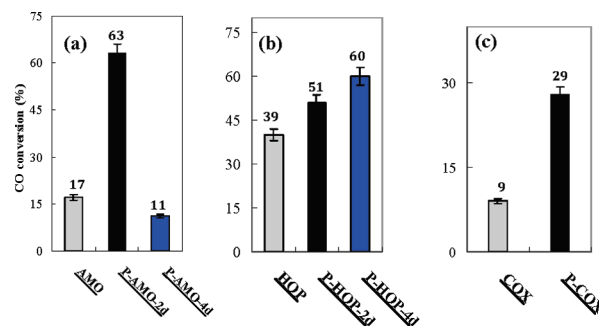


Figure 3. Catalytic performance of polymer-coated and uncoated materials under wet conditions. The comparisons of (a) amorphous manganese oxide system performed at 100 °C; (b) commercial Hopcalite system performed at 70 °C; (c) Co_3O_4 system performed at 100 °C.

as compared to uncoated **AMO** after a long time storage under ambient conditions (> 1 month). The second weight loss between 250 and 600 °C is 2.3% for **AMO**, 2.8% for **P-AMO-2d**, and 3.2% for **P-AMO-4d**. The additional weight loss of these coated samples is due to the decomposition of the surface hydrophobic PDMS and shows that longer coating times deposit more PDMS on the catalyst surface.

The result of water tolerance under the wet condition is shown in Figure 3. A general trend is demonstrated that hydrophobic coating enables materials to perform higher CO conversions compared to that of uncoated materials. In the AMO system (Figure 3a), the two-day polymer coated sample, **P-AMO-2d**, shows a CO conversion of 63%, around 3.7 times more compared to the 17% conversion for pure **AMO** at 100 °C. The conversion of the four-day coated sample, **P-AMO-4d**, however, dropped to 11%. Our TGA results show that this sample has the highest amount of PDMS deposition compared to **AMO** and **P-AMO-2d**, suggesting the decrease in conversion of this sample is presumably caused by limited diffusion of gaseous molecules (CO , O_2 and CO_2) through the PDMS layer. For the commercial Hopcalite system (Figure 3b), its conversion at 70 °C increased from 39% (**HOP**) to 60% (**P-HOP-4d**) with increasing coating time. The four-day coating process on **HOP** does not inhibit the performance of Hopcalite compared to that of the AMO system. The **P-HOP-4d** sample shows the best conversion of all the coated **HOP** samples, which indicates that the optimum coating amount differs for various catalysts. For the crystalline cobalt oxide catalysts (Figure 3c), the polymer coated Co_3O_4 catalyst (**P-COX**) causes 29% CO conversion, which is three times that of the untreated Co_3O_4 (**COX**) at 100 °C.

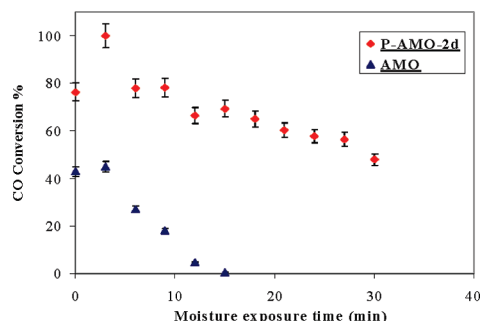


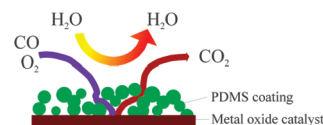
Figure 4. Water deactivation study of AMO system as a function of exposure time under wet conditions at 40 °C.

Detailed studies of the AMO system under dry and wet conditions were performed to investigate the influence of water deactivation. In the wet condition of Figure S5, moisture significantly inhibits the catalytic activity at all test temperatures compared to the results from the dry condition. In the dry condition, the uncoated AMO should be having better CO conversion than that of the coated samples as there is no active-site blocking due to the PDMS coating. The results, however, show that **P-AMO-2d** has a higher conversion than pure AMO, indicating that even a trace amount of water in the feed gas could significantly poison the catalytic sites.⁹ In the wet condition, all the test samples are significantly deactivated below 40 °C, and only **P-AMO-2d** has a perceptible conversion (11%) at 70 °C. At 100 °C, the **P-AMO-2d** increases the CO conversion (63%) dramatically and reaches a total conversion at 130 °C, whereas the AMO shows only a 53% conversion.

To understand the water deactivation with the moisture exposure time, a time-resolved study of CO conversion was applied to the coated **P-AMO-2d** and pure AMO samples at 40 °C. This particular temperature was chosen based on the result of the temperature effect studies (see Figure S5b in the Supporting Information), at which both samples are still highly deactivated but also close to regaining some activity. In Figure 4, the uncoated AMO was totally deactivated within 15 min of water exposure, which is similar to the reported data by Kramer et al.¹⁰ With the hydrophobic protection on **P-AMO-2d**, this sample shows a much slower decay and still possesses about 70% conversion, whereas the uncoated AMO becomes inactive. The dependence of the conversion on time is linear and the extrapolated lifetime is 80 min (see Figure S6 in the Supporting Information), which is 5.3 times longer than that for the unprotected AMO sample. In addition, this coating works even better than the noble metal (platinum) incorporated system.¹⁰

Detailed studies to reveal the mechanism of coating protection are undergoing. Current results suggest that

Scheme 1. Illustration of Protective Hydrophobic PDMS Coating on the Surface of Metal Oxide Catalysts^a



^a PDMS coating serves as a porous membrane and selectively allows CO oxidation reagents and products to diffuse through but inhibit moisture.

the hydrophobic PDMS polymer might form a porous layer on the surface of the catalyst with a selective permeability of CO, O₂, and CO₂ but not to water molecules (Scheme 1).¹¹ The GPC analysis shows that the polymer molecules of the hydrophobic coating have a weight average molecular weight of 5000 with a small dispersity index (PDI = 1.08), which could form a hydrophobic layer with a uniform pore size to significantly enhance the water tolerance of the coated samples. Previous studies have shown that the microstructure of coating, including coverage, porosity, and the orientation of the PDMS chain can be controlled, and a superhydrophobic and highly selective protected surface can be produced.¹² More work on the control and characterization of the polymer coating and its depositing process are desired as the optimum coverage and porosity may vary with properties of different materials, including surface area, functional groups, roughness, active site distributions, elemental compositions, particle sizes, and crystallinity.

In summary, an effective strategy of producing highly moisture-tolerated catalysts for CO oxidation without using noble metals has been successfully developed. The procedure is simple, low-cost, and general for all kinds of possible current active catalysts with various chemical compositions and crystallinity. Additional water resistance can be simply raised to the literature-reported catalysts already having certain levels of moisture tolerance. This strategy can also be applied to other water sensitive catalysis or applications. Further studies on different coating materials and controlled surface deposition are underway.

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Supporting Information Available: Experimental procedures and characterization results (XRD, TEM, EDXS, IR, and TGA) (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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