

ALD PROCESS FOR THE PREPARATION OF NOBLE-METAL-FREE MONOLITHIC CATALYSTS

Naoufal Bahlawane ^a, Katharina Kohse-Höinghaus ^a, Jin-Seong Park ^b, Roy G. Gordon ^b

^aPhysikalische Chemie I, Universität Bielefeld, Universitätsstr. 25, 33615 Bielefeld,
Germany

^bDepartment of Chemistry and Chemical Biology, Harvard University, 12 Oxford Street,
Cambridge, MA 02138, USA

ABSTRACT

Deposition of cobalt oxide on honeycomb substrates was performed using atomic layer deposition (ALD) technique. The obtained films were characterized and tested for their ability to induce the catalytic combustion of different hydrocarbons including methane. The threshold of oxidation for all investigated hydrocarbons correlates well with the reduction temperature of Co_3O_4 . The catalyst deactivation was significant when the catalyst was heated up to 800 °C, and the deposition of an alumina diffusion barrier did not bring any noticeable improvement. Nonetheless, even the severely deactivated cobalt oxide was noted to suppress the production of contaminants, such as formic acid and propene at high temperatures. Furthermore, the occurrence of the partial oxidation and the methanation reactions under oxygen-deficient conditions prevents sooting and suggests the complete reduction of the catalyst as the most probable cause of deactivation.

INTRODUCTION

Catalytic combustion is attracting great attention because of its potential in producing environmentally clean energy. This process enables full oxidation of lean fuel mixtures outside the usual flammability limits. The resulting reduction of the peak temperature in the combustion process leads to low thermal NO_x formation. Catalytic combustion is further exploited for efficient removal of a wide range of pollutants including carbon monoxide, unburned hydrocarbons and soot. Despite the well-recognized advantages of catalytic combustion, the large commercial application in power and heat production lacks an ideal catalyst. The presently available catalysts are either short-lived at high temperatures or insufficiently active at low temperatures (1).

Typical catalyst compositions involve precious metals such as Pt and Pd. Each presents an optimal catalytic activity toward a specific class of gases. Palladium is most suitable for the deep oxidation of CO and methane in addition to unsaturated hydrocarbons, while platinum is more suitable for alkanes (2). However, their high cost motivates the proposition of alternative materials. The most investigated noble-metal-free catalysts are spinels (3-8) and perovskites (9-12). These crystalline structures are ideal hosts for many transition- or non-transition-metal ion solid solutions, which is useful for the optimization of the catalyst performance.

The catalytic deep oxidation of methane is regularly selected as performance test reaction for the synthesized catalysts (1, 6, 8-12), because methane is the most difficult hydrocarbon to oxidize. Furthermore, being the main component of natural gas, methane is considered economically and environmentally one of the most important fossil fuels. Highly active catalysts are suspected to initiate the methane combustion to CO₂ at reasonably low temperatures and high flow rates, and to withstand high operation temperatures.

The catalyst performance is repeatedly reported to depend on the preparation process. The conventionally used liquid-phase synthesis processes depend highly on the physicochemical properties of the supports and considerably influence the surface area and the porosity of the support, which makes the gas phase synthesis a successful substitute. Okumura et al (13) demonstrated that CVD was successful in the deposition of highly dispersed gold catalysts on acidic supports while liquid-phase preparation methods failed. Keränen et al (14, 15) have conducted a comparative study between gas phase (ALD) and liquid phase (impregnation) synthesis methods. These authors concluded that, in contrast to impregnation, ALD produced highly dispersed catalysts with homogeneous distribution on different phases of the support material. Consequently, the catalytic activity was greater. Another comparative study, performed by Kainulainen et al (16), showed that the gas-phase deposited Co/SiO₂ catalyst was 3 times as active as that prepared by impregnation and experienced higher stability. Several recent works use gas-phase processes for the preparation of catalysts for different purposes including deep oxidation (6, 7, 17) and NO decomposition (18). In the present study, ALD-deposited cobalt oxide is investigated as deep oxidation catalyst with an emphasis on the deactivation process.

EXPERIMENTAL METHODS

The support material for the catalyst preparation was cordierite monolith with square channels and different densities (400, 600 and 900 cpsi). These monoliths exhibit a void fraction from 70 to 88% and allow a pressure drop below 10 mbar/m. The purchased monolith samples were cut to the diameter of 25 mm and the length of 50 mm and used for the deposition process without any pretreatment.

Cobalt monoxide (CoO) thin films were made by alternating exposure of the catalyst support at 250 °C to bis(N,N'-diisopropylacetamidinato)cobalt(II) vapor and water vapor using ALD; details are given in (19). The Co precursor was vaporized from a precursor bubbler at 65 °C, and the water vapor came from a bubbler at room temperature. The dose of cobalt precursor was 5×10^{-9} moles/cm² and the water dose was 8×10^{-8} moles/cm². These doses were kept in the reactor for 10 seconds after each injection, in order to allow full penetration in the holes of the honeycomb, which had an aspect ratio of about 40:1. After each 10-second exposure, nitrogen gas flowed through the reactor for 45 seconds in order to remove excess reagent. The film growth rate was about 0.025 nm per cycle of precursor and water. The alternating precursor and water exposures were repeated 1000 times to deposit a uniform, conformal film of CoO about 25 nm thick on all surfaces of the monolith, including inside the channels.

For testing the catalytic activity and investigating the redox properties, conventional horizontal quartz plug-flow reactors were used at atmospheric pressure with a temperature ramp of ~ 2.5 K/min. The monoliths were wrapped in high-temperature ceramic wool in order to force the gas to flow through the channels. The temperature of the reactor was controlled referring to that of the outer wall. During each test, the inlet and the outlet gas temperatures were simultaneously measured at ~ 1 mm away from both sides of the monolith sample. In order to identify the homogeneously occurring reactions, each test is automatically reproduced with a non-coated sample. The combustion tests were performed using 2 v% of the hydrocarbon gas and 2 v% of calibration gas (argon) in synthetic air at a total flow rate of 100 sccm under atmospheric pressure. The temperature-programmed reduction measurements (TPR) were performed using 50 sccm of argon flow rate containing 5 v% of hydrogen. The exhaust gas was analyzed using mass spectrometry (Quadrupole Mass Spectrometer, MKS-Spectra). The gas flow rates were adjusted using electronic mass flow controllers (MKS Instruments).

RESULTS AND DISCUSSION

The deposited films using ALD were revealed to present the cobalt monoxide stoichiometry using Rutherford backscattering analysis. Nevertheless, it was also demonstrated that the deposited films convert to Co_3O_4 ($\text{C/O} = 1.28$) upon heating up to 350°C in air. For this analysis, films were deposited on carbon substrates to avoid the presence of oxygen background.

Experimental tests of non-catalytic combustion were carried out using non-coated monoliths. It is shown in the Fig. 1 a, b and c that the oxidation of methane started at 600°C , which corresponds to its homogeneous combustion. Propane oxidized starting at 550°C , and the oxidation process was completed above 600°C . The non-catalytic combustion of *n*-octane shows a complex trend with the formation of methane and hydrogen at intermediate temperatures. The process takes place in two steps, the first starts at 200°C and leads to the conversion of 20% of carbon to CO_2 . The second step starts at a much higher temperature (600°C) and leads to complete combustion.

The TPR profile of the Co_3O_4 films shows two peaks that correspond to its sequential reduction to cobalt monoxide and then to metallic cobalt. The first reduction takes place between 200°C and 300°C . As can be appreciated from Fig. 1d, the first reduction peak correlates well with the temperature where cobalt oxide is catalytically active for the oxidation of hydrocarbons.

It is worth noting that the combustion of methane was investigated using cordierite monoliths with a cell density of 600 cpsi while that of propane and octane were done using the 400 cpsi samples. This choice was motivated by the high surface area, which is required to observe the heterogeneous combustion of methane. The occurrence of the catalytic action starting at 250°C was already reported for planar model catalysts prepared by CVD using the catalytic combustion of propane and ethanol as test reactions (7).

The thermal stability of the catalyst was investigated by performing successive catalytic screenings of methane combustion. The selected samples for this test were monoliths with high density (900 cpsi) and low cobalt loading. The first screening cycle,

Fig. 2a, shows that only a part of methane was heterogeneously oxidized at low temperature. The major fraction was homogeneously oxidized above 650 °C, with steep increase of the reaction yield with temperature.

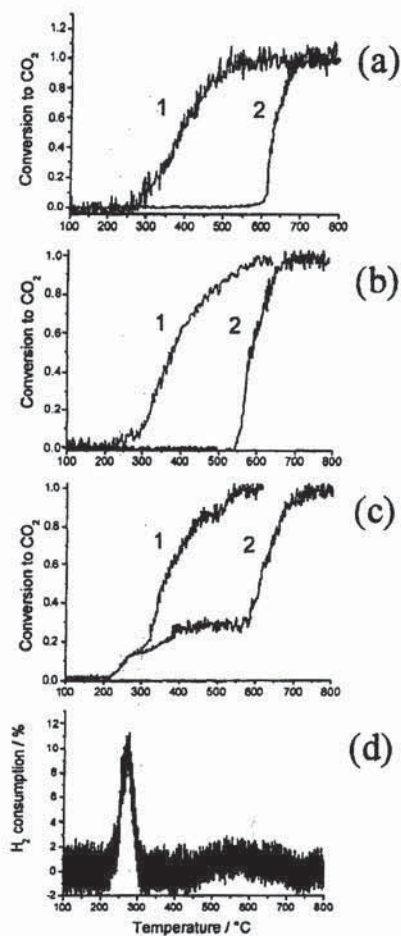


Fig. 1: Catalytic (1) and non-catalytic (2) combustion of methane (a), propane (b), and *n*-octane (c) in comparison with the registered TPR profile (d) using the same temperature ramp.

The measured temperature difference between both sides of the catalyst shows a single peak corresponding to the steep increase of the reaction yield (Fig. 2b). Because of

the heat dissipation, the slow thermally activated heterogeneous reaction did not induce any measurable temperature change. The linearly increasing maximal amplitude of this temperature difference (Fig. 2c) suggests that the fraction of the heterogeneously oxidized methane decreased with the number of cycles; therefore, the catalyst shows a constant rate of deactivation. The deactivation can either be associated with interfacial reaction between the deposit and the support material or with the surface modification of the deposit. The deposition of an interlayer of aluminum oxide using ALD did not decrease the rate of deactivation, which is not consistent with the first hypothesis. The remaining plausible causes of deactivation are the growth of carbon species on the surface of the catalyst during the screening cycles or the deep reduction of cobalt oxide.

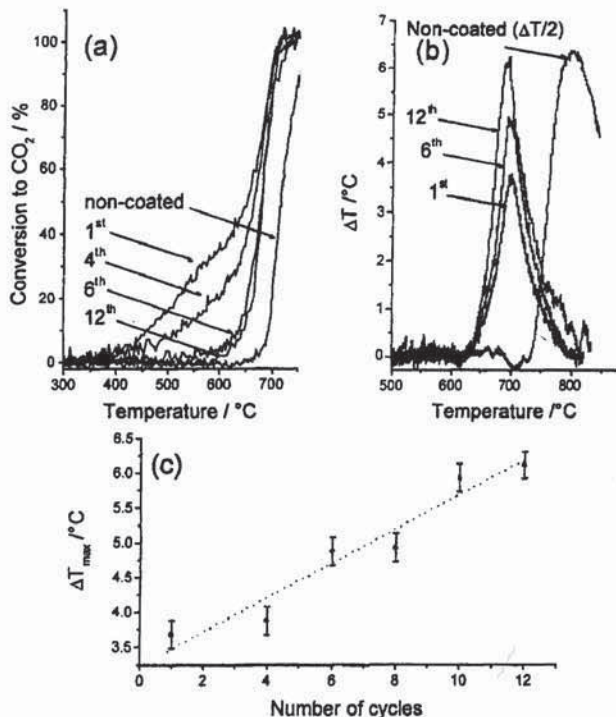


Fig. 2: Successive light-off curves (a) of methane with the corresponding temperature difference between both sides of the catalyst (b). The graph (c) presents the maximal amplitude of the temperature increase as a function of the number of performed cycles.

The hypothesis of carbon growth was also rejected because the heavily deactivated catalysts are still able to suppress the formation of contaminants. In fact, CO₂ is not the only by-product of non-catalytic combustion. Traces of formic acid were observed above 700 °C during the non-catalytic combustion of both methane and propane, while propene and methane were produced during the non-catalytic combustion of propane. All these

species are not observed during catalytic combustion even after heavy deactivation as shown in Fig. 3

The hypothesis of deep reduction of the catalyst was confirmed by the ability of the deactivated catalysts to catalyze the reforming reaction of *n*-pentane as shown in Fig. 4. The observed peak with $m/z = 72$ corresponds to *n*-pentane, while $m/z = 44$ (CO_2) reveals deep oxidation, $m/z = 15$ corresponds to a product of methanation reaction (CH_4 detected as CH_3^+) and $m/z = 2$ (H_2) is a product of the reforming reaction.

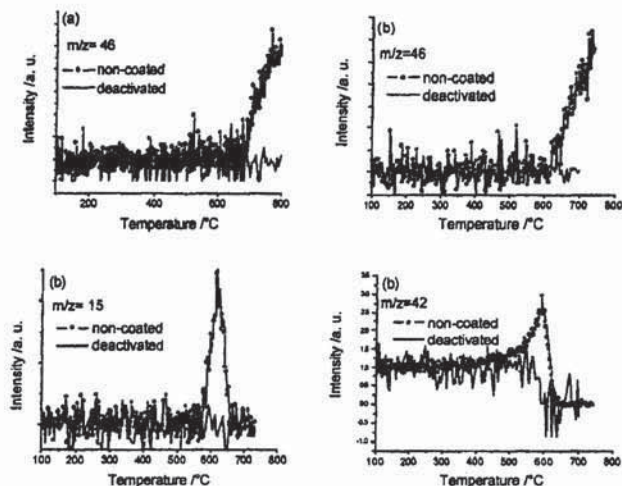
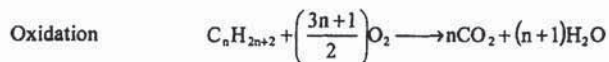


Fig. 3: Intensities of the produced contaminants during the combustion of methane (a) and propane (b) over non-coated support and deactivated catalysts ($m/z = 15$: methane detected as CH_3^+ , $m/z = 42$: propene and $m/z = 46$: formic acid).

Non-catalytic combustion is observed in the temperature interval 290-340 °C, followed by a large temperature interval where only a slight increase of CO_2 is seen. At 450 °C, a second process is activated where signals of all carbon-containing molecules drop to a minimal value, including CO_2 . The second step was revealed from the visual inspection to correspond to the sooting process. Both steps are exothermal as seen from the corresponding differential thermal curve.

Using the deactivated catalyst did not influence the first step that corresponds to the combustion; however, the second process that describes soot production was completely suppressed. The deconvolution of the differential thermal curve shows at least the occurrence of three reactions other than the oxidation starting at 290 °C. Above 450 °C, a large amount of hydrogen was produced in addition to methane. During this step, the following reactions are potentially involved in the production of hydrogen:



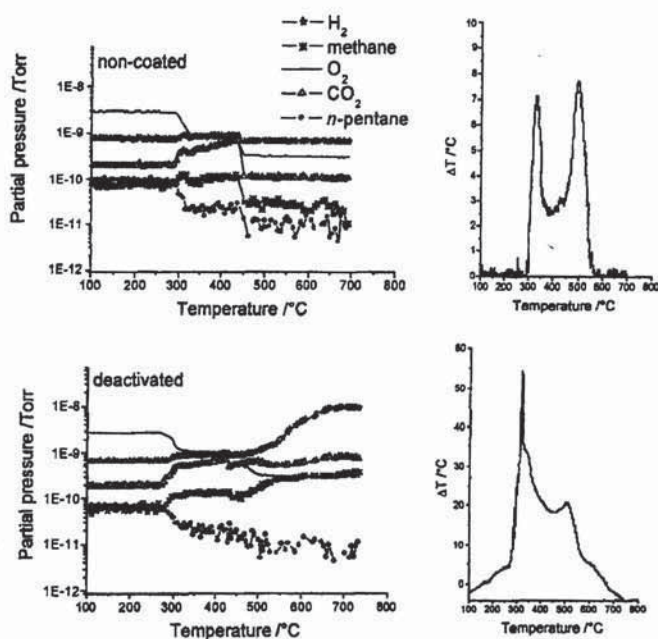
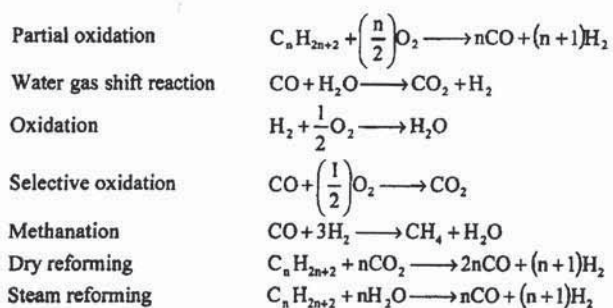


Fig. 4: Partial pressures of relevant species during the combustion of *n*-pentane over the non-coated and the deactivated cobalt oxide catalyst, and their corresponding differential thermal analyses.

In fact, several recent reports point out the promising role that the metallic cobalt might play for the conversion of hydrocarbons to hydrogen either through the steam (20), dry (21) reforming, or by partial oxidation (22). Furthermore, the methanation reaction is also reported as side reaction during the steam reforming (22). These observations suggest that deep reduction is the major cause of cobalt oxide deactivation.

CONCLUSIONS

The present work confirms the fact that cobalt oxide is highly active as deep oxidation catalyst and that ALD is a valuable process for the preparation of monolithic catalysts. The catalytic activity of cobalt oxide is positively correlated to the reversible oxidation-reduction reaction of Co_3O_4 to CoO around 250 °C. It was also demonstrated that cobalt oxide deactivates rapidly when exposed to heating cycles up to 800 °C. This deactivation can neither be explained by the reaction of cobalt oxide with the support material nor by the surface growth of carbon-containing species. Once deactivated, the catalyst became effective for reforming reactions and still suppresses the formation of contaminants, such as formic acid, during high-temperature oxidation of hydrocarbons. Therefore, optimizing cobalt oxide for deep oxidation reaction should consist of lowering the temperature of the first reduction $\text{M}_x\text{Co}_{3-x}\text{O}_4$ to $\text{M}_{x/3}\text{Co}_{1-x/3}\text{O}$ so that the oxidation of hydrocarbons starts at lower temperatures. Second, the reduction process $\text{M}_{x/3}\text{Co}_{1-x/3}\text{O}$ to $\text{M}_{x/3}\text{Co}_{1-x/3}$ should be retarded to expand the interval of the catalyst thermal activity

REFERENCES

1. S. Cimino, L. Lisi, R. Pirone and G. Russo, *Ind. Eng. Chem. Res.*, **43**, 6670 (2004).
2. S.A. Yashnik, V.V. Kuznetsov, Z.R. Ismagilov, V.V. Ushakov, N.M. Danchenko and S.P. Denisov, *Top. Catal.*, **30/31**, 293 (2004).
3. Md. H. Zahir, S. Katayama and M. Awano, *Mater. Chem. Phys.*, **86**, 99 (2004).
4. V. Matei, L. Patron, D. Matei, C. Suci, A. Borcea and D. Petre, *Prog. Catal.*, **11**, 51 (2002).
5. B. Chi, J.-B. Li, Y.-S. Han and J.-H. Dai, *Mater. Lett.*, **58**, 1415 (2004).
6. W. Li and Y. Lin, *Chem. Lett.*, **31**, 84 (2002).
7. N. Bahlawane, E. Fischer Rivera, K. Kohse-Höinghaus, A. Brechling and U. Kleinberg, *Appl. Catal. B*, **53**, 245 (2004).
8. E. Fischer Rivera, B. Atakan and K. Kohse-Höinghaus, *P. Electrochem. Soc.*, **2**, 1455 (2003).
9. S. Cimino, S. Colonna, S. De Rossi, M. Faticanti, L. Lisi, I. Pettiti and P. Porta, *J. Catal.*, **205**, 309 (2002).
10. J. Kirchnerova, M. Alifanti and B. Delmon, *Appl. Catal. A*, **231**, 65 (2002).
11. R. Spinici, A. Delmastro, S. Ronchetti and A. Tofanari, *Mater. Chem. Phys.*, **78**, 393 (2002).
12. S. Cimino, R. Pirone and G. Russo, *Ind. Eng. Chem. Res.*, **40**, 80 (2001).
13. M. Okumura, S. Nakamura, S. Tsubota, T. Nakamura, M. Azuma and M. Haruta, *Catal. Lett.*, **51**, 53 (1998).
14. J. Keränen, C. Guimon, A. Auroux, E. I. Iiskola and L. Niinistö, *Phys. Chem. Chem. Phys.*, **5**, 5333 (2003).
15. J. Keränen, P. Camiti, A. Gervasini, E. Iiskola, A. Auroux and L. Niinistö, *Catal. Today*, **91-92**, 67 (2004).
16. T. A. Kainulainen, M. K. Niemelä and A. O. I. Krause, *Catal. Lett.*, **53**, 97 (1998).
17. V. Cominos and A. Gavriilidis, *Chem. Eng. Res. Des.*, **79(A7)**, 795 (2001).
18. Y. Kuroda, K. Yagi, N. Horiguchi, Y. Yoshikawa, R. Kumashiro and M. Nagao, *Phys. Chem. Chem. Phys.*, **5**, 3318 (2003).
19. B. S. Lim, A. Rahtu and R. G. Gordon, *Nat. Mater.*, **2**, 749 (2003).
20. T. Furusawa and A. Tsutsumi, *Appl. Catal. A*, **278**, 195 (2005).
21. K. Omata, N. Nukui, T. Hottai, Y. Showa and M. Yamada, *Catal. Commun.*, **5**, 755 (2004).
22. M. S. Batista, R. K. S. Santos, E. M. Assaf, J. M. Assaf and E. A. Ticianelli, *J. Power Sources*, **124**, 99 (2003).