GERMANY/HONG KONG JOINT RESEARCH SCHEME
THE PROJECT REPORT
(for Project Completion)

Project Number: G_HK003/11

Title

Engineering the Oxygen Mobility of High Performance Catalysts for Preferential Oxidation of Carbon Monoxide (CO-PrOx)

Particulars

	Hong Kong team	German team
Name of Project Co-ordinator (with title)	Ir. Dr. Wey Yang TEOH	Prof. Dr.-Ing. Lutz Mädler
Name of Co-Investigator (if any)		
Institution or Institutional affiliation	☑ CityU ☐ HKU ☐ CUHK ☐ HKUST ☐ HKBU ☐ LU ☐ HKIEd ☐ PolyU	☑ University of Bremen ☐ Others:
Other project team members (if any)		

Funding Period

	1st year	2nd year (if applicable)
Start Date	1 January 2012	1 January 2013
Completion Date	31 December 2012	31 December 2013

Objective(s) as per original application

1. To design novel CO-PrOx catalysts with tunable operating temperatures through the engineering of lattice oxygen mobility
2. To advance the understanding of CO-PrOx mechanism over FeO_x-based catalysts and the influence of oxygen mobility

Details of Report [Please attach relevant document(s)]

i) Outline of proposed research and results obtained

1. Synthesis of novel catalyst for the low-temperature preferential oxidation of carbon monoxide (CO-PrOx) in H_2-rich stream, using the two-nozzle flame synthesis technique.

Through the proposal, we have designed a new class of Pt-FeO_x/CeO_2 catalyst with extremely high activity for CO-PrOx reactions. By controlling of the intersection distance of the Pt-FeO_x-laden aerosol flame and that of CeO_2, we were able to tune the interactions of the two active and complementary phases. At intersection distance of 22 cm, we obtained the most active catalysts where excellent interparticle mixing could be obtained (Figure 1). At closer distance, drastic atomic mixing of Fe-Ce phases take place which later impaired interfacial oxygen transfer within each nanocrystallite.

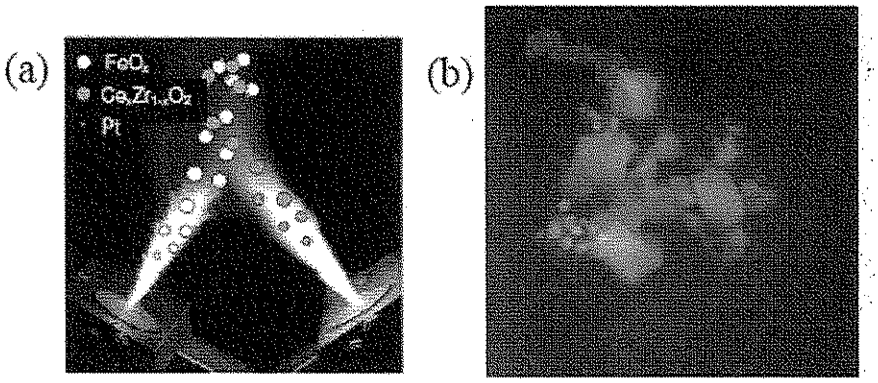

Figure 1. The flame spray synthesis of FeO_x-CeO_2 catalysts in a two-nozzle configuration to control the extent of interactions of FeOx and CeO_2 phases (right). Also shown is the scanning-transmission electron microscopy (STEM) image of the FeO_x-CeO2 catalysts, with the large rhombohedral particles belong to the CeO_2 crystals. In this case, it is show that the extent of interactions can be minimized when the spray flames are interfaced at large distance.

2. Assessment of two-nozzle flame catalysts

The flame-made catalysts were assessed for PrOx reactions at low temperatures as shown in Figure 2. High activity and selectivity are the two desirable characteristics of a good PrOx catalyst. Catalyst synthesized with the highest inter-nozzle distance, Pt-Fe|h|CeO_2 (black circle) shows the highest activity below 100 °C, and importantly, high selectivity towards the oxidation of CO_2. The catalytic selectivity basically decreases with decreasing inter-nozzle distance (Pt-Fe|s|CeO_2 and Pt-Fe|m|CeO_2). Physically-mixed analogue of Pt-FeO_x and CeO_2 (Pt-Fe|h|CeO_2, grey square) resulted in inter-aggregate mixing and hence could not reproduce the same extent of low-temperature activity. In the absence of CeO_2, Pt-FeO_x reference catalyst, which was reported to be one of the most active catalysts, produces low activity and selectivity compared to the composite Pt-Fe|d|CeO_2 catalysts synthesised in the two-nozzle flame.

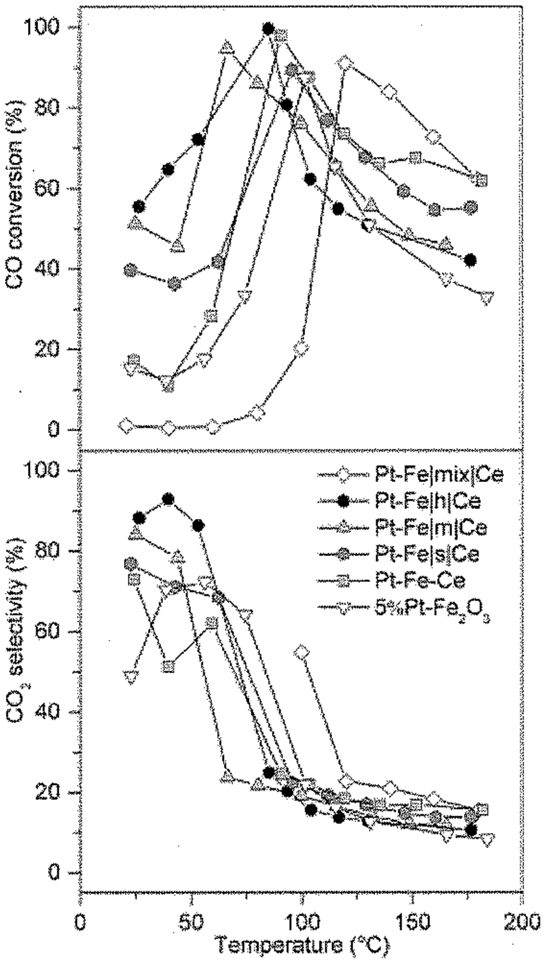

Figure 2. (a) CO conversion and (b) CO_2 selectivity of the Pt-Fe||Ce catalysts synthesized at different flame spray pyrolysis nozzle distances, Pt-Fe-Ce synthesized in a single nozzle and the analogous mechanically mixed Pt-FeO_x and CeO_2. Amount of catalysts = 20 mg, 50 mL min^{-1} of PROX gas mixture (1% CO, 2% O_2, 88% H_2 in He; O/CO ratio of λ=4).

3. Elucidating the reaction mechanism of the PrOx reaction

The low temperature reducibility of the flame-made catalysts was the main reason for the low temperature activity of the PrOx catalysts. This is well reflected by the H_2 temperature-programmed reduction spectra (Figure 3), where low temperature reduction infers easier oxygen mobility for participation in the CO oxidation. In other words, it is likely that the low temperature activity involve the Mars-van Kravalen (MvK)-like mechanism whereby surface/lattice oxygen was the source of O for CO oxidation. For this to take place efficiently, the interparticle contact between the Pt-FeO_x and CeO_2 (O source) is critical without doping of Fe in CeO_2, which essentially decreased the lattice oxygen mobility of the CeO_2 crystallite.

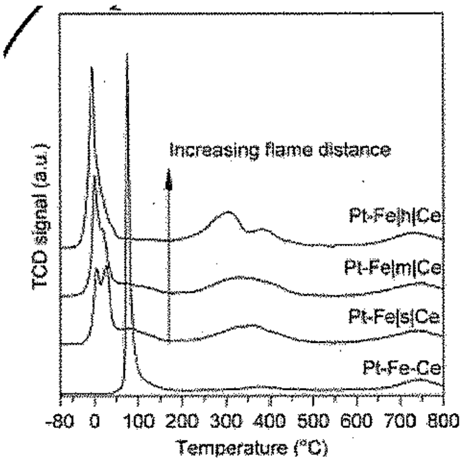

Figure 3. H2-TPR profiles of Pt-FeOx|d|CeO2 samples synthesized by two-nozzle flame spray pyrolysis

at different nozzle distances (hereby marked |s| = 6.5, |m| = 8.4 and |h| = 12 cm), as well as Pt-FeOx-CeO2 synthesized in a single nozzle flame spray pyrolysis.

To further probe the mechanism of oxygen transport contributing to the two different zones of PrOx activity, i.e., below and above 90 °C, we further assessed the stability of the catalysts at 40 and 100 °C (Figure 4). Here it can be seen that the activity of CO oxidation at 40 °C basically decreases with time on stream, inferring that the oxidation reaction is limited by the oxygen transport beyond the regions adjacent to the Pt sites, where CO molecules adsorb. At 100 °C, the activity remains relatively stable over the assessed 20 h period. The efficient rate of interparticle oxygen transport from CeO_2 to FeO_x and further oxygen mobility on the latter sustained the rate of oxidation reaction taking place on the Pt.

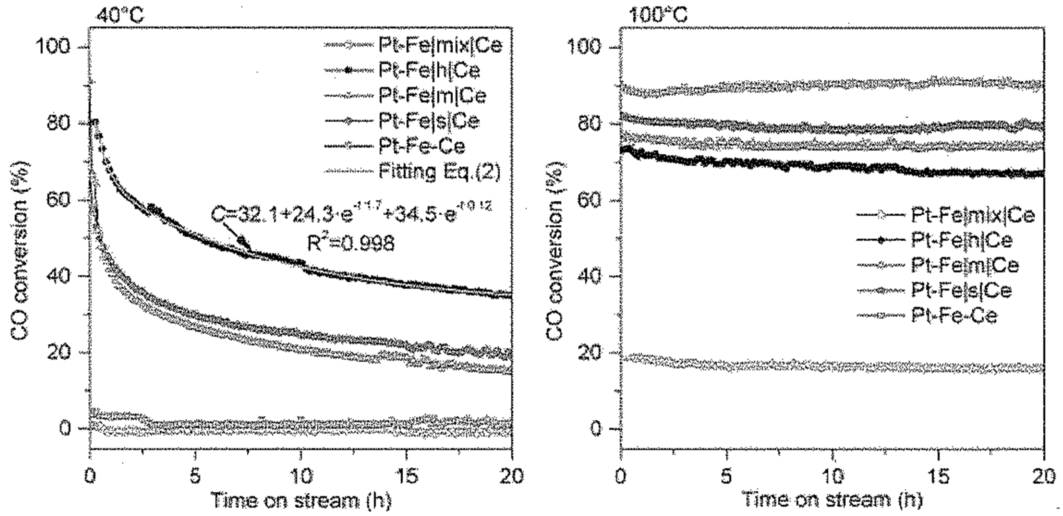

Figure 4. CO-PROX durability assessments over Pt-FeO_x||CeO_2 synthesized by two-nozzle flame spray pyrolysis at different nozzle distances, Pt-FeO_x-CeO_2 synthesized in a single nozzle and the analogous mechanically mixed Pt-FeO_x and CeO_2, at (a) 40 and (b) 100 °C. Amount of catalysts = 20 mg, 50 mL min^{-1} of PrOx gas mixture (1% CO, 2% O_2, 88% H_2 in He; O/CO ratio of λ=4).

ii) Significance of research results

The research demonstrates the versatile nature of the two-nozzle flame synthesis in fabricating novel class of highly efficient catalysts. The PrOx catalysts produced in this work is a clear proof-of-concept, while also shedding fundamental information on the reaction mechanism. The knowledge gained is further applicable to the elucidation of other PrOx catalysts, further forming the precursor of even more efficient catalysts.

iii) Research output

Part of the work has been presented at the ARC Advances in Functional Nanomaterials for Energy and Environmental Applications (15-16 November 2012). The abstract of the presentation is as below:

Hydrogen (H_2) is mainly produced by reforming and/or indirect partial oxidation of hydrocarbons. Even after a water-gas shift (WGS) reaction the resulting gas mixture contains 1000-10000 ppm CO. In order to utilize such H_2 rich gas mixtures for ammonia synthesis or feed gas for Polymer Electrolyte Fuel Cell (PEMFC) , it is essential to further reduce the CO concentration.The preferred oxidation (PrOx) of CO in H_2 rich streams is a promising approach in this context. In the ideal case all CO is oxidized to CO_2 (activity) while no H_2 is oxidized to H_2O (selectivity). Here, we present a novel flame made CeO_2/FeO_x catalyst, which is expected to exhibits higher activity and selectivity than its single metal oxides (CeO_2 or Fe_2O_3).

Part of the work has been presented at the Tokyo Catalysis Conference (1-6 June 2014). The short abstract of the presentation is as below, and extended abstract as attached:

A novel Pt/FeO_x-CeO_2 catalyst was designed by two-nozzle flame spray pyrolysis. By depositing Pt on FeO_x (in Flame 1) and interfacing with CeO_2 (Flame 2) at controlled interfacial distance, the catalyst reducibility and CO-PROX activity can be enhanced.

A manuscript is currently in preparation for submission to the Journal of Catalysis.

iv) Potential for or impact on further research collaboration

The results obtained through this proposal form the basis for further collaboration between the two groups for the exploration of other advanced catalysts beyond PrOx. Examples include catalysts for CO_2 reduction and biomass conversion. Joint grant applications such as those funded by Hong Kong General Research Fund and European Research Council will be considered for further support of such activities.