



Methanation of carbon monoxide over promoted flame-synthesized cobalt clusters stabilized in zirconia matrix



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ABSTRACT

Methanation catalysts based on 20% Co–ZrO₂ were synthesized in a one-step flame spray pyrolysis that at the same time allows the doping of noble metal promoters, hereby demonstrated with 0.4 wt.% Pd, Rh, Pt, Ru, and Ag. Unlike conventional catalysts, the cobalt content is internally dispersed and stabilized within the zirconia matrix, allowing the formation of very fine surface Co⁰ clusters (1–2 nm) upon reduction as unraveled from its dispersion. *In situ* X-ray absorption spectroscopy (XAS) showed that doping of noble metal promoters significantly improved the reducibility of cobalt in the order of undoped < Ag < Ru < Pt < Rh < Pd, as assisted by the H-spillover. The number of active Co⁰ sites on the surface was enhanced by almost 2-fold upon addition of promoters, and so are the corresponding rates of CO conversion. Detailed characterization by XAS and X-ray photoelectron spectroscopy (XPS) unraveled that homogeneously dispersed promoters (Rh, Pt, and Ru) merely enhanced the reducibility of cobalt and did not affect the turnover frequencies (TOFs, based on CO conversion) relative to that of the bare Co–ZrO₂ catalyst. On the contrary, surface-enriched promoters (Pd and Ag) lowered the apparent TOFs due to the mixed influence of the noble metals and Co⁰. We further found in the representative case of Rh-promoted Co–ZrO₂ that the promoter ameliorated hydrogenation and hence resulted in higher CH₄ selectivity with increasing H₂ partial pressure (i.e., higher reaction order), compared to the unpromoted catalyst.

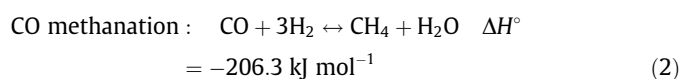
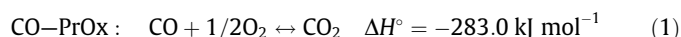
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1. Introduction

Securing clean H₂ fuel is a prerequisite to the realization of hydrogen-based economy, where the direct conversion to electricity is predominantly centered on chemical fuel cells [1,2]. In the foreseeable future, solar hydrogen generated using photocatalytic, solar-thermal, and bio-mediated water splitting, as well as that from the electrolysis of water using fully renewable resources such as wind and tidal energy are expected to be the workhorse for carbon-free H₂ production [3]. In the interim period, carbon-based resources such as coal, natural gas, and biomass continue to be an integral part of the energy mix strategy [4,5], including the industrial production of H₂ (currently the largest source of H₂). Despite possessing a highly efficient chemical-to-electricity conversion (efficiency reaching ~90%), the susceptibility of polymer electrolyte membrane-based H₂ fuel cells (PEMFC) to CO poisoning has been the bottleneck to their applications [6]. This is especially a

major challenge as far as the current production of H₂ from carbon-based resources is concerned, that is, through hydrocarbon reforming or partial oxidation followed by water–gas shift (WGS) reaction. The product syngas (CO and H₂ mixture) after WGS typically contains 2–10% CO [6–8]. It is not possible to further remove the residual CO as it is essentially limited by the thermodynamic equilibrium of the WGS reaction, which is reached by many active catalysts at the typical reaction temperatures of above 250 °C.

An additional reaction step is necessary to reduce the trace CO concentration in the reformat gas to a suitable level (<100 ppm) for the direct utilization in PEMFC. The two forefront catalytic technologies to address this issue are the preferential oxidation of carbon monoxide (CO–PrOx, Eq. (1)) and methanation reactions (Eq. (2)).



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The CO–PrOx reaction requires the introduction of close to stoichiometric O₂ over catalysts such as CuO/CeO₂, Pt/FeO_x, Au/TiO₂, or Au/MgAl₂O₄ that preferentially oxidizes CO in the presence of H₂-rich stream [9–13]. For this, tight and fast response process control over PrOx catalysts (with exclusive CO adsorption) during onboard conversion is necessary [14]. On the other hand, the CO methanation targets the hydrogenation reaction to convert CO to CH₄ (Eq. (2)). By capitalizing on the abundance of H₂ in the stream, a small amount of H₂ is sacrificed for the conversion of the trace CO. This maintains the simplicity of the reactor system design by circumventing the needs to control the O₂ concentration, and importantly preventing the oxidation of H₂.

In the past, CO methanation has largely focused on Ni [15,16] and noble metal-based catalysts, particularly Ru [17–19] and Pt [20] supported on zeolites, TiO₂, or Al₂O₃. These active metals exhibit strong affinity toward CO adsorption [21]. Catalysts based on Group VIII metals such as Co- and Fe-based methanation catalysts have attracted attention as economical alternatives [22–27]. Fe-based catalysts are known to possess intrinsically high WGS activity, a competing reaction to the hydrogenation reaction that Co-based catalysts are known for [28]. Among the long-standing challenges of Co-based catalysts are the requirements to obtain highly dispersed metals for maximum reactivity and at the same time, maintain high reducibility of the Co species. While strong metal-support interaction (SMSI) between Co oxides and support prevents the sintering of the active metals, it necessitates high reduction temperatures. Such high temperatures during the synthesis or pretreatments may lead to the formation of irreducible mixed oxide phases such as cobalt aluminate (for Al₂O₃ support) [29,30] and cobalt silicate (for SiO₂ support) [31]. In this regard, the addition of noble metal promoters is a possible strategy to lower the reduction temperature of the cobalt-based catalysts [32,33].

Herein, we report the flame spray synthesis of cobalt clusters stabilized in a zirconia matrix (Co–ZrO₂) for the methanation of CO. The flame spray pyrolysis (FSP) technique is a rapid (milliseconds) and scalable technique for the synthesis of highly crystalline nanoparticles with precisely controlled chemical compositions [34,35]. In the recent years, FSP has emerged as one of the mainstream techniques for synthesizing ready-to-use catalysts (see extensive review by Schimmoeller et al. [36]). The one-step FSP yields Co–ZrO₂ catalyst with a unique structure where Co is internally dispersed within the ZrO₂ matrix, but not forming mixed oxide phase of cobalt zirconate [37]. This allows chemical reducibility of the Co, and more importantly for the surface exposed Co to take part in catalytic reactions while preserving their fine structures as stabilized by the ZrO₂ matrix. Our preliminary studies leading to the current work found the formation of irreducible cobalt aluminate, silicate, and titanate when flame-spraying the mixtures of Co with Al, Si, and Ti precursors, respectively, rendering them not usable as methanation catalysts. We further investigate the role of different noble metal promoters, i.e., Pd, Rh, Pt, Ru, and Ag, all of which are introduced in precise trace amount during the flame synthesis of Co–ZrO₂. We show that the addition of noble metals significantly enhanced the reducibility of the Co oxides and depending on their morphologies, could also affect the catalytic properties of the catalysts.

2. Experimental

2.1. Catalysts preparation

Cobalt–zirconia (20 wt.% Co–ZrO₂) catalysts were synthesized using the one-step flame spray pyrolysis (FSP) as described in our earlier work [37]. Zirconium propoxide (0.5 M, 70% in 1-propanol, Aldrich) and cobalt 2-ethylhexanoate (0.2 M, 65% in mineral

spirits, Aldrich) were dissolved in xylene-based solvent (Table 1). Small amount of acetonitrile (ACN, HPLC grade, Aldrich) or 2-ethylhexanoic acid (2-EHA, ≥99%, Aldrich) was added to the solvent to enhance the solubility of metal acetylacetonate or metal benzoate, respectively. A range of noble metal precursors listed in Table 1 were dissolved in the solvent to give the final loading of 0.4 wt.% metal with respect to Co–ZrO₂. During the FSP synthesis [38], liquid precursor was delivered to the nozzle tip at 5 mL min⁻¹ using a syringe pump (Inotech), where it was dispersed by 5 L min⁻¹ O₂ flow (1.5 bar). Combustion of the dispersed droplets was initiated by supporting oxygen–methane flame (1.5 L min⁻¹ CH₄, 3.2 L min⁻¹ O₂) to form the primary aerosol flame (Scheme 1a). Additional 5 L min⁻¹ sheath O₂ was delivered around the aerosol flame. The Co–ZrO₂ aerosol leaving the flame was collected on a fiberglass filter (Whatmann GF-D, 25.7 cm) with the assistance of a vacuum pump (Alcatel SD series). The catalyst particles were scraped from the filter and used as-prepared without further treatment. All catalysts are labeled according to their nominal loadings, for example, 0.4M–20Co–ZrO₂ denotes a catalyst with 0.4 wt.% noble metal promoter M = Pd (molecular weight, M_w = 106.4), Rh (M_w = 102.9), Pt (M_w = 195.1), Ru (M_w = 101.1), Ag (M_w = 107.9), in metallic form), 20 wt.% Co (in metallic form), and the rest as ZrO₂.

2.2. Catalysts characterization

The specific surface area of the catalysts was measured by N₂ adsorption (BET) at –196 °C on a Micromeritics Tristar 3000. Prior to the measurement, the catalysts were treated at 150 °C under vacuum for at least 1 h to remove moisture and volatile organics. The surface composition was determined by X-ray photoelectron spectroscopy (XPS) on an ESCALab 220i-XL (VG Scientific), equipped with Ar⁺ sputtering (5 keV) for depth profile analyses. Monochromatic AlKα was used as the radiation source with energy scale calibrated and corrected for charging by using the C 1s (284.9 eV) line as the reference binding energy. The XPS spectra were treated and analyzed on commercial Avantage software using Shirley background and the Al-Scofield peak sensitivity library.

The X-ray absorption spectra (XAS) were recorded at ANKA synchrotron radiation source (XAS beamline; Co K and Pt L₃ absorption edges) and at the European Synchrotron Radiation Facility (ESRF, DUBBLE beamline; Pd K, Rh K, Ru K, and Ag K absorption edges). In both cases, a Si(111) double-crystal monochromator was used for selecting the energy of X-ray photons and the spectra were recorded in fluorescence and transmission modes. Co K-edge EXAFS spectra were recorded using pellets of the as-prepared

Table 1
Formulation of liquid precursors for the flame spray synthesis of bare and noble metal-promoted Co–ZrO₂.

Catalyst ^a	Noble metal precursor	Solvent ^b
0.4Pd–20Co–ZrO ₂	Pd(II) acetylacetonate (99%, Aldrich)	7.8 vol.% ACN, 92.2 vol.% xylene
0.4Rh–20Co–ZrO ₂	Rh(III) acetylacetonate (97%, Aldrich)	7.8 vol.% ACN, 92.2 vol.% xylene
0.4Pt–20Co–ZrO ₂	Pt(II) acetylacetonate (97%, Aldrich)	7.8 vol.% ACN, 92.2 vol.% xylene
0.4Ru–20Co–ZrO ₂	Ru(III) acetylacetonate (97%, Aldrich)	7.8 vol.% ACN, 92.2 vol.% xylene
0.4Ag–20Co–ZrO ₂	Ag benzoate (99%, Aldrich)	19.5 vol.% 2-EHA, 80.5 vol.% xylene
20Co–ZrO ₂	–	100% xylene

^a The cobalt precursor is 0.2 M cobalt 2-EHA (65% in mineral spirit, Aldrich), and the zirconium precursor is 0.5 M zirconium propoxide (70% in 1-propanol, Aldrich).

^b Acetonitrile (ACN, HPLC grade, Aldrich) and 2-ethylhexanoic acid (2-EHA, ≥99%, Aldrich).

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