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Water-gas shift reaction over platinum/strontium apatite catalysts

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ABSTRACT

Platinum supported on calcium hydroxy (CaHAP) and fluoroapatite (CaFAP) exhibits excellent water-gas shift (WGS) activity comparable to the best Pt WGS catalysts on reducible oxides. The high activity of these unusual WGS catalysts is attributed to the parallel activation of CO on the noble metal and H_2O on the ionic phosphates with formate species apparently being the major reaction intermediates. We have studied Pt supported on strontium hydroxy and fluoroapatites with varying cation and noble metal contents now in order to elucidate the role of the apatite cations and anions on WGS activity. Initial Pt dispersions approached 100% for loadings up to 3% (weight) with mean particle sizes of 1–2 nm according to H_2 chemisorption and EXAFS results (coordination number of 6.6). TEM analyses show further that the Pt aggregates grew slightly during catalytic testing up to 723 K with 1.5–2.5 nm particles being most abundant afterwards. Moreover, Pt^{n+} reduction is much facilitated on these apatites as revealed by temperature programmed reduction coupled with *in situ* X-ray absorption spectroscopy (XAS). The WGS reaction rates in a reformate-type gas mixture increased strongly with Sr/P ratio in the apatite, with the rates over the most active Pt/SrHAP and Pt/SrFAP catalysts being among the highest reported to date. In particular, Pt/SrHAP and Pt/SrFAP rates surpassed the rates over analogous Ca^{2+} substituted catalysts by ca. 30% at 573 K. This demonstrates that apatite cations have a strong impact on WGS conversion over these systems opening a route to catalysts with potentially even higher WGS activity.

1. Introduction

The water-gas shift (WGS) reaction ($CO + H_2O \leftrightarrows CO_2 + H_2$, $\Delta H = -41.1\ kJ\ mol^{-1}$) is a very attractive option for CO clean up in decentralized production of high-purity H_2 for fuel cells because it does not consume H_2 but delivers additional fuel instead. In particular, its combination with micro and membrane reactor technology [1,2] is intriguing as compact devices can be obtained enabling on site H_2 production for transportation and residential proton exchange membrane fuel cell (PEMFC) applications [3,4]. However, conventional ferrochrome and Cu based catalysts are unsuitable for such systems due to their large weight and volume, long start-up times, insufficient durability under steady state and transient conditions, and high susceptibility to condensation and poisoning [5,6]. High-temperature WGS reactors with integrated Pd membranes are also an intriguing option for pre-combustion CO_2 capture in large-scale power generation from fossil fuels [7–9]. This carbon capture scheme will benefit greatly from more active WGS catalysts because costly Pd membrane area can be reduced [2]. Hence, WGS catalysis has moved back to the forefront of research [5,6,10–18]. Gold and especially platinum supported on reducible oxides are the most promising alternatives for these WGS applications [5,6,10–14] although noble metal and rare earth element costs are a major concern [14]. These catalysts may also not be sufficiently stable under typical reformer outlet conditions [19,20].

Intrigued by an earlier study on the WGS reaction over apatite supported Au and Ru catalysts [21], we recently found that Pt supported on calcium hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, CaHAP) exhibits excellent high-temperature WGS activity on par with the best ceria supported Pt catalysts reported in the literature and without showing propensity for methanation [22]. The variation of WGS activity with Ca^{2+} surface concentration suggested that the apatite

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cations play a crucial role in the WGS catalysis on these irreducible, ionic oxides. This hypothesis is supported by quantum chemical calculations which showed that H_2O is strongly activated on apatite surfaces via simultaneous coordination to Lewis acidic Ca^{2+} ions and H-bonding to basic O atoms of PO_4^{3-} units [23,24]. Such simulations also revealed that formate ions are readily stabilized through similar bonding on CaHAP surfaces [25]. Interestingly, this species and its protonation product formic acid were the only WGS reaction intermediates that we detected by infrared (IR) spectroscopy on Pt/CaHAP catalysts [22].

Ionic apatites combine amphoteric acid and base functions and high hydrophilicity with good high-temperature stability [26–31]. These properties as well as the Ca^{2+} concentration can be readily modified through formation of non-stoichiometric formulations $Ca_{10-Z}(HPO_4)_Z(PO_4)_{6-Z}(OH)_{2-Z}$ with $0 \leq Z \leq 1$ (i.e. $1.5 \leq Ca/P \leq 1.67$) and isomorphous cation and anion substitution [32]. Non-stoichiometric forms can be conveniently obtained by shifting the equilibrium between phosphate ions PO_4^{3-} and its hydrogenated forms HPO_4^{2-} and $H_2PO_4^-$ through variation of the pH value during precipitation of these materials from aqueous mixtures with concomitant adjustment of the number of charge balancing earth alkaline cations [31]. The Ca/P ratio can be even raised above the stoichiometric limit (1.67) with excess Ca^{2+} ions being charge balanced by anions such as carbonate CO_3^{2-} [26]. Since the WGS activity of Pt/CaHAP catalysts correlated strongly with Ca^{2+} surface concentration [22], we have studied Pt supported on Sr^{2+} exchanged hydroxyapatites and fluoroapatites now in order to further elucidate the impact of the support cations on the WGS activity of these materials. In addition to the Sr^{2+} surface concentration we varied the Pt loading and carried out *in situ* XAS measurements to gain a better understanding of the interplay between the precious metal and apatites in WGS catalysis.

2. Experimental section

2.1. Catalyst preparation

All chemicals were of analytical grade, used without further purification and procured from Kermel unless otherwise noted. Strontium apatite powders were synthesized in analogous manner to previously studied Ca apatites [22] using aqueous solutions of $Sr(NO_3)_2$ and $(NH_4)_2HPO_4$ as precursors and aqueous ammonia (25%) for adjustment of the solutions pH values at 10, 10.5 and 11, respectively. Typically 100 mL aqueous 0.20 mol L^{-1} $(NH_4)_2HPO_4$ solution (e.g. at pH 11) was added dropwise under vigorous magnetic stirring to 100 mL aqueous 0.33 mol L^{-1} $Sr(NO_3)_2$ solution (e.g. at pH 11) at room temperature. The resulting suspension was kept stirring in a water bath for 2 h at 363 K and then cooled to room temperature and aged for 6 h. Next the precipitate was centrifuged, washed repeatedly with purified water until pH ~7, dried at 333 K for 12 h and finally calcined for 4 h in air at 773 K in a muffle furnace. The obtained powders were denoted SrHAP-10, SrHAP-10.5 and SrHAP-11 according to pH of the synthesis solutions. Fluoride substituted apatite (denoted SrFAP) was prepared by adding 0.247 g NH_4F to the $(NH_4)_2HPO_4$ solution before combination with the $Sr(NO_3)_2$ solution (both at pH 11). The remaining procedural steps were the same as for preparation of the SrHAP powders.

Catalysts with nominally 1% Pt were prepared by impregnation of the calcined apatite powders at room temperature using appropriate amounts of aqueous 15.8 mg mL^{-1} H_2PtCl_6 (Sinopharm Chemical Reagent Co.) solutions. The resulting suspensions were kept at room temperature for about 24 h before the samples were dried at 333 K for 12 h and calcined again for 4 h in air at 773 K in a muffle furnace. Pt/SrHAP-11 samples with different nominal Pt amounts (0.2–3%) were also prepared using the same method. All Pt concentrations are based on catalyst weight unless otherwise noted and nominal Pt loading is prepended to catalyst designations where required for clarity (e.g. 1% Pt/SrHAP-11).

2.2. Catalyst characterization

The bulk Sr/P ratio and Pt content were analyzed with an inductively coupled plasma optical emission spectrometer (ICP-OES, Perkin-Elmer Optima 7300DV). For that purpose catalyst samples were digested with aqua regia in a hydrothermal reactor at 423 K for 2 h. Surface compositions of the as-prepared catalysts were determined by X-ray photoelectron spectroscopy (XPS) carried out with a Thermo ESCALAB 250Xi instrument using Al K_α radiation ($h\nu$ = 1486.6 eV). The C1s peak was set at 284.8 eV and taken as reference for binding energy calibration. The software XPSPEAK was used for fitting of XPS spectra employing a Shirley background and a 90/10 mixture of Gaussian and Lorentzian functions. Platinum dispersions were derived from H_2 chemisorption measurements at 323 K assuming that the molar ratio of adsorbed H_2 to exposed Pt is 0.5. Each catalyst (50 mg) was first reduced in flowing 10% H_2/Ar at 573 K for 1 h, heated to 698 K under Ar and kept at that temperature for 1 h to purge H_2, and then cooled to 323 K in Ar. Chemisorption measurements were performed at that temperature by injecting a series of 10% H_2/Ar pulses till saturation adsorption was reached.

The specific surface area was analyzed by the BET method carrying out N_2 adsorption measurements at 77 K on a QuadraSorb SI instrument (Quantachrome). All samples were used as powders and degassed at 573 K for 6 h in vacuum before N_2 adsorption. X-ray diffraction (XRD) patterns of the catalyst powders were recorded with a PANalytic Empyrean instrument using Cu K_α radiation (λ = 0.1541 nm). Transmission electron microscopy (TEM) images were obtained with a JEM-2100 system (JEOL) with an acceleration voltage of 200 kV. The samples were ultrasonically suspended in ethanol and dropped onto a carbon film supported over a Cu grid for that purpose. Fourier transform infrared (FTIR) spectra were recorded in the 400–4000 cm^{-1} range at a resolution of 4 cm^{-1} on a Bruker Tensor 27 spectrometer equipped with a deuterated triglycinesulfate (DTGS) detector. Carefully ground catalyst samples were diluted with KBr (mass ratio = 1:200) and pressed into thin wafers for those measurements.

X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectra of the 3% Pt/SrHAP-11 sample were recorded at ANKA-XAS at Angströmquelle Karlsruhe (ANKA, KIT, Germany) [33]. Measurements were performed at the Pt L_3-edge (11564 eV) in fluorescence mode using a Si(111) double crystal monochromator. A Pt foil was used for energy calibration. The intensity of the Pt L_α-fluorescence (9.4 keV) was measured with an energy-dispersive 5-element solid-state Ge detector (Canberra, selected region: 9.1-9.7 keV, line width 300 eV). During temperature programmed reduction (TPR), XANES spectra were recorded in a continuous scanning mode (QEXAFS mode, scan duration 120 s). For this purpose, the 100–200 μm sieve fraction of the catalyst powder was loaded in a quartz capillary (outer diameter = 1.5 mm, wall thickness = 0.02 mm) between two quartz wool plugs. A gas blower (FMB Oxford) placed below the capillary was used for heating the sample from room temperature to 673 K at 5 K min^{-1} while flowing a 5% H_2/He mixture (50 ml min^{-1}) through the capillary [34]. Before and after reduction EXAFS spectra were acquired in step scanning mode under steady state conditions at room temperature in flowing helium (50 ml min^{-1}). XANES and EXAFS data analysis was conducted using the Athena and Artemis interfaces of the IFEFFIT software package (version 0.8.056) [35]. The spectra were energy calibrated, normalized and background subtracted using Athena. Athena was also used for linear combination (LC) fitting of the XANES spectra to determine the relative concentrations of oxidized and reduced Pt species during TPR. LC analysis of XANES