

## The Effect of Sodium in Activity Enhancement of Nano-sized Pt/CeO<sub>2</sub> Catalyst for Water Gas Shift Reaction at Low Temperature

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Water gas shift reaction (WGS) is a key step in H<sub>2</sub> production for fuel cell application.<sup>1</sup> Pt/CeO<sub>2</sub> is one of the most studied catalysts in WGS.<sup>2</sup> The Pt/CeO<sub>2</sub> catalysts are known to be bi-functional; in which both nano-sized Pt metal and CeO<sub>2</sub> supports adsorb and activate CO and H<sub>2</sub>O respectively. The activity/stability of Pt/CeO<sub>2</sub> catalysts strongly depends on the presence of oxidized species of Pt formed at the surface.<sup>3</sup>

Recently, Zhai *et al.* reported that alkali ions (sodium and potassium) added in small amounts activate platinum adsorbed on irreducible supports such as alumina and silica for low temperature WGS.<sup>4</sup> The alkali ion-associated surface OH groups are activated by CO at low temperature in the presence of atomically dispersed Pt.<sup>4</sup> It is also known that the nano-sized CeO<sub>2</sub> with hydroxyl species in contact with nano-sized platinum is able to stabilize these species to limited extent; which are known to be active species for WGS.<sup>2</sup> In this study, we have demonstrated sodium has a beneficial effect on stabilizing only oxidized species of Pt at the surface, resulting in the improvement of the activity of Pt/CeO<sub>2</sub> catalyst for WGS at low temperature. To the best of our knowledge, this is the first report that oxidized species of Pt are stabilized by Na in Pt/CeO<sub>2</sub>, which is confirmed by TPR.

The nano-sized CeO<sub>2</sub> with high surface area ~117 m<sup>2</sup>/g was prepared from Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and 15% solution of KOH by a simple protocol without using any template by a simultaneous precipitation/digestion technique described earlier by our group.<sup>2</sup> Pt/CeO<sub>2</sub> catalyst was prepared by an incipient wetness impregnation method with Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> (99%, Aldrich). The amount of Pt loading was fixed at 1 wt %. Pt-Na/CeO<sub>2</sub> catalyst was prepared by an incipient wetness impregnation method with aqueous NaNO<sub>3</sub> (99%, Duksan) and Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> (99%, Aldrich) at the same

time. The amount of sodium loading was fixed at 2%. The prepared catalysts were calcined at 500 °C for 6 h. Activity tests were carried out from 200 to 320 °C at 1 atm in a fixed-bed micro-tubular quartz reactor. CO<sub>2</sub> selectivity is defined as follows: CO<sub>2</sub> selectivity = CO<sub>2</sub> formed/CO converted. Table 1 describes the characteristics of Pt-Na/CeO<sub>2</sub> and Pt/CeO<sub>2</sub> catalysts. The addition of sodium in Pt/CeO<sub>2</sub> catalyst

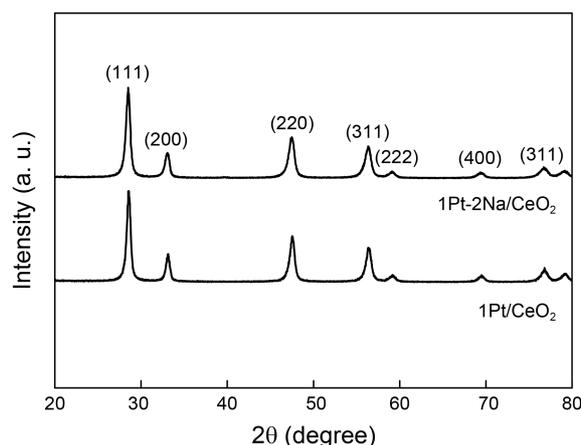


Figure 1. XRD patterns of Pt-Na/CeO<sub>2</sub> and Pt/CeO<sub>2</sub> catalysts.

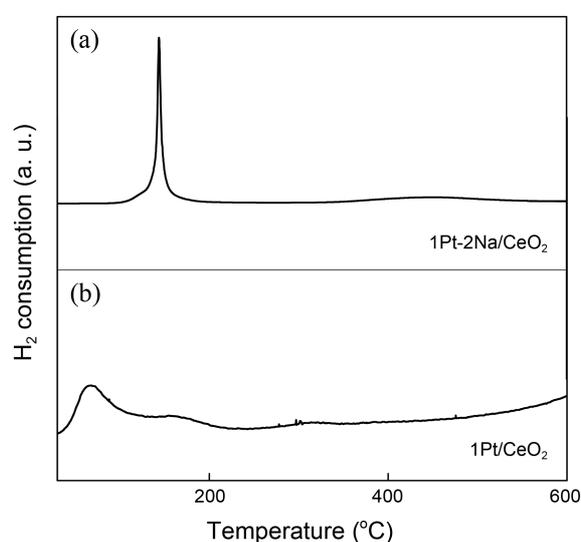


Figure 2. TPR patterns of (a) Pt-Na/CeO<sub>2</sub> and (b) Pt/CeO<sub>2</sub> catalysts.

**Table 1.** Characteristics of Pt-Na/CeO<sub>2</sub> and Pt/CeO<sub>2</sub> catalysts

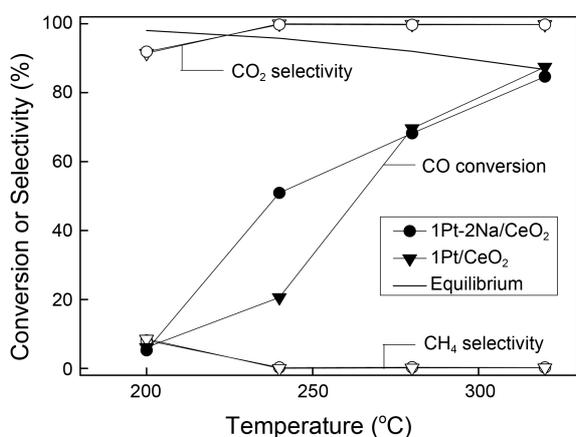
Catalyst	S.A. <sup>a</sup> (m <sup>2</sup> /g)	Dispersion <sup>b</sup> (%)	Pt S.A. <sup>b</sup> (m <sup>2</sup> /g)	Pt Size <sup>b</sup> (nm)
1Pt-2Na/CeO <sub>2</sub>	109	51.7	1.28	2.2
1Pt/CeO <sub>2</sub>	104	37.6	0.92	3.0

<sup>a</sup>Estimated from N<sub>2</sub> adsorption at -196 °C. <sup>b</sup>Estimated from CO-chemisorption at 50 °C

reduced the Pt crystallite size from 3.0 to 2.2 nm resulting in better dispersion of 51.7% in sodium added catalyst as compared to that of 37.6% in a catalyst without sodium.

Figure 1 shows X-ray diffraction (XRD) patterns of Pt-Na/CeO<sub>2</sub> and Pt/CeO<sub>2</sub> catalysts, which depict the fluorite structure. The Pt species (Pt, PtO, and PtO<sub>2</sub>) diffraction peaks are absent in XRD patterns, suggesting that the Pt species are highly dispersed on CeO<sub>2</sub>. To identify the nature of Pt species on the surface of these catalysts, TPR patterns of Pt-Na/CeO<sub>2</sub> and Pt/CeO<sub>2</sub> catalysts are shown in Figure 2. The Pt-Na/CeO<sub>2</sub> catalyst shows a strong peak at 143 °C attributable to only oxidized Pt species on the surface and a very weak peak above 450 °C corresponding to the reduction of bulk CeO<sub>2</sub>. On the contrary, Pt/CeO<sub>2</sub> catalyst shows three peaks at 65, 156 and 314 °C, respectively. These peaks are assigned to the reduction of surface CeO<sub>2</sub> in contact with Pt<sup>0</sup> species, PtO<sub>x</sub> and PtO<sub>x</sub> species interacting with CeO<sub>2</sub> support based on the literature data.<sup>3</sup>

The reduction of bulk CeO<sub>2</sub> starts above 500 °C. As a result, Pt-Na/CeO<sub>2</sub> catalyst shows the presence of only PtO<sub>x</sub> species while Pt/CeO<sub>2</sub> catalyst shows the presence of metallic Pt<sup>0</sup> and oxidized species of Pt. Thus, it has been confirmed that the addition of sodium has a beneficial effect on converting Pt<sup>0</sup> species into oxidized species of Pt at the surface of catalyst, which are known to be active species for WGS at low temperature.<sup>5</sup> Figure 3 illustrates the activity profiles of Pt-Na/CeO<sub>2</sub> and Pt/CeO<sub>2</sub> catalysts for WGS at a very high gas hourly space velocity (GHSV) of 45,515 h<sup>-1</sup>. At 200 °C, both catalysts showed very low CO conversion. At the reaction temperature of 240 °C, the CO conversion of Pt-Na/CeO<sub>2</sub> catalyst was 2.5 times higher than that of Pt/CeO<sub>2</sub> catalyst. In addition, selectivity to CH<sub>4</sub> and CO<sub>2</sub> remains unaffected in both catalysts as shown in Figure 3. The enhancement in CO conversion at 240 °C can be explained on the basis of increased oxidized species of Pt in catalyst with sodium.



**Figure 3.** CO conversion and selectivity to CO<sub>2</sub> and CH<sub>4</sub> with reaction temperature over Pt-Na/CeO<sub>2</sub> and Pt/CeO<sub>2</sub> catalysts (H<sub>2</sub>O/(CH<sub>4</sub>+CO+CO<sub>2</sub>) = 2.0; GHSV = 45,515 h<sup>-1</sup>).

It is reported that alkali ions stabilize atomically dispersed, oxidized species of Pt on silica surface.<sup>4</sup> The presence of such species can catalyze WGS on nano-sized Pt/CeO<sub>2</sub> catalyst at low temperature. It is interesting to note that the enhancement in WGS at low temperature has been realized by adding small amount of sodium. It is known that nano-sized ceria (CeO<sub>2</sub>) has a high oxygen storage capacity (OSC), redox couple and oxygen defects in its lattice.<sup>6</sup> It is also reported that the Ce-O bond is weakened because of the presence of nano-sized Pt or Au particles and this oxygen becomes reactive at lower temperatures.<sup>7</sup> The addition of sodium helps to create only Ce-PtO<sub>x</sub> species which may increase available oxygen at the surface for WGS at low temperature. As a result, the CeO<sub>2</sub> support can give mobile O<sub>2</sub> species to oxidize CO to CO<sub>2</sub> by temporarily reducing Ce<sup>4+</sup> → Ce<sup>3+</sup>, and then is re-oxidized by taking oxygen from the H<sub>2</sub>O molecule.<sup>5</sup> A dynamic equilibrium is quickly set up at the surface of catalyst involving Ce<sup>4+</sup>, Ce<sup>3+</sup> and lattice oxygen species under given reaction conditions involving reduction/oxidation processes during the WGS. This dynamic equilibrium at the surface of nano-sized Pt/CeO<sub>2</sub> catalyst in present study is fine tuned by addition of sodium in such a way that the enhanced activity for WGS at low temperature is achieved. Reproducibility of catalyst preparation with respect to its physicochemical characterization as well as the activity measurement for WGS is found to be excellent.

In summary, the addition of small amount of sodium while impregnating 1 wt % Pt on nano-sized Pt/CeO<sub>2</sub> catalyst helps to convert Pt<sup>0</sup> species into oxidized Pt species with higher dispersion, resulting in enhancing the activity of WGS at low temperature.

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