

Low temperature water-gas shift: weakening of formate C-H bond observed with alkali doping of Pt/ZrO₂ catalysts

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Introduction

In 2005, Brooks et al. [1] from Honda Research Institute USA, Inc., in conjunction with Symyx Technologies, Inc., reported findings from over 250,000 experiments conducted by combinatorial catalysis. Catalyst libraries were synthesized on 4" wafers in 16 × 16 arrays, and screened using a Symyx high throughput scanning mass spectrometer. Among the promising compositions found, an important improvement in catalyst activity was observed when Pt/ZrO₂ was doped with the alkalis Li, Na, and K, with Na yielding the greatest enhancement. In 2006, Pigos et al. [2] reported results of DRIFTS spectroscopy suggesting that formate species were more reactive on the Na promoted catalysts relative to Pt/ZrO₂ alone. In this contribution, the aim is to explore further the nature of the promoting effect of alkali dopants on 2%Pt/ZrO₂ catalysts by examining the impact of Li, Na, or K addition to the stability of formate species. Three separate tests were conducted to probe formate stability, including (1) steady state CO adsorption and water-gas shift experiments at 225°C, (2) transient formate decomposition studies at 130°C in the presence of steam, and (3) formate decomposition tests under dry conditions using hydrogen-deuterium exchange at 225°C.

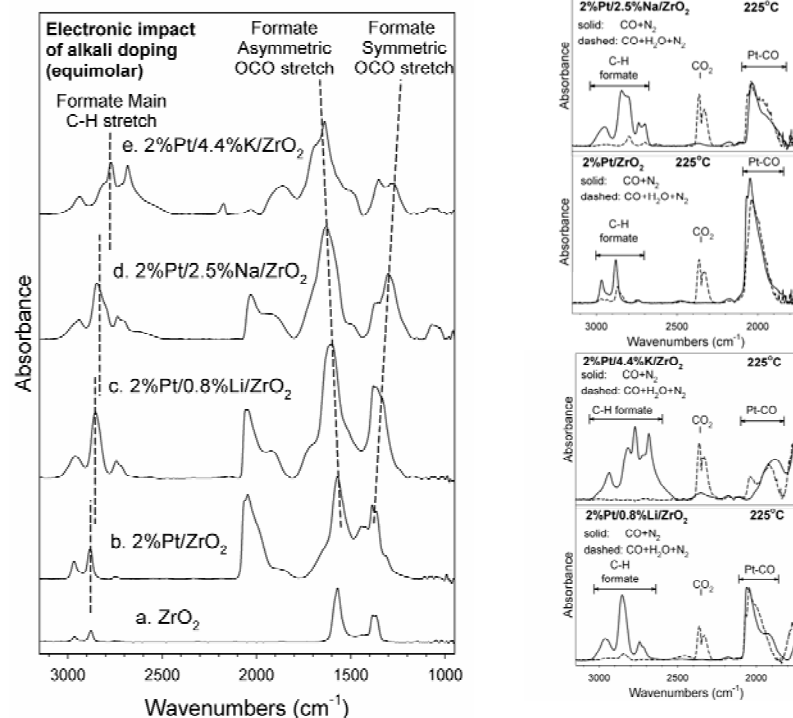
Materials and Methods

Catalyst samples were prepared by the incipient wetness impregnation method. Commercial high surface area zirconium support Gobain NorPro (BET surface area of 117 m²/g) was impregnated with aqueous platinum and either lithium, sodium, or potassium salt containing solutions. The impregnated catalysts were dried in an oven at 110°C for 24 hours and then calcined at 300°C for 3 hours in a furnace. Sequential impregnations were carried out by drying and calcining after each metal addition.

Results and Discussion

Using combinatorial methods, doping Pt/ZrO₂ with alkali cations such as Li, especially Na, and K, was found to have a positive impact on the low temperature water-gas shift rate. Formate species have been reported to be likely intermediates in water-gas shift (3,4). In this investigation, DRIFTS results indicate that the alkali cation significantly shifts the formate C-H band positions toward lower wave-numbers in the order K (2774 cm⁻¹) < Na (2842-2804 cm⁻¹) < Li (2858 cm⁻¹) < none (2880 cm⁻¹). Not only were the bands shifted, but the overall intensities were found to be higher with the addition of alkali promoter. Three separate tests were conducted to probe the stability of formates, including (1) steady state experiments at 225°C, (2) transient formate decomposition studies at 130°C in steam, and (3) dry hydrogen-deuterium exchange tests at 225°C. In each case, the alkali significantly impacted the formate decomposition rate, due to the weakening of the formate C-H bond. The results suggest a new direction in water gas shift catalyst design.

Figure 1. (Left) CO addition 225°C after H₂ reduction at 300°C. (Right) Formates are reaction rate limited upon switching to WGS conditions. Alkali addition further limits the band intensities, suggesting an increase in their turnover rates.



Significance

Alkali doping of Pt/ZrO₂ catalysts altered the intensity and stability of formate species, proposed intermediates in the low temperature water-gas shift reaction mechanism. Weakening of the formate C-H bond led to improved formate turnover rates, suggesting a new direction in water gas shift catalyst design.

References

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