

# Alkali-stabilized atomic Au- and Pt-OH<sub>x</sub> species supported on L-zeolite and MCM-41 catalyze the low-temperature water-gas shift reaction

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## Introduction

The water-gas shift reaction (WGS) is important in upgrading hydrogen-rich gas streams during fuel gas processing. For this reaction, atomically dispersed supported gold and platinum species, Au- and Pt-O<sub>x</sub>-support, have been found to be the active sites [1-6]. When depositing Au and Pt on supports like ceria and doped ceria that contain a large number of reducible surface oxygen, a facile thermal oxidation treatment suffices to anchor the Au and Pt species on the support [1, 2]. When the “capacity” of anchoring sites of ceria is exceeded, any additional precious metal will form particles that are spectator species for the WGS reaction. However, for many earth-abundant cheaper supports, such as alumina, silica, and zeolites, precious metal anchoring and stabilization at reaction conditions is more difficult. A promoter is necessary in these cases. To demonstrate that the same Au- and Pt-O<sub>x</sub>- sites can be created on any support, we have investigated the promotional effect of alkali metals on Au-OH<sub>x</sub> and Pt-OH<sub>x</sub> species loaded in alumino-silicate supports, such as zeolites (L type and MCM-41), as new low-temperature WGS catalysts.

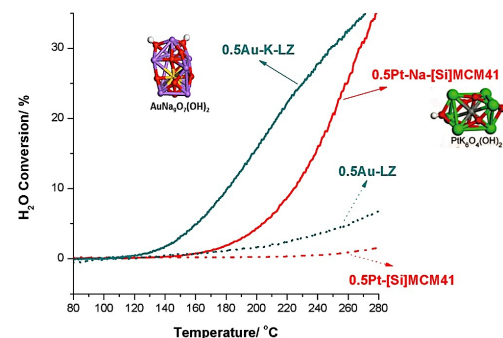
## Materials and Methods

The preparation technique is adapted from the method already reported by our group for Pt catalysts on silica and alumina [3, 6]. Accordingly, alkali promoters are used to provide vicinal –OH groups to Pt atoms [3]. In this work, Au(I) and Pt(II) precursors were mixed with the alkali base by solid state or wet impregnation and followed by careful thermal treatment up to 673 K. The K L-zeolites were supplied by TOSOH, while the MCM-41 materials were made by the Huang group at the U. Sydney. The catalysts were tested in a quartz packed-bed flow reactor in temperature-programmed surface reaction (TPSR) dynamic mode and at steady state in realistic reformate gas conditions. Gas streams were analyzed on-line by mass spectrometry and a TCD detector. ICP, XPS, XRD, XAS, and HAADF-STEM were used to characterize the samples. To get a better understanding of the underlying reaction mechanism, we used periodic, self-consistent DFT calculations, in the framework of *ab-initio* molecular dynamics (AIMD).

## Results and Discussion

Active and stable (up to 673 K) alumino-silicate supported gold and platinum catalysts were developed in this work (Figure 1). Without the addition of alkali metals, both the

gold and platinum catalysts were inactive for the low-temperature WGS reactions, and the formation of metallic particles (> 5 nm) was observed. Modifying only the zeolites supports by ion exchange of alkali metals does not improve the catalytic activity if the Au or Pt-O-alkali interaction is not established. The metal atom-centric (Au or Pt)-OH<sub>x</sub>-O-(Na, K) ensemble is identified to be the active site. The addition of alkali metals does not change the apparent activation energy of Pt- or Au-O<sub>x</sub> for this reaction, which is the same as on reducible oxide supports. Thus, again we find that the support effects are indirect for the WGS reaction on Au and Pt catalysts. Typical promising active structures identified by our DFT studies are shown in Figure 1. The Bader charge of platinum in these structures is close to Pt(II), and for gold it is close to the Au(I) state, which agrees well with the XPS and XAS analyses. The H<sub>2</sub>O activation is facile on the Au- and Pt-OH<sub>x</sub> sites.



**Figure 1.** Dynamic light-off of the WGS reaction over the 0.5 wt.% Au/L-zeolite and 0.5 wt.% Pt /MCM41 samples with and without alkali metals (heating rate: 5 K/min; 10 % CO-3 % H<sub>2</sub>O- He, 30 mL/min; 100 mg sample). Two promising active structures are illustrated in the figure (Au: yellow, Pt: gray; Na: purple; K: green; O: red; H: white).

## Significance

In this work, we have investigated alkali oxide-promoted gold and platinum on alumino-silicate supports as catalysts for the WGS reaction. The promotion is due to creation of (Au or Pt)-OH<sub>x</sub>-O-(Na or K) ensembles, where vicinal –OH species are supplied to the Au and Pt sites and the adsorbed CO. Our kinetic results show that the atomic Au- or Pt-OH<sub>x</sub> sites can catalyze the low-temperature WGS reaction on any support with the same intrinsic activity. This paves the way for using earth-abundant “inert” oxides to disperse and stabilize precious metal atoms by alkali promoters for the WGS and potentially other fuel processing reactions.

## Acknowledgement

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