

Characterization of PtRe/carbon catalysts used for conversion of sugars to hydrocarbons

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Introduction

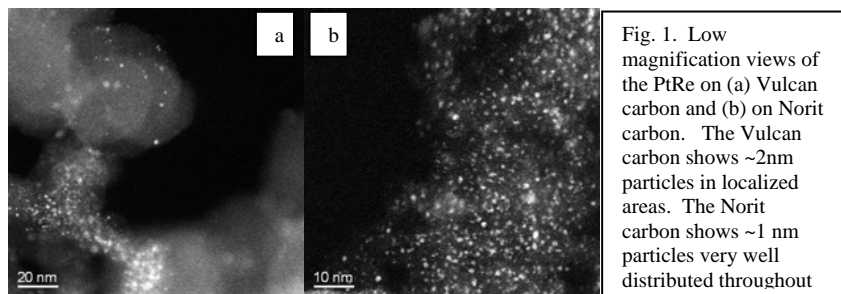
PtRe/carbon catalysts have been recently shown to convert sorbitol and glucose at temperatures near 500 K to a hydrophobic organic liquid containing alcohols, ketones, carboxylic acids, and alkanes containing four, five, or six carbon atoms, as well as heterocyclic tetrahydrofuran and tetrahydropyran compounds [1]. At 503 K and 18 bar, Pt-Re/C showed excellent stability for longer than 1 month time-on-stream [1]. In this work we present a detailed characterization of the nature of the Pt and Re components in this catalyst and the evolution of the catalyst after use in these reactions. Of particular interest are the preparation conditions of the catalysts and the morphology of the carbon support and the surface sites on the carbon that may be responsible for the remarkable activity and stability of these catalysts under reaction conditions. Two types of carbon support were used, an activated carbon (Norit -SX1G) and a carbon black (Vulcan XC 72).

Materials and Methods

The carbon-supported Pt-Re catalysts were prepared by incipient wetness impregnation with an aqueous solution of $H_2PtCl_6 \cdot 6H_2O$ and $HReO_4$ (Strem Chemicals) to yield a catalyst with loadings of 5.1 wt% Pt and 4.9 wt% Re (atomic Pt:Re ratio of 1:1). Transmission electron microscopy was carried out using a JEOL 2200 FS aberration corrected electron microscope (ACEM) and also a FEI CM 200 FEG microscope.

Results and Discussion

The images in figure 1 show how the nucleation of the PtRe metal particles is very different on the two carbon supports. On Vulcan carbon, the PtRe particles are located in specific regions of the support. This leads to a lower CO chemisorption uptake (150 $\mu\text{mol/g}$) and larger particle size (2nm) on the Vulcan carbon compared to on the Norit carbon (200 $\mu\text{mol/g}$ and 1 nm average diameter). Examination of these samples with the aberration-



corrected STEM allows us to see the atomic scale details of surface features on the carbon support where the PtRe particles are located.

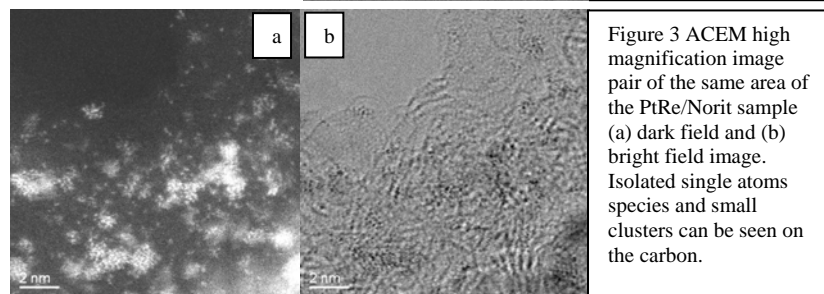
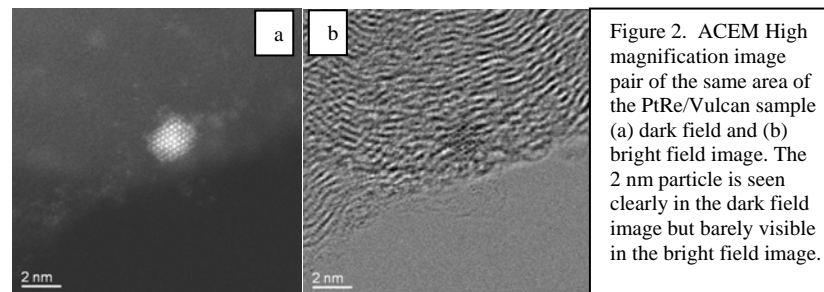


Figure 2 helps us understand the low nucleation density on the spherical particles of Vulcan carbon that exhibits convex surfaces of graphitic layers that expose the basal planes. These basal planes are apparently not conducive to the nucleation of the metal particles. The 2 nm particle has formed at a location that exposes more reactive (edge) sites. Figure 3 shows an image pair from the PtRe/Norit carbon. Here, we can see smaller clusters of the metal phase, and even isolated single atoms. The morphology of the carbon support is very different, with a very low degree of stacking of the graphitic sheets. The metal clusters appear to form in areas where we see concave regions of the support, with isolated atoms on the flat graphene sheets.

Significance

The atomic resolution images provide us with an opportunity to see a dispersed metal phase that is indeed very stable during aqueous phase catalysis. Similar images were obtained from spent catalysts that had been used for one month. The presentation will correlate information from other characterization techniques –EELS, XRD, EXAFS with the reactivity of these catalysts. Understanding the anchoring of metal on carbon and the role of particle size and morphology on conversion of biomass derived reactants will help in the design of new processes for production of chemicals and fuels from biorenewables [2].

References

1. Kunkes, E., et al., Science 322, 417 (2008).
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