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Microstructural Development of Supported $Pt/ZrO_2/SiO_2$ Catalysts: The Effect of ZrO_2 Nanoligands

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Supported platinum metal catalysts play an important role in numerous applications such as hydrogenation, naptha reforming, and in fuel cells. The catalytic performance of supported metal catalysts can be improved via the control of the metal particle size and the metal/support interaction. For some structure sensitive reactions (e.g., the oxidation of H_2 to H_2O in excess H_2 over a Pt catalyst), it has been shown that the catalytic activity can increase with a decrease in the domain size of the catalytically active sites. Previous studies have also revealed that the metal/support interaction can affect the electronic and molecular structure of the supported metal component and thus affect the catalytic properties [1]. It has recently been shown that on "double-supported" metal oxide catalysts, the electronic and molecular structure of the catalytically active sites can also be tuned by the metal oxide nanoligand size, which controls the activity [2]. The present investigation focuses on the microstructural development of supported Pt domains on a nanostructured ZrO_2/SiO_2 substrate.

A series of double-supported $Pt/ZrO_2/SiO_2$ catalysts were prepared by a two step impregnation method in which the ZrO_2 loading on SiO_2 was varied and Pt loading kept constant. The catalysts were subsequently dried, calcined, and analyzed by a variety of electron microscopy techniques. Low electron dose imaging conditions were used during TEM analysis in order to minimize beam damage to the samples. The STEM annular dark field (ADF) images presented have been low-pass filtered to reduce high frequency background noise.

Bright field (BF) TEM images (Figs 1A-C) show that with ZrO_2 loadings below 12wt%, the ZrO_x species are highly dispersed on the SiO_2 surface below monolayer coverage. Complimentary UV-vis spectroscopy analysis revealed a systematic change of supported ZrO_2 domain size from isolated surface species to polymeric surface species for these samples. ZrO_2 nanoparticles with sizes varying between 1.5 and 3nm became visible on the SiO_2 support surface when the ZrO_2 loading exceeded 12wt%. The size and number density of these ZrO_2 nanoparticles increases systematically with increasing ZrO_2 loading. Thus, the ZrO_2 domain size on SiO_2 is a direct function of ZrO_2 loading.

Pt particles having size in the 10-70 nm range were found in catalysts having ZrO_2 loadings below 25wt% as shown by backscattered electron (BSE) SEM images (Figs 2), and the number density of observable Pt particles decreases with increasing ZrO_2 loading. Pt particles were not observed by this technique in the catalysts with ZrO_2 loadings higher than 25%. Correlation of Pt particle number density and ZrO_2 loading suggests that Pt atoms are primarily dispersed on the surface of the ZrO_2 species and that the residual Pt component forms larger particles after saturation of the available ZrO_2 surface sites. This conjecture is supported by STEM-ADF imaging (Fig 3A) from a high ZrO_2 loading catalyst. In this image some brighter spots can be noticed on the 2-3nm ZrO_2 domains having moderate intensity especially in the indicated area (represented in Fig 3B with a temperature scale), and they may well be associated Pt atoms dispersed on the ZrO_2 particle surface. Electron microscopy analyses suggest that Pt atoms have high affinity to sit directly on the surface of ZrO_2 species (as compared to SiO_2) and that Pt dispersion can be tuned by adjusting the ZrO_2 domains size.

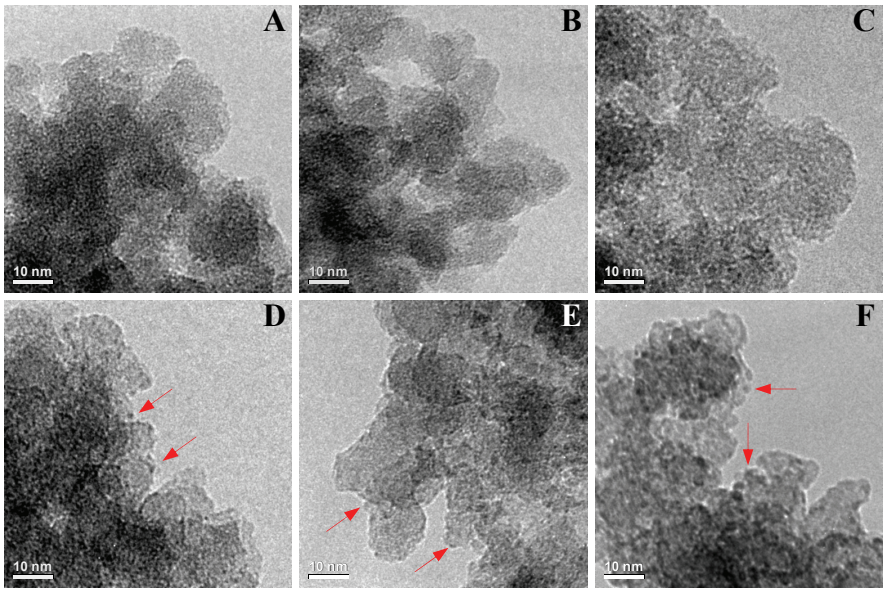

Figure 1. Representative BF TEM images of:
(A) pure SiO_2 support,
(B) 0.1%Pt/1%ZrO_2/SiO_2,
(C) 0.1%Pt/10%ZrO_2/SiO_2,
(D) 0.1%Pt/12%ZrO_2/SiO_2,
(E) 0.1%Pt/15%ZrO_2/SiO_2,
(F) 0.1%Pt/50%ZrO_2/SiO_2.

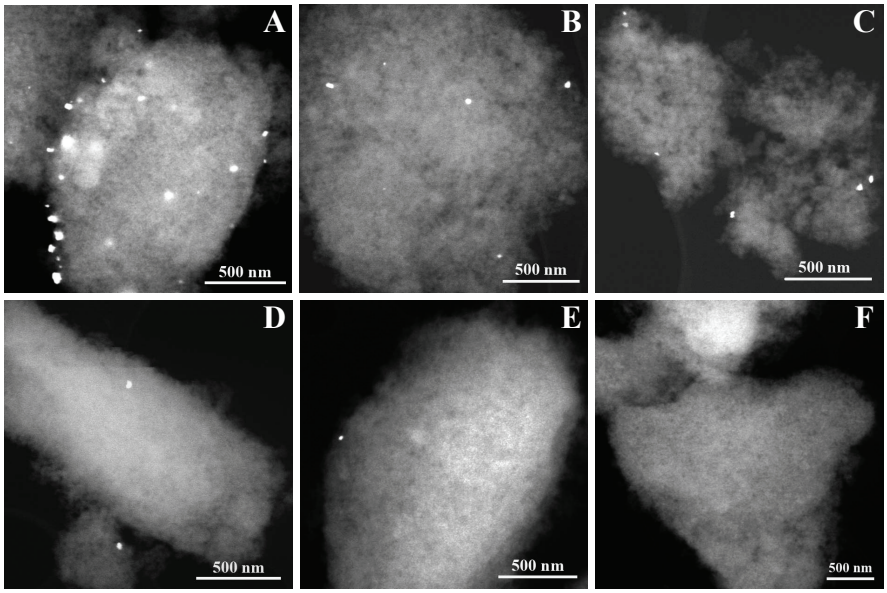

Figure 2. Representative SEM BSE images of:
(A) 0.1%Pt/1%ZrO_2/SiO_2,
(B) 0.1%Pt/10%ZrO_2/SiO_2,
(C) 0.1%Pt/12%ZrO_2/SiO_2,
(D) 0.1%Pt/15%ZrO_2/SiO_2,
(E) 0.1%Pt/20%ZrO_2/SiO_2,
(F) 0.1%Pt/25%ZrO_2/SiO_2.

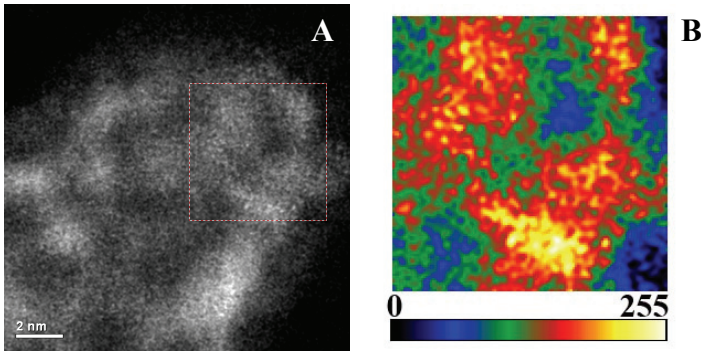

Figure 3. (A) STEM ADF image of the 0.1%Pt/50%ZrO_2/SiO_2 catalyst and (B) a temperature scale ADF image from the area indicated in (A).

References:
[1] W. Lin, A.A. Herzing, C.J. Kiely, and I.E. Wachs, *J. Phys. Chem. C*, **112**, (2008), 5942
[2] E.I. Ross-Medgaarden *et al.*, *J. Am. Chem. Soc.*, **131**, (2009), 680
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