

Influence of ZrO₂ Nanoligands on the Catalytic Performance of Supported Pt/ZrO₂/SiO₂ Catalysts

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Introduction

One of the most important parameters in designing an improved catalyst is the control of the catalytic active site particle size. It has been demonstrated for supported metal catalysis that in certain reactions the particle size of the metal can have a significant effect on the activity of the catalyst [1]. These studies have focused on the size of the active site but no studies have looked at the influence of the domain size of a metal oxide support on the catalytic active site. These metal oxide support nanoligands can change the electronic and molecular structure of the catalytic active site and, thus, influence the catalytic performance.

This study will focus on examining how the domain size of ZrO₂ nanoligands can affect the activity of Pt active sites. *In situ* Raman and UV-vis spectroscopy and electron microscopy characterization were used to determine the electron and molecular structures of the catalysts. The reactivity of the supported Pt phase was chemically probed with CH₃OH oxidation using both steady-state and CH₃OH-temperature programmed surface reaction (TPSR) spectroscopy.

Materials and Methods

The catalysts were synthesized by first impregnating zirconium tert-butoxide, Zr[OC(CH₃)₃]₄, onto the SiO₂ support via the incipient wetness impregnation. In the second step, aqueous platinum tetraammine nitrate, Pt(NH₃)₄(NO₃)₂, was impregnated onto the ZrO₂/SiO₂ to form the final double-supported Pt/ZrO₂/SiO₂ catalyst. The ZrO₂ loading was varied between 1% and 50% and the Pt loading was maintained constant at 0.1%. *In situ* Raman spectroscopy was performed on a single-stage Horiba-Jobin Yvon Lab Ram-HR Raman spectrometer with a 15X objective using UV laser excitation (325 nm). UV-vis spectroscopy was performed on a Varian Cary 5E UV-vis spectrophotometer employing the integration sphere diffuse reflectance attachment (Harrick Praying Mantis Attachment, DRA-2). Scanning electron microscopy (SEM) backscattered electron (BSE) images, giving Z-contrast information, were collected on a Hitachi 4300LV SEM equipped with a STEM holder. CH₃OH TPSR spectroscopy was performed Altamira temperature programmed system (AMI-200) coupled with an online mass spectrometer (Dycor Dymaxion DME200MS). The steady-state CH₃OH reaction was carried out at 150 °C at atmospheric pressure. The reactant gas contained CH₃OH/O₂/He composition (%) 7/14/79 with a total flow rate of ~100 ml/min. The products were analyzed using an on-line gas chromatograph (HP-5890 series II).

Results and Discussion

Electron microscopy showed that the domain size of the ZrO₂ increased in size from 1.5 – 3 nm as the ZrO₂ loading was increased. It also reveals that Pt nanoparticles in the size range 10-70 nm were found in samples with less than 25%ZrO₂ with a greater particle density in lower loadings as shown in Fig 1. These particles are not found at 25% ZrO₂ and higher loadings and Pt exists as a highly dispersed surface species.

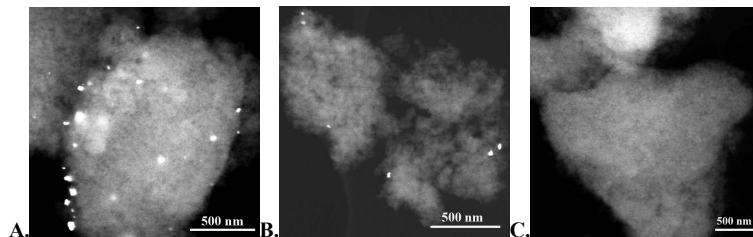


Figure 1. Representative SEM BSE images of (A) 0.1%Pt/1%ZrO₂/SiO₂, (B) 0.1%Pt/12%ZrO₂/SiO₂, (C) 0.1%Pt/25%ZrO₂/SiO₂.

Kinetic parameters were calculated from the CH₃OH TPSR experiments and the k_{rds} values are plotted as a function of ZrO₂ loading in Fig 2. A greater activity was seen within samples with a higher density of Pt nanoparticles.

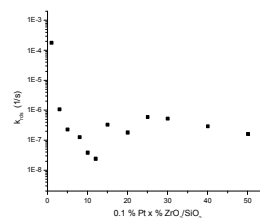


Figure 2. k_{rds} as a function of % ZrO₂ loading.

Significance

The domain size of the ZrO₂ was successfully varied on the SiO₂ support. The activity of the catalysts was found to increase with the number density of the Pt NPs, which also corresponds to lower ZrO₂ domain size. Thus, the reactivity and domain size of the Pt catalytic active sites could be tuned by the domain size of the ZrO₂ nanoligands.

References

1. Boudart, M., *Kinetics of Catalytic Processes*. Princeton: Princeton University Press, 1984.