

Selective Oxidation of Ethanol over Zeolite-Supported Gold Catalysts

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Introduction

Selective oxidation of alcohols to aldehydes, acids and esters is required in the production of numerous products in the chemical industry. Some current commercial technologies use non-catalytic stoichiometric reactions with oxidants, such as chromate or permanganate, which are expensive and toxic. It is, therefore, highly desirable for green chemistry and improved efficiency to replace these current technologies with catalytic processes using gas-phase oxygen as the oxidant. In this work, Au/ZSM-5 catalysts were synthesized, characterized and tested for ethanol selective oxidation. Effects of the Au loading, zeolite acidity as well as proximity of Au and zeolite acid sites were studied with X-ray diffraction (XRD), transmission electron microscopy (TEM), diffuse reflectance ultraviolet-visible spectroscopy (UV-vis DRS), in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and density functional theory (DFT) calculations.

Materials and Methods

Two sets of supported Au catalysts were synthesized. In the first set, the support was varied while the Au loading was kept constant at 1 wt %. The Si/Al ratio of the ZSM-5 support was varied from 15 to 140. In addition, S-1 silicalite and amorphous SiO₂ were used as supports. In the second set, the Au loading was varied from 0.25 to 2 wt % while the support was kept constant: ZSM-5 (Si/Al=15). The Au catalysts were tested in a flow reactor with 30 mol % O₂/He and ethanol, which was mixed with the gas flow and vaporized in a preheater. The partial pressure of ethanol was below its saturation pressure. The reaction products were analyzed with online sampling using a gas chromatograph. DFT calculations with clusters and periodic unit-cell structures using the DMol³ DFT code in Materials Studio 2017 software by Dassault Systèmes BIOVIA were employed for determining the preferential anchoring sites and structures of Au on the ZSM-5 support.

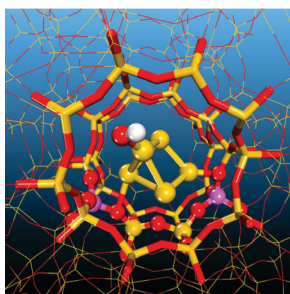


Figure 1. DFT model for an Au₅ cluster anchored on a double Al-atom site in the ZSM-5 framework.

Results and Discussion

The reaction products were ethyl acetate, acetaldehyde and acetic acid. Undesirable overoxidation reactions to CO and CO₂ were completely avoided. The ethanol reaction rate at 333 K increased by a factor of 3 when 1 wt % Au was deposited on S-1 silicalite compared to the same Au loading on an amorphous SiO₂ support. This effect was attributed to a better

dispersion of Au particles on the MFI structure of S-1 based on TEM and XRD measurements. When the same 1 wt % Au was deposited on ZSM-5 (Si/Al=15, the same MFI structure, Figure 1), the reaction rate increased to 58 mol ethanol/mol of Au/h, by a factor of 26 higher than that for 1 wt % Au/SiO₂. The presence of Al sites in the MFI structure, thus, dramatically increased the catalytic activity. Moreover, the catalytic activity declined with decreasing concentration of framework Al sites (higher Si/Al ratios in Figure 2a). This effect can be due to either the activity of Al sites by themselves or synergy between Al and Au sites. Reaction testing results of physical mixtures with different ratios of 1 wt % Au/S-1 and ZSM-5 (Si/Al=15) without Au in Figure 2b demonstrate that the mere presence of zeolite Al sites does not change the reaction rate. Therefore, the Al sites are not active by themselves, and the synergistic effect requires proximity of Au and Al sites. In addition to the increased activity, 1 wt % Au/ZSM-5 exhibited better stability than the SiO₂-supported catalyst.

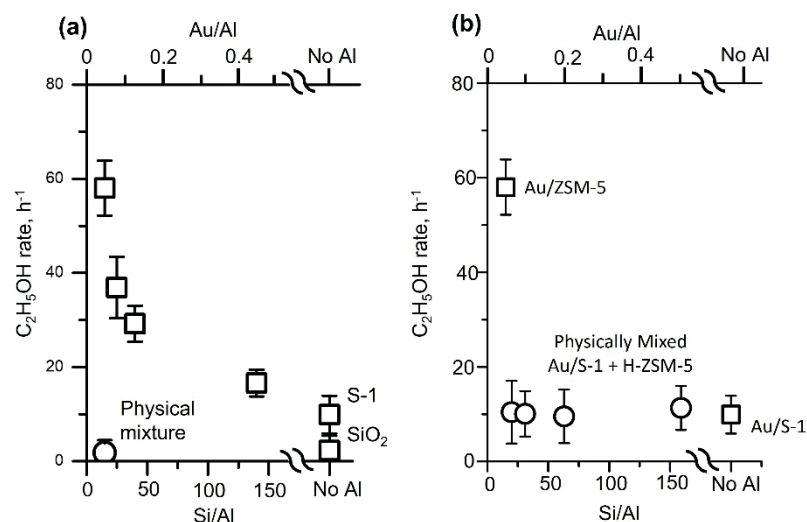


Figure 2. Effects of Si/Al ratios for (a) 1 wt % Au/ZSM-5 (Si/Al=15-140 plus S-1), 1 wt % Au/SiO₂ is shown for comparison and (b) physical mixtures of 1 wt % Au/S-1 and ZSM-5 (Si/Al=15) without Au (□ - catalysts prepared by incipient wetness impregnation of Au, ○ - physical mixtures). 333 K, atmospheric pressure.

Significance

Au/ZSM-5 catalysts are active, selective and stable in ethanol selective oxidation. The obtained information on the effects of the Au loading and Si/Al ratio as well as the synergistic effects between Au and Al zeolite sites will be useful in the development of more efficient catalysts for selective oxidation of ethanol and other primary alcohols.