

Selective Desulfurization of Hydrocarbon Fuels by Ag/TiO₂: Preparation, Performance and Characterization

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Introduction

Selective sorption of sulfur containing species from complex liquid fuels can be used to protect downstream components sensitive to sulfur poisoning such as fuel cells and associated reformation catalysts. Potential benefits of this approach include the opportunity to reduce the weight and volume of fuel processing systems while reducing the processing severity and hydrogen consumption normally associated with hydrosulfurization. Several liquid phase adsorbents have been reported to be effective desulfurization agents[1-3]. We report here the preparation, performance, characterization, mechanistic discrimination, and facile regeneration of a family of Ag/TiO₂ selective adsorbents used in conjunction with JP-5 and a variety of model fuel mixtures. Efforts are undertaken to determine the highly selective nature and competitive adsorption mechanism of Ag/TiO₂ which strongly adsorbs one sulfur-containing heterocycle (to an equilibrium concentration below 1 ppmw) per two silver atoms even in the presence of a 160-fold excess of other aromatics found in the fuel (i.e., JP-5).

Materials and Methods

Ag/TiO₂ sorbents were prepared by incipient wetness using AgNO₃ precursors. Both JP-5 fuel (1172 ppmw sulfur) and model fuel mixtures of various sulfur heterocycles in n-octane were studied. Tests were conducted in a packed bed configuration at ambient temperature and pressure. Sulfur concentrations at the bed outlet were determined by total sulfur analysis to 20 ppbw and by species specific gas chromatography (a sulfur selective pulsed flame photometric detector) to 50 ppbw. Sorbents were characterized by X-Ray Photoelectron Spectroscopy (XPS) and Electron Spin Resonance (ESR). Sulfur removal, sorbent regeneration, Ag dispersion and redox behavior were studied by Temperature Programmed Desorption (TPD), Temperature Programmed Oxidation/Reduction (TPO/TPR) and pulsed and static oxygen chemisorption. XRD was inconclusive. Competitive adsorption and adsorption/reaction models were evaluated in conjunction with measured heats of adsorption and observed surface reaction behavior.

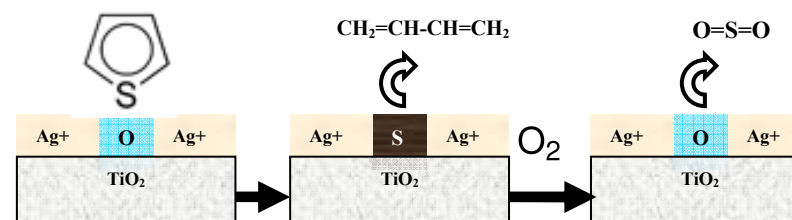
Results and Discussion

XPS spectra show Ag, Ti, and O, indicating complete decomposition of the Ag precursor. The oxidation state of Ag was found by XPS via the Auger parameter[4-5], and by ESR[6], and is Ag⁺. Minor amounts of Ag are present as: Ag²⁺ and Ag_{2n+1}⁺ or Ag_{2n+1}⁰. A maximum sulfur saturation capacity of 7 mg/g from JP-5 occurred at an intermediate loading of 4 wt% Ag/TiO₂. Oxygen chemisorption and TPO/TPR also indicate the presence of highly dispersed Ag⁺ as the active component. When tested with model fuels containing up to 3500

ppmw of various sulfur heterocycles in n-octane, saturation capacity increased to 9 mg/g. Typical breakthrough characteristics do not exhibit significant loss in capacity or selectivity following multiple regenerations in flowing air. Variations in sulfur saturation capacity between JP-5 (contains >200 distinct sulfur species) and model fuels containing selected sulfur heterocycles, as well as the shapes of their respective breakthrough curves, were correlated to steric hindrances associated with specific heterocycles as well as the sequential competitive adsorption/desorption events occurring within a bed as it dynamically reaches maximum sulfur saturation/retention. Experiments with model fuels show that adsorption, desorption, and surface reaction all depend on molecular structure. Thiophene shows molecular desorption at ~370 K, C-S bond scission[7] at ~370-500 K (desorption of C₄H₆), and SO₂ emission at >700 K in O₂. Dibenzothiophene “chemisorbs”, and releases SO₂ at >700 K, via oxidation of the surface sulfide.

Significance

High sulfur heterocycle capacity and selectivity in the presence of other aromatics is noteworthy especially as it occurs with a stoichiometry of one heterocycle per two surface Ag atoms. Facile regenerability in air is also beneficial. Other attributes include large particle sizes and large pore sizes resulting in low pressure drop, good intraparticle transport/effectiveness, easy bed packing, and scalable preparation and application.



Scheme 1. Proposed desulfurization and regeneration mechanisms for Ag/TiO₂.

References

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