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Preparation And Characterization Of Nanodispersed Ag-Based Sorbent For Removal Of Sulfur From Logistic Fuels

The Ag/TiO₂-based adsorbent for selective removal of sulfur from logistic fuels was prepared by incipient wetness impregnation of titania with AgNO₃, with the subsequent calcination, and characterized. The survey XPS spectra obtained with the “calcined” sorbents with typical nominal loadings from 0.5% to 8% wt. Ag show the similar features. The following elements were identified in the specimens: Ag, Ti, O and spurious carbon as expected. No residual nitrogen was detected in the calcined samples, thus indicating that complete decomposition of AgNO₃ deposited onto the sample during the incipient wet impregnation step does occur during the calcination step. To determine the valence state of Ag in the calcined samples of the sorbent, XPS line scans for Ag were performed and standard curve fitting procedures executed. Binding energy of the XPS peaks of Ag, including the spectroscopically most important 3d_{3/2} and 3d_{5/2} lines, is known to be insensitive to the valence state and coordination environment of Ag. Therefore, the Auger parameter was used to determine the oxidation state of Ag: Ag metal vs Ag⁺. The Auger parameter α is known to be especially useful for processing XPS spectra of the insulating samples e.g. titania-supported sorbents, since its value is independent on the electrostatic charging of the specimens. The Ag Auger lines M₄N₄₅N₄₅ and M₅N₄₅N₄₅ lines and XPS lines 3d_{3/2} and 3d_{5/2} were used to calculate the Auger parameter for Ag. Moreover, model sorbents Ag/TiO₂ were prepared, containing only Ag⁺ (freshly impregnated and dried specimen) and only Ag metal (calcined specimen reduced in hydrogen). Auger parameter α was calculated to find the oxidation state of Ag in the dried, calcined and reduced samples. The dried samples have the smallest value of α , the reduced samples – the highest, and the calcined samples have the intermediate value. Literature indicates that metal Ag shows the highest value of α , while Ag⁺ shows the smallest value. Thus, the obtained data indicate that in the calcined samples that are commonly used for desulfurization, significant fraction of Ag is present as metal silver. Another indication of the presence of metal silver in the “calcined” samples is their low aptitude towards electrostatic charging under XPS conditions. “Dried” samples showed significant charging (up to 3 eV), while both the “reduced” and “calcined” samples showed rather small and similar charging (less than 1 eV). Dispersion of silver on titania was studied by XRD and SEM, and occurs at nanoscopic dimensions. Studies of adsorption and desorption pathways of several sulfur-containing polyaromatic hydrocarbon (S-PAH) molecules typically present in logistic fuels – Thiophene (T), Benzothiophene (BT) and Dibenzothiophene (DBT) - on the surface of the sorbent was performed by Temperature-Programmed Desorption (TPD) and Temperature-Programmed Reaction Spectroscopy (TPRS). The adsorption of selected S-PAHs onto the sorbent was carried out from their solutions in octane that represent chemical composition of sulfur-containing liquid fuels. Next, the sorbent was excessively rinsed with octane, to remove the excess of S-PAHs, either entrapped in the pores of the sorbent or weakly bound to the surface sites. The sorbent was then dried, and studied by the TPD

and TPRS in presence of oxygen under High Vacuum (HV) conditions. The data show that desorption pathways proceed differently for S-PAHs molecules with different molecular structure. For thiophene (T), significant fraction of adsorbed molecules binds reversibly to the surface sites, and desorbs without decomposition (“molecular desorption”) at about 350 K. The rest of adsorbed thiophene reacts chemically with the surface, forming products of C-S bond scission (butadiene) and surface-supported silver sulfide. The presence of the latter is found due to high-temperature TPRS band of sulfur dioxide SO₂ that is formed from silver sulfide in presence of molecular oxygen. In contrast, products of molecular desorption were not identified for DBT, yet C-S bond scission products (biphenyl) were found. Upon TPRS in presence of oxygen, strong SO₂ desorption band at ~725 K suggests that in case of DBT, chemisorption pathway with formation of titania-supported silver sulfide takes place.