

Interaction of silver atoms with ethylene in Ag-SAPO-11 molecular sieve

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The studies on the interaction between metal cations or small metal clusters and adsorbed molecules are essential to understand the mechanism of catalytic reactions on metal active sites in heterogeneous systems. The interaction of silver, copper or nickel with ethylene in inert gas matrices under cryogenic conditions has been studied by different techniques for many years. Their ethylene complexes show a single intense adsorption in visible region band and less pronounced UV bands¹⁻³.

Based on EPR results the formation of silver – ethylene complexes in inert gas matrices has been reported. In argon matrix Kasai^{4,5} proposed the formation of $\text{Ag}(\text{C}_2\text{H}_4)_n$, $n = (1, 2)$ complexes. In frozen hydrocarbon matrices at 77 K Howard⁶ identified complexes of silver and its clusters with ethylene with various stoichiometry such as $\text{Ag}(\text{C}_2\text{H}_4)$, $\text{Ag}(\text{C}_2\text{H}_4)_2$, $\text{Ag}_3(\text{C}_2\text{H}_4)$ and $\text{Ag}_7(\text{C}_2\text{H}_4)_n$, $n \geq 1$. The formation of such complexes in real catalytic systems has not been reported till now.

We examined the paramagnetic species formed in Ag-SAPO-11 molecular sieve exposed to C_2H_4 and γ -irradiated at 77 K. At 100 K the EPR spectra of silver atoms, $^{107}\text{Ag}^0$: ($A_{\text{iso}} = 57,9$ mT and $^{109}\text{Ag}^0$: $A_{\text{iso}} = 66,9$ mT) and ethyl radicals $^{\bullet}\text{C}_2\text{H}_5$: ($A_{\perp}(2\text{H}_{\alpha}) = 2,01$ mT, $A_{\parallel}(2\text{H}_{\alpha}) = 2,87$ mT and $A_{\perp}(3\text{H}_{\beta}) = 2,68$ mT, $A_{\parallel}(3\text{H}_{\beta}) = 2,80$ mT) have been recorded. The anisotropy of $^{\bullet}\text{C}_2\text{H}_5$ hyperfine splitting indicates that radicals trapped inside SAPO-11 channels are unable to rotate freely. Above 270 K those signals decay completely and a new spectrum composed of six lines is recorded. It was simulated with the following EPR parameters: $g_x = 2,004$, $g_y = 1,977$, $g_z = 2,003$; 1Ag : $A_x = 0,9$ mT, $A_y = 2,34$ mT, $A_z = 2,19$ mT, 8H : $A_{\text{iso}} = 0,3$ mT, and was assigned to $\text{Ag}^0(\text{C}_2\text{H}_4)_2$ complex. The „gas phase” geometries of $\text{Ag}(\text{C}_2\text{H}_4)$ and $\text{Ag}(\text{C}_2\text{H}_4)_2$ complexes, and respective hyperfine coupling constants were calculated applying DFT quantum chemical methods. The hyperfine coupling constants calculated for $\text{Ag}(\text{C}_2\text{H}_4)_2$ complex of D_{2h} symmetry are in very good agreement with those obtained experimentally. The ligands are located at opposite sides of Ag^0 adopting an eclipsed parallel conformation.

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