Kinetic study of the hydrodechlorination reaction for $CH_{4-x}Cl_x$ (x=1-4) and $CF_{4-x}Cl_x$ (x=1-3) compounds on Pd/Carbon catalyst

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The hydrodechlorination reaction kinetics on $CH_{4-x}Cl_x$ (x=1-4) and $CF_{4-x}Cl_x$ (x=1-3) compounds was measured on Pd/carbon catalysts. It was found that the hydrodechlorination reaction rates correlated with the value of the C-Cl bond energy. The C-Cl bond energy could be used to predict the relative hydrodechlorination reaction rates of these compounds, and the theoretical prediction agreed well with experimental results. It was thus concluded that the first C-Cl bond scission on the surface is the rate determining step of the hydrodechlorination reaction. The observed hydrodechlorination reaction kinetics of the seven compounds supports a previously proposed Langmuir-Hinshelwood type of hydrodechlorination reaction mechanism. That is, (1) gas phase H_2 and HCl are in equilibrium with surface H and Cl; (2) adsorbed Cl is the most abundant surface intermediate and (3) irreversible scission of the first C-Cl bond is the rate-determining step. The overall hydrodechlorination reaction rate for these series of compounds can be written as $r=k'[CFC]/(1+K'[HCl]/[H_2]^{0.5})$. Based on this model, the activation energy for the hydrodechlorination rate determining step for these compounds was calculated and it was found out they were linearly related to the bond strength of the first C-Cl bond to break during reaction. During hydrodechlorination with D_2 the C-H bond exchanged with deuterium in only 2%, 6% and 9% of products when the reactants were CH_3Cl, CH_2Cl_2 and $CHCl_3$ respectively. Surface DFT (density functional theory) calculations were performed to study the reaction energetics of the elementary steps of hydrodechlorination reaction, such as adsorption of CFC species on catalyst surface, C-Cl and C-F bond dissociation, and C-H bond formation. The calculation results were used to identify the hydrodechlorination reaction rate limiting step, to explain the product distribution of $CF_{4-x}Cl_x$ (x=1-3) compounds, and to explore the reason for the structure insensitivity of hydrodechlorination reaction.