

Understanding the selective dechlorination during adsorption of chlorinated ethylenes

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Abstract: Dissociative adsorption of chlorinated ethylenes, particularly the different adsorption patterns over the Pd, Cu and CrOx-Y zeolite, is discussed with the aid of molecular orbital calculation. In this work, the dechlorination mechanism is proposed to begin with 1) dissociative Cl-metal interaction through electron donation from Cl or 2) associative adsorption through C or C=C.

Keywords: dechlorination, selective adsorption, perchloroethylene, trichloroethylene, hydrofluorocarbon

1. Introduction

The global market size of chlorinated olefins, perchloroethylene (PCE) and trichloroethylene (TCE), has been increasing and is expected to expand for another decade by 1% annually largely due to the solvent applications whilst their health and environmental issues have been receiving significant attention.¹ Thus, tremendous efforts have been devoted to establish methods to efficiently eliminate chloro-olefins in particular, PCE and TCE. A common method is thermal treatment.²⁻⁵ Among them, oxidation of chlorinated olefins are feasible, however, potential safety issue is associated to generate toxic substances, such as phosgene, in the presence of water.⁴ With consideration of safety aspect, selective chlorine removal from chlorinated carbons is the most ideal, but only a few studies were reported on the surface of metal (Pd,⁶⁻⁸ Cu,⁷ Ni⁹ and Fe¹⁰), metal alloy,¹¹⁻¹³ and oxide (CrOx,^{8, 14} Al₂O₃⁸). In this work, the molecular orbital calculation was unitized to explain the initial step of selective chlorine removal which is more focused on dissociative adsorption with the previously reported results.

2. Theoretical

Computer-aided molecular orbital, bond order and electron density calculations of chlorinated ethylene compounds were performed using a semi-empirical quantum chemistry method (the PM3 method) in computer-aided chemistry (CACHe) molecular orbital package (MOPAC) 2000, version 1.34. The PM3 method determines both the optimum geometry and electronic properties of molecules using the PM3 semi-empirical Hamiltonians.

3. Results and discussion

The initial step of adsorption of chlorinated ethylene was discussed with the difference of C-Cl stretching frequency between gas phase and adsorbed chlorinated olefins from the previously reported IR spectroscopy results summarized in Table 1. The C-Cl stretching band of trans-DCE over Pd and Cu shifted from 817 cm⁻¹ to 808 or 814 cm⁻¹, respectively at the low temperature. This indicates weakening of the C-Cl bonds through the Cl-metal interaction in adsorption. Additionally, the adsorption of trans-DCE on Pd occurred through π -bond of DCE at the elevated temperature. This suggests that an adsorption configuration of chlorinated ethylenes differ particularly over Pd surface at the different temperature. On the other hand, the stronger shift of the C=C stretching vibration of PEC and DCE over the CrOx on Y zeolite was observed in comparison with the shift of C-Cl stretching. The stronger shift of the C=C stretching is ascribed as the cause of localization of electrons on C=C bond of PEC and DCE.

Combination of calculated molecular orbitals, bond order, and electron density of each atom of chlorinated ethylenes with results of spectroscopy explains the different reactivity of PCE, TCE and DCE with the individual active site of catalysts. In this work, interaction of Cl and surface was discussed as the initial step in dechlorination.

Table 1. Reported $\nu(\text{C-Cl})$ vibrational stretching frequency of perchloroethylene, trichloroethylene and dichloroethylene

Adsorbate	Gas Phase	Adsorbent		
		Pd ¹⁵	Cu ¹⁶⁻¹⁷	CrOx-Y ¹⁴
PCE	916 ¹⁴			916 at 298K
				912 at 403K
	781 ¹⁴			779 at 298K
				777 at 403K
TCE	939 ¹¹			943 at 298K
	941 ¹⁸			943 at 373K
trans-DCE	817 ^{16, 19}	808 at 85K	814 at 85K	
		837 at 133K	815 at 408K	
cis-DCE	610 ¹⁴			610 at 298K
	793 ¹⁴			793 at 298K

4. Conclusions

Molecular orbital calculation of chlorinated ethylenes were utilized to discuss the initial step of adsorption over Pd, Cu and Cr-Y zeolite with previously reported IR spectroscopy results. Due to the strong electron donation capability of Cl, chlorinated ethylenes dissociatively adsorb on particularly electron deficient site, Pd and Cu. Over CrOx, chlorinated ethylenes adsorb through its C or C=C bonding with surface oxygen over the oxide surface. With understanding of active site of catalysts, an ideal adsorbent selection can be made for the selective dechlorination process.

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