In situ FTIR study of *o*-DCB interaction over Pd-Co loaded mordenite and sulfated zirconia

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Introduction

Catalytic oxidation is considered one of the best methods for the control of polychlorinated dibenzodioxin and furan (PCDD/F) emissions from stationary sources [1,2].V_2O_5/TiO_2-based catalysts are commercially employed in most incinerators for the combined destruction of such PCDD/F compounds and NOx [2,3]. In situ FTIR studies have been used to explore the reactant-catalyst interactions and to develop a basic understanding of the surface chemistry involved in PCDD/F oxidation on V_2O_5/TiO_2 [2]. Due to the high toxicity of the original compounds, chlorinated benzenes and phenols, and most commonly 1,2-dichlorobenzene (*o*-DCB), have been employed as models in these studies [1,2,4]. Recently, additional inorganic materials, including H-MOR and H-ZSM5 zeolites, have been also investigated for the adsorption and destruction of organochlorinated and dibenzodioxin-type of compounds [1,3,4]. The concentration and strength of surface hydroxyl groups, the amount of Lewis acid sites and diffusional pore effects have been found in these cases to affect the adsorption and reaction processes [2,4]. Additionally, Pd and Co-containing zeolites [5] and sulfated zirconia [6] have been found to be promising catalysts for the reduction of NOx with methane. In this work we report the results of in situ FTIR studies of the adsorption and oxidation of *o*-DCB over Pd and Co-containing mordenite and sulfated zirconia with the goal of exploring the nature and properties of the surface active sites.

Materials and Methods

Co-HMOR was prepared by ion exchange of NH_4-MOR according to the method described elsewhere [5]. Sulfated zirconia and Co-SZ were synthesized following a reported procedure [6] in which cobalt was added during the gelation step. Pd-containing samples were obtained by impregnation of Co-HMOR or Co-SZ samples with an aqueous solution containing 0.0049 g of $Pd(NH_3)_4.Cl_2$ H_2O to obtain a Pd loading of approximately 0.2 wt-%. After drying at 60 °C, catalyst samples were heated at 500 °C for 4 h in flowing helium. Catalyst samples were characterized by XRD, TGA, BET and TPR. In situ FTIR spectra were collected with a Nicolet 740 spectrometer equipped with a MCT-B detector cooled by liquid nitrogen. A homemade flow cell was used for the in situ measurements and approximately 30 mg of catalyst was placed into the sample cell in the form of a self-supported wafer. Transmission spectra were collected in the single-beam mode by recording 128 scans and a resolution of 4 cm^{-1}. Before each experiment, samples were pretreated in flowing helium at 360 °C for 2 h. The cell was then cooled down to the desired temperature in flowing He. Adsorption and reaction studies were conducted by exposing the catalyst samples to a stream of approximately 500 ppm *o*-DCB or 500 ppm *o*-DCB/8% O_2 in He. In situ FTIR spectra were collected at different time intervals until a steady state was reached. Finally, the cell was flushed with He and/or an 8% O_2/He mixture to examine the strength of adsorption and the reactivity of the different surface species formed.

Results and Discussion

The adsorption of *o*-DCB over SZ, Co-SZ, Pd/Co-SZ, Co-HMOR and Pd/Co-HMOR catalysts at 250 °C resulted in the formation of a well defined strong FTIR band centered at approximately 1668 cm^{-1} (Figure 1). This band is neither removed by flushing with a He stream or by increasing temperature to 300 °C. Since it is not observed in the FTIR spectra of HZSM-5, H-MOR and SiO_2, this band can be assigned to strongly adsorbed *o*-DCB on Lewis acid sites. On Pd-containing catalysts the 1668 cm^{-1} band slowly decreases upon flushing He and faster in flowing oxygen. In the later case reaction between the adsorbed species and O_2 leads to partial oxidation products, as indicated by the ap-pearance of additional bands at 1581, 1576, 1532 1453 and 1348 cm^{-1}; that can be assigned to a mixture of oxygenate species.

The strong band at 1668 cm^{-1} was not observed on Co-HMOR and Pd/Co-HMOR samples during reaction conditions (*o*-DCB/O_2 mixture flowing over the sample). Additionally, water formation was observed under these conditions, which may be associated with loss of Lewis acid sites and correspondingly the generation of Brønsted acid sites. Such a hypothesis was further supported by an increase in the intensity of the, IR bands in the 3800-3500 cm^{-1} region associated with bridging hydroxyl groups .

Significance

Overall, the results of the FTIR studies suggest a common strong interaction between adsorbed *o*-DCB and the Lewis acid sites of SZ and Co-HMOR materials. The adsorbed species formed can further react towards partial oxidation products. Such a reaction is faster in the presence of Pd and gas-phase oxygen.

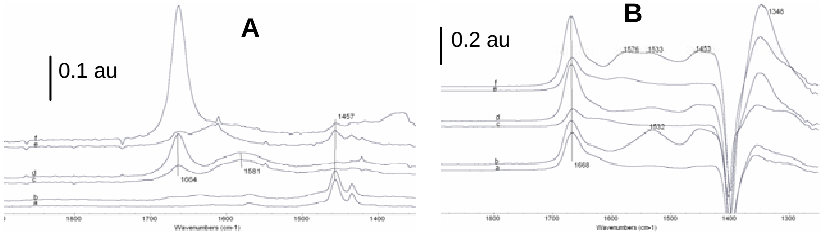

Figure 1. . In situ FTIR spectra collected at 250 °C after flowing 500 ppm *o*-DCB/He stream on **(A)** (a) 10 and (b) 120 min on H-MOR, (c) 10 and (d) 120 min on Pd/Co-HMOR, (e) 10 and (f) 120 min on Co-HMOR; **(B)** (a) 10 and (b) 120 min on SZ, (c) 10 and (d) 120 min on Co-SZ, (e) 10 and (f) 120 min on Pd/Co-SZ

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