

Catalytic destruction of polychlorinated organics over commercial SCR catalysts

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Introduction

Dioxins and other chlorinated aromatic compounds are emitted in small quantities from municipal and medical waste incinerators. Although these emissions can be partially reduced by the modification of the burners, such a strategy cannot always satisfy the strict emission limits that are in place in several countries [1]. Recently much attention has focused on the catalytic destruction of these compounds as an effective method for their removal from the exhaust stream [2-4]. Although several catalysts are marketed commercially for these applications, the understanding of the surface chemistry taking place on these catalysts is rather limited. Because of the high toxicity of dioxins, model compounds are frequently utilized in laboratory studies [5-7]. In our previous work [8,9] we used 1,2-dichlorobenzene as such a model compound. Even more structurally similar to the polychlorinated dibenzodioxins and furans is the 2,4,6-trichlorophenol, since in addition to the chlorine it also contains an oxygen atom. Using this compound as a model for the catalytic destruction of PCDD/PCDFs we anticipate obtaining more accurate information about the reaction(s) that actually take place on the catalyst.

Vanadia/titania based catalysts represent the state-of-the-art for NO_x control and are also known to be active for PCDD/PCDFs destruction [2]. In the present study we examine the catalytic destruction of 2,4,6-trichlorophenol over commercial vanadia-tungsta/titania SCR catalysts at a low temperature range (i.e. 180-250°C). This study focuses on the initial adsorption/desorption characteristics of these catalysts, their steady state activity, and the effect of water vapor on in the catalytic behavior.

Experimental

The two catalysts used in this work are commercial vanadia-tungsta/titania and vanadia/titania SCR catalysts with two different vanadia loadings. The catalyst A (CatA) has the higher, and catalyst B (CatB) has the lower amount of vanadia. Their surface areas are <100m²g.

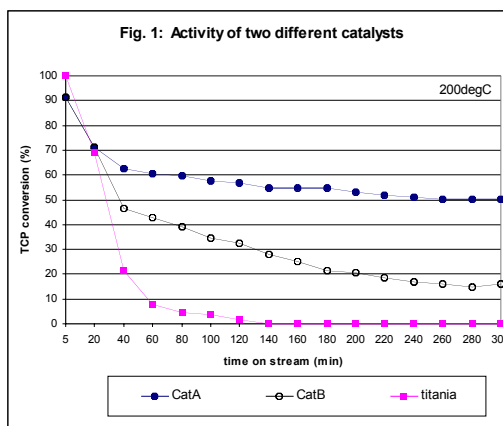
Catalytic measurements were carried out in a single-pass fixed bed reactor, filled with 15mg or 30mg of catalyst diluted in 45 or 30 mg of quartz, respectively. The total flow rate over the catalyst was equal to 200ml/min. 2,4,6-trichlorophenol (TCP) was obtained from Aldrich Chemicals and was introduced to the reactor feed by passage of helium through a saturator maintained at 70°C. The saturator stream was then mixed with an O₂/He stream to obtain the following reacting gas mixture composition: TCP – 12ppm, O₂ – 5%, balance He. In some experiments water vapor was also introduced into the reactor (3.5-40vol%) using a syringe pump.

The reaction products were analyzed on-line using a gas chromatograph (GC) model 910 manufactured by Buck Scientific equipped with a flame ionization detector (FID). The column used for separation of the products was carbograph 3CW, and was 20cm long.

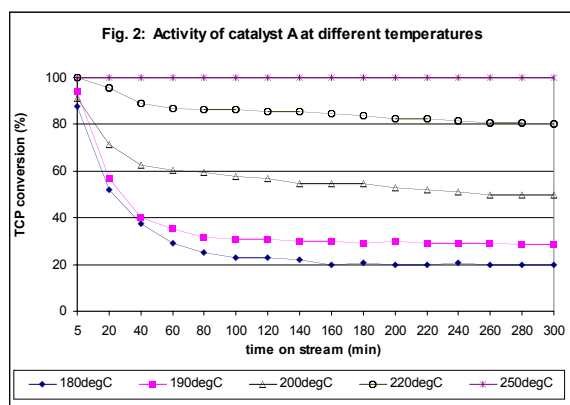
Results and Discussion

The activity of the vanadia-tungsta/titania catalysts tested, expressed as percent removal of TCP from the reacting mixture at 200°C is shown as a function of time on stream in Fig.1. The removal capacity of the pure titania support is also shown in the same figure. The results show that at steady state the catalyst with higher vanadia content (CatA) exhibits a higher activity for the destruction of TCP when compared to the catalyst with the vanadia content (CatB).

The same catalysts exhibited a lower activity for the destruction of o-DCB. We attribute this effect to the presence of phenol group in the benzene ring, may weaken the adjacent carbon-bond. In both cases, an initial drop in TCP removal capacity was observed few hours were required before state was reached. The titania support similar behavior, initially removing a significant fraction of the TCP, but after two hours on stream a zero activity steady state is reached. This transient behavior can be attributed to adsorption of TCP on the catalyst. At steady state the surface is saturated with reactants and/or products.



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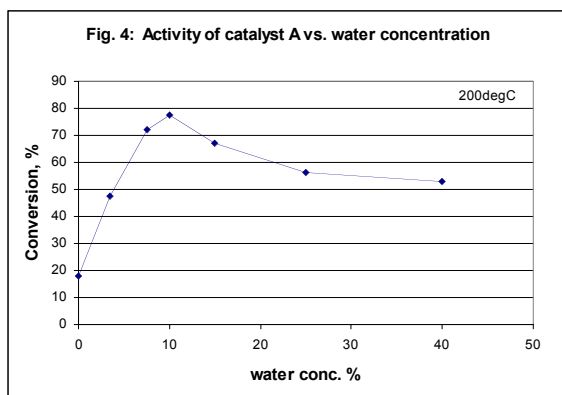
The transient behavior observed during experiments performed at different temperatures (Fig. 2), supports this hypothesis. At higher temperatures the drop of TCP removal capacity during the transient phase is lower, consistent with anticipated lower adsorption capacity. Similar results were also obtained with the titania support saturated faster at 250°C rather than at 200°C. These observations are in agreement with results reported by Weber et al [2], which suggest that significant amount of polychlorinated

aromatic compounds can adsorb on the surface of vanadia/titania catalyst in the temperature range of interest.

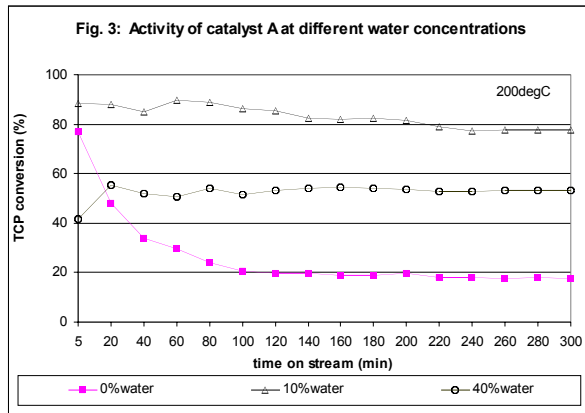
To further demonstrate that initial TCP removal capacity is a result of adsorption on the catalyst, we attempted to reverse the transient behavior, by treating the steady state catalyst in air as well as helium for two hours at 200 and 250°C. The results indicate that the initial TCP removal capacity is restored as the result of these treatments and the same transient behavior is once again observed. This process was faster when air was used at elevated temperatures, suggesting that the adsorbed species can react with oxygen faster than they desorb.

The activity of the two catalysts examined for the destruction of is strongly affected by the presence of water vapor. In general the presence of water results in an increase in the activity of the catalysts (Fig. 3). Furthermore, the transient behavior is eliminated and the catalyst reach steady state in a period of time. Finally there is a distinct maximum in activity water concentration at approximately 10%vol (Fig.4).

The effect of water can be attributed to the reaction surface hydroxyl groups and Cl adsorbed on the surface leading to the formation of HCl, which can easily desorb from the surface. On the contrary, in the absence of water Cl accumulates on the catalyst (a point confirmed by elemental analysis of the spent catalyst) and blocks reaction sites. However, if the gas phase water concentration reaches a certain level (in our case approximately 10%vol) the excessive concentration of surface hydroxyls can also reduce the number of TCP adsorption sites, and hence, have an adverse effect on catalytic activity. This can explain why the activity vs. water concentration profile is characterized by a maximum.



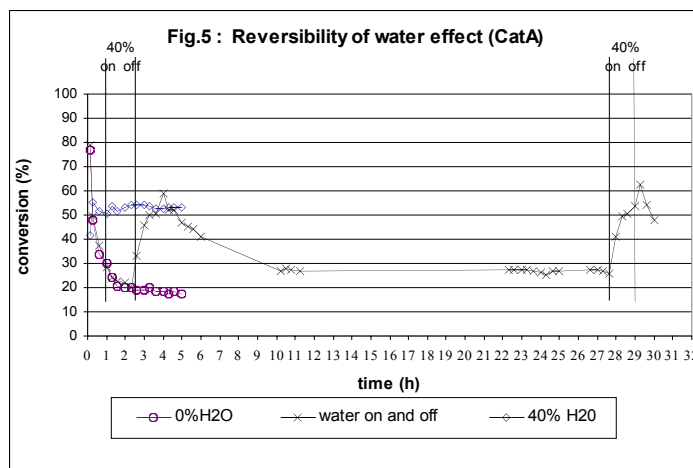
where the 40% water content was present from the beginning. Removing the water from the reaction mixture caused a decrease in activity to a level slightly higher than what was previously observed in the absence of water. The same procedure was repeated after 28h on stream and resulted in the same behavior, confirming the reversibility of the observed behavior.



TCP

short

with



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