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Strategies to enhance the stability of h-bea zeolite in the catalytic oxidation of Cl-VOCs: 1,2-Dichloroethane

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ABSTRACT

The objective of this work was to evaluate the feasibility of oxy-combustion treatments with the aim of restoring the catalytic activity and properties of H-zeolites deactivated in the oxidation of Cl-VOCs, namely DCA. The efficiency of regeneration treatments was analyzed by submitting the fresh H-BEA to cycles of reaction-regeneration-reaction. Conversion of DCA was monitored with time on stream and acidity, coke content and chlorine content on the catalyst surface was characterized before each step of the cycle. We found that deactivation process was reversible, since it was associated mainly to coking. Wet air regeneration was more efficient than dry air regeneration, especially for chlorine removal, although coke was only removed above 500 °C. The effect of multiple cycles of reaction and regeneration steps has been also quantified.

1. Introduction

The economical feasibility of any industrial catalytic process is based on the catalyst activity, selectivity and durability, but also in the possibility of regeneration and re-use. It concerns especially to catalytic processes for cleaning up of pollutant emissions, such as volatile organic compounds (VOCs), since the driving force is not making higher value added products, but reducing environmental impact and complying the environmental regulations.

Although the catalytic oxidation of chlorinated volatile organic compounds (Cl-VOCs) is a known and well-established technology, regeneration of deactivated catalysts is a relatively new field of study, and papers in the literature are scarce.

The interaction of the catalyst with chlorine is the main problem met in the design of catalysts for the combustion of Cl-VOCs. Although at a different extent, almost all types of catalysts are deactivated by chlorine attack or poisoning, e.g. supported noble metals [1], cerium oxides [2] and zeolites [3]. Transition metal oxides, but particularly chromium, tend to form volatile metal oxychlorides with the subsequent loss of active material [4]. The volatilization of the active phase has also been reported for V_2O_5/TiO_2-SiO_2 catalysts [5] and for perovskite type catalysts ($LaCoCO_3$) [6]. Dai et al. [2] and de Rivas et al. [7] found out that Ce/Zr mixed oxides were easily deactivated by thermal sintering. Formation of coke has been reported to be the main reason for the deactivation of protonic [8] and metal exchanged zeolites [9].

The properties of the catalysts deactivated by volatilization of the active phase or by physicochemical changes in the catalyst structure are difficult to restore (irreversible deactivation). However, when coking or poisoning is the source of deactivation, it is possible to regenerate the catalyst partly or even completely (reversible).

The combustion of coke formed over catalysts used for oxidation of non-chlorinated VOCs is widely reported in the literature [10,11], but less in the case of deactivated catalysts used in the oxidation of Cl-VOCs [12]. The most commonly used method to remove coke is burning it with oxygen, usually using air as the source of oxygen. The main disadvantage of this method is that it requires an accurate control of temperature, since the combustion reaction is highly exothermic, and thus catalyst may be damaged. To prevent uncontrolled increase of temperature, water vapor is often added to the oxygen-providing stream, so coke gasification ($C + H_2O \rightarrow CO + H_2$) takes place at lower temperatures. Furthermore, the produced syngas continues regenerating the catalyst [13,14].

Some papers in the literature also propose high temperature treatments in dry or wet air streams to regenerate catalysts deactivated by chlorine poisoning. Vu et al. [15] found out that catalysts made of Mn-Cu mixed-oxides, heating up to 350 °C for 5 h in dry air flow, retrieved almost completely its initial activity in the oxidation of chlorobenzene, although the removal of chlorine from

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the catalyst structure was not complete. Dai et al. [2] concluded that the elimination of chlorine in CeO_2 catalysts, used in the oxidation of trichloroethylene (TCE), was a slow process, thus only a long treatment under wet air could completely remove the adsorbed chlorine and restore the activity.

In a previous paper, we reported the main causes of the deactivation of H-ZSM-5, H-BEA and H-MOR in the oxidation of 1,2-dichloroethane (DCA) [8]. A rapid deactivation of the H-zeolites was found, due mainly to the coke formation and in a lesser extent due to the chlorine attack. It was found that the effect of coking on the stability of H-zeolites depended strongly on their pore channel system and total amount of acid sites. We also found that coke was formed via vinyl chloride intermediate, which was formed by previous hydrodechlorination of DCA.

Given the rapid deactivation of these investigated catalysts [8], the industrial viability of the process is conditioned by the catalyst regeneration. The objective of this work is to evaluate the feasibility of oxy-combustion treatments with the aim of restoring the catalytic activity and properties of H-zeolites in the oxidation of Cl-VOCs, namely DCA, in order to extend the catalyst lifetime. Based on the knowledge gained from our previous work on the deactivation of different protonic zeolites [8], this work was restricted to deactivated H-BEA, since it contained the greater amount of coke and chlorine, enabling higher resolution in analysis and establishing decisive conclusions.

2. Material and methods

2.1. Preparation and characterization of the catalyst

The catalyst was prepared by calcining the NH_4-BEA zeolite supplied by Zeolyst International (Si/Al molar ratio of 12.5) in air at 550 °C for 3 h and then pelletized under 29 kN during 3 min (Specac hydraulic press). The resulting pellets were crushed and sieved to a particle size of 0.3–0.5 mm. Before reaction run, zeolite catalysts were dried in situ at the reactor under a 450 $cm^3\,min^{-1}$ stream of dry air at 200 °C for 2 h.

Temperature-programmed desorption of ammonia (NH_3-TPD) was performed on a Micromeritics AutoChem 2910 instrument. Prior to adsorption experiments, the samples (80–90 mg) were pretreated in a quartz U-tube under a N_2 stream at 500 °C. Then, they were cooled down at 100 °C in a N_2 flow (20 $cm^3\,min^{-1}$) and after that, the NH_3 adsorption step was performed by admitting small pulses of NH_3 in Ar at 100 °C up to saturation. Subsequently, the samples were exposed to a flow of Ar (50 $cm^3\,min^{-1}$) for 2 h at 100 °C in order to remove reversibly and physically bound NH_3 from the surface. Finally, the desorption was carried out from 100 to 500 °C at a heating rate of 10 °C min^{-1} in Ar stream (50 $cm^3\,min^{-1}$). This temperature was maintained for 15 min until the adsorbate was completely desorbed. The amount of ammonia desorbed at a given temperature range was taken as a measure of the acid site concentration. All the samples showed two major desorption peaks, the one around 180–200 °C was considered weak acid sites, and the other in the range 350–450 °C as corresponding to strong acid sites. The profiles were simulated according to two Gaussian functions associated with the desorption at low and high temperatures, respectively, as shown elsewhere [8]. The fitting quality of the deconvolution, measured as correlation coefficient (R^2) of least square fitting was always higher than 0.997.

Coke content was determined by heating the spent catalyst up to 850 °C at a rate of 5 °C min^{-1} under synthetic air flow (300 N $cm^3\,min^{-1}$, 100 kPa) in a thermogravimetric analyser (Setaram Setsys Evolution).

Chlorine content was measured by scanning electron microscopy analysis combined with energy dispersive X-ray analysis (SEM–EDX) on a JEOL JSM6400 scanning microscope operating at 5 kV of field emission, 1 nA of beam current and 15 mm of working distance. The powder samples were placed on a brass holder with a carbon conductive tape. A conductive layer of graphite of 15 6 nm thick was deposited over them.

2.2. Experimental reaction set-up

The experimental reaction set-up is shown in Fig. 1. The Cl-VOC feed consisted of a dry compressed air stream, regulated by a gas mass flow controller (Bronkhorst® High-Tech El-Flow F-201C-FAC-20-V), and DCA liquid stream, dosed by a mass flow controller (Bronkhorst® High-Tech μ-Flow L01-AAA-99-0-20S). The complete evaporation of the liquid stream and homogenous blend with the gas stream was performed in a controlled-evaporator-mixer (Bronkhorst® High-Tech CEM W-101A-111-K). The regeneration feed also consisted of a dry compressed air stream, regulated by a mass flow controller and H_2O liquid stream dosed by mass flow controller (Bronkhorst® High-Tech μ-Flow L01-AAA-99-0-20S). The blending point was electrically heated to ensure complete evaporation. The resulting gaseous stream went through the fixed catalytic bed inside a U formed tubular quartz reactor, which was heated into a convective-flow oven. An on-line gas chromatograph

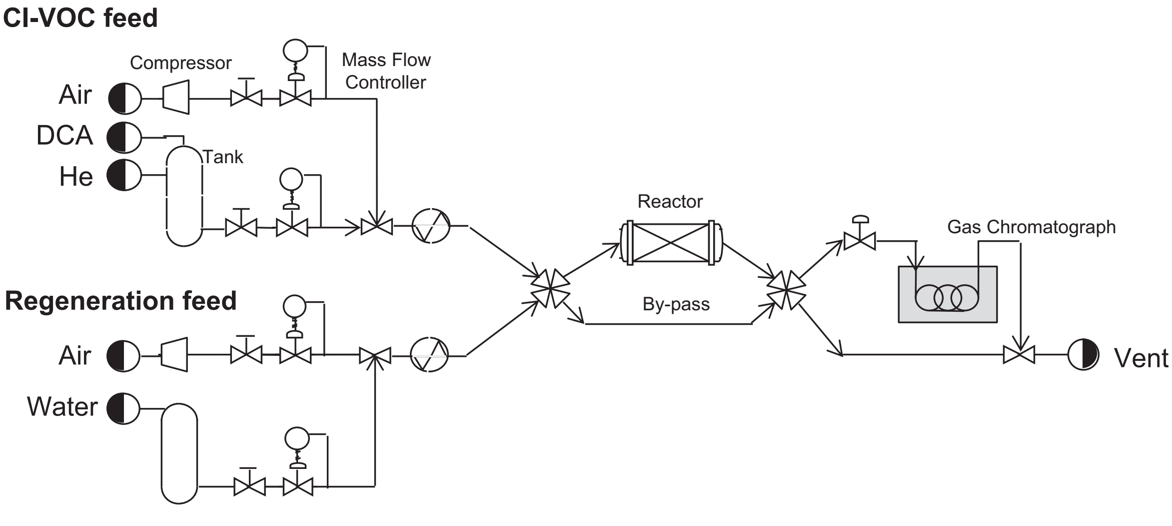

Fig. 1. The experimental set-up for the catalytic oxidation of DCA and dry and wet regeneration experiments.