Catalytic destruction of PCDD/Fs. Effect of temperature and catalyst loading on efficiency of 1,2-dichlorobrnzene destruction on V2O5-WO3/Al2O3-TiO2 catalyst

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Introduction

Catalytic degradation is the most important method for the reduction of PCDD/Fs emissions from incineration processes. The method has been known since the end of the 1980s, but it is still a subject of extensive studies. Research carried out by Hagenmeier[1] proved that a vanadium-tungsten catalyst (V_2O_5-WO_3) on a titanium dioxide carrier (TiO_2) efficiently decomposes PCDD/Fs with a release of CO_2, H_2O and HCl. This catalyst is widely used in the catalytic reduction of nitric oxides (with the addition of ammonium)[2-6] in the process known as SCR (**S**elective **C**atalytic **R**eduction). Further studies[7-11] have shown that on a properly prepared V_2O_5-WO_3/TiO_2 catalyst in the presence of ammonium, it is possible to efficiently reduce the emission of both nitric oxides and PCDD/Fs.

When analysing the literature on the subject, it can be assumed that in the catalytic dioxin decomposition the following catalysts are applied:

- vanadium, vanadium-tungsten and vanadium-molybdenum,
- chromium,
- perovskite.

The most frequently used carrier is TiO_2 which has catalytic properties, and the process is most often conducted at temperature ranging from 230 to 300°C (for vanadium catalysts), 300 to 400°C (for chromium catalysts) and 500 to 600°C (for perovskite catalysts). The highest efficiencies of PCDD/Fs reduction to CO_2, H_2O and HCl are obtained for catalyst load equal to 5000-10000 1/h.

Due to significant technical problems with obtaining a stable air stream containing trace (several ng/m^3) concentrations of PCDD/Fs, many researchers carried out their studies using other chloro-organic compounds, e.g. o-dichlorobenzene, trichloroethylene, tetrachloroethylene, etc. The best PCFDD/Fs "simulator" is considered to be o-dichlorobenzene, which has a chemical structure similar to that of the half molecule of tetrachlorodibenzo-p-dioxin.

Methods and Materials

Studies on the catalytic dioxin decomposition were carried out in a specially constructed semi-commercial apparatus, whose most important element was a catalytic reactor with a monolithic catalyst in the form of $150 \times 150 \times 100$ mm cubes. The catalyst had the specific surface about 1050 m^2/m^3. On a catalyst made from cordierite an active layer of the following composition was deposited:

$$
\begin{array}{lcl}
Al_2O_3 & - & 64\%\ wt. \\
TiO_2 & - & 26\%\ wt. \\
V_2O_5 & - & 6.6\%\ wt \\
WO_3 & - & 3.4\%\ wt.
\end{array}
$$

The reactor made it possible to carry out the process in the temperature range 150-400°C, at a variable catalyst load and changing gas flow velocity through the reactor. It had 4 independent gas flow lines which allowed 1 catalyst cube to be placed in a horizontal system of each line, and to place 4 catalyst cubes one above the other in the vertical system. Schematic diagram of the experimental set-up is shown in Fig. 1.
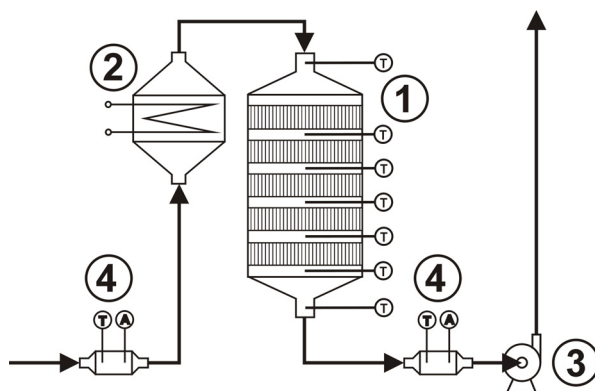

Figure 1. Schematic diagram of the experimental set-up. (1) – catalytic reactor, (2) electric heater, (3) fan, (4) point of temperature, pressure, flow rate and concentration control

The air flow through the installation could be adjusted in the range 100-400 m^3/h. Using a special micro-feeder o-dichlorobenzene was fed to the stream of gases supplied to the installation before the point of process parameters control (4). The initial concentration of o-dichlorobenzene in the air was around 2 mg/m^3.

The content of o-dichlorobenzene in the air was analysed by the chromatographic method. A precisely measured volume of gases from inlet and outlet streams was passed through absorbing tubes filled with a sorption bed composed of 1 g activated carbon (Merck Aktivkohle 0.3-0.5 mm). The gas was aspirated at the velocity about 1 dm^3/min with ca. 40 dm^3 gas passing through one pipe. The pipes were transported immediately to a laboratory. O-dichlorobenzene was extracted from the sorption bed of 1 g activated carbon with 10 ml benzene of chromatographic purity. After being desorbed for 15 minutes at room temperature, the solution was filtered and diluted in the 1:10 ratio with benzene in a measuring flask 10 ml in volume and taking 1 ml of the filtered extract. The o-dichlorobenzene solutions were analysed by capillary gas chromatography using HP-6890 chromatograph equipped with an electron capture detector ECD. Samples were fed by the Splitless

technique. Using an EQUITY 5 capillary column of length 30 m and inner diameter 0.32 mm, the stationary phase thickness 0.25 μm and the following temperature program: 60°C 1 min, the accretion 10°/min to 80°C, the time of o-dichlorobenzene retention was 2 min 41 s. The mixture of o-dichlorobenzene in benzene at concentrations: 10 ng/ml 100 ng/ml, 1 μg/ml and 10 μg/ml was used as a standard. In this range of concentrations, a linear range of the values of peak surface fields of standard substances was recorded as a function of the concentration (a linear range of ECD response). Each analysis was repeated three times. Using the Dixon test, the precision of determination was checked. To calculate o-dichlorobenzene concentration in the stream of inlet and outlet gases from the catalyst, a mean value of three determinations was used. The boundary of the method determinability was calculated to be 2 μg/m^3 o-dichlorobenzene (for the sample 40 dm^3 in volume).

Results and Discussion

Several series of experiments were made to specify the effect of selected parameters on the process of catalytic decomposition of o-dichlorobenzene. In the first series the effect of linear flow velocity through the catalyst capillaries on the process rate was analysed. To accomplish this a trial was made in which first 3 catalyst cubes were placed in the vertical system (1 x 3) in one flow line (linear flow velocity u = 2.7 m/s), and next 3 catalyst cubes were placed in the horizontal system (3 x 1) in 3 flow lines (u = 0.9 m/s). In both working systems the same catalyst load equal to ca. 50 000 1/h was retained at different linear flow velocities through the catalyst (different mass transfer coefficients in the gas phase). Next, this trial was repeated for 4 catalyst cubes placed in the system 4 x 1, 2 x 2 and 1 x 4 cubes. No effect of the configuration, and hence no influence of mass transfer processes in the gas phase was found.

In consecutive series, the effect of process temperature on destruction efficiency was studied. These trials were conducted at various loads of the catalyst being about 33 500 1/h, 16 600 1/h, 10 900 1/h and 8 200 1/h. The investigations were carried out for several temperatures ranging from 175 to 298°C. Results are shown in Fig. 2.
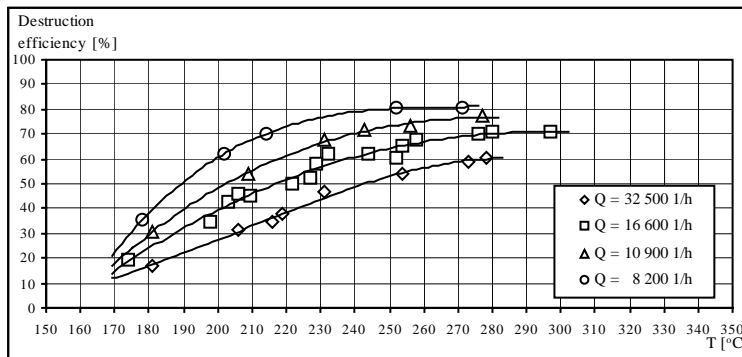
Figure 2. Effect of temperature on o-dichlorobenzene destruction efficiency at various catalyst loading (Q [1/h]).

The next measuring series were supposed to answer the question of the effect of the catalyst load on the efficiency of o-dichlorobenzene destruction. Several trials were made at mean temperature, i.e. ca. 207°C and ca. 254°C for 4, 8, 12 and 16 catalyst cubes placed in the reactor. That corresponded to the catalyst load equal to ca. 33 500 1/h, 16 600 1/h, 10 900 1/h and 8 200 1/h. Results are illustrated in Fig. 3.
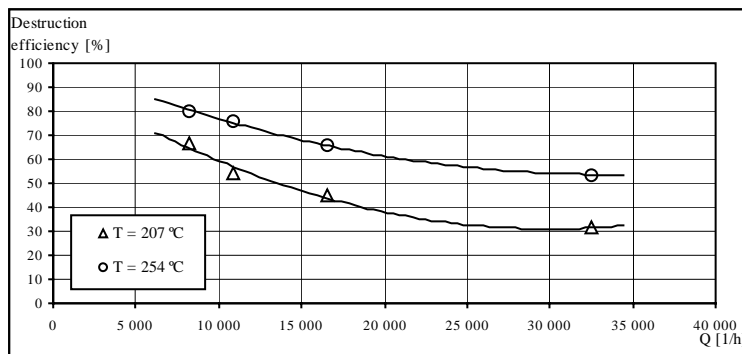

Figure 3. Effect of catalyst loading on o-dichlorobenzene decomposition efficiency at various temperatures.

As a result of these investigation a distinct effect of the catalyst load and temperature on the efficiency of o-dichlorobenzene decomposition was observed. No influence of the linear flow velocity through the catalyst on the obtained o-dichlorobenzene decomposition efficiency was observed. The vanadium-tungsten catalyst on a monolithic carrier made from $TiO_2/\gamma\text{-}Al_2O_3$ revealed a very good activity, which enabled 80% efficiency of o-dichlorobenzene destruction at the temperature about 250°C with the catalyst load reaching around 8 200 1/h. Research on the catalytic decomposition of dioxins will be continued after connecting the semi-commercial installation described in this paper to the real incineration plant for hazardous wastes of the capacity about 3500 Mg/year. It will be performed on real flue gases using the catalyst presented in this paper.

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