



## Structure sensitivity of dimethylamine deep oxidation over Pt/Al<sub>2</sub>O<sub>3</sub> catalysts

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### ABSTRACT

The deep oxidation of dimethylamine (DMA) was studied over Pt/Al<sub>2</sub>O<sub>3</sub> catalysts with small (1 nm) and large (7.8–15.5 nm) Pt crystallite sizes. The turnover frequency (TOF) was higher for the large than for the small Pt crystallites, indicating that the reaction is structure sensitive. Two kinetic models were used to interpret the obtained results, i.e., the Mars van Krevelen and a mechanism based on the adsorption of oxygen and adsorption of dimethylamine on different active sites were employed. Both models showed that the activation energy for the oxygen chemisorption rate constant ( $k_o$ ) decreased with increasing of Pt crystallite size and that the activation energy for the surface reaction rate constant ( $k_i$ ) was independent of the Pt crystallite size. The structure sensitivity may be explained by differences in the reactivity of the oxygen adsorbed on these Pt crystallites.

The Mars van Krevelen model fits the TOF values very well at concentrations of DMA higher than 1500 ppm, while in the lower concentrations region, the model under predicts the experimental data. The model based on the adsorption of oxygen and DMA on different active sites fits the experimental data quite well over the whole temperature and concentration range. The fitted values of the Henry adsorption constant are independent of the Pt crystallite size.

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### 1. Introduction

Deep catalytic oxidation of volatile organic compounds (VOCs) on noble metals is a widely used method to remove VOCs from industrial waste gases, especially in processes with high flow rates of waste gases and low concentrations of VOCs [1,2]. Typical catalysts for deep oxidation of VOCs are based on precious metals. As a general rule, any surface reaction over a supported metal catalyst the rate of which is affected by a change in the metal particle size is considered to be structure sensitive [3]. Several studies have reported that the intrinsic rate of the deep oxidation of VOCs over supported platinum and palladium catalysts are dependent on the particle size, i.e., the specific activity (activity per exposed metal atom) of supported noble metal is influenced by the metal crystallite size [4–10]. There are numerous papers indicating that the strength of the oxygen adsorption plays a key role in the observed structure sensitivity of these reactions [11–18]. In addition, some authors interpret the structure sensitivity of the deep oxidation of VOCs considering the adsorption of hydrocarbons as the rate-determining step and the readiness of the rupture of the weakest C–H bonds is affected by the metal crystallite size [19–21]. However, there is agreement that changes

in the specific activity can be attributed to morphological effects rather than to the chemical state.

An understanding of the root causes of structure sensitivity is an important challenge, both for the fundamental study or practical use of catalysts. The structure sensitivity can be clearly evidenced and well explained using a detailed determination of the kinetic parameters, such as activation energy for each elementary step of the oxidation of VOCs, for catalysts with different Pt particle sizes. The results of a previous study [11] of the kinetics of toluene and *n*-hexane oxidation over Pt/Al<sub>2</sub>O<sub>3</sub> catalysts with platinum mean crystallite sizes ranging from 1.0 to 15.5 nm showed that both the kinetic parameters and the turnover frequency are affected by the mean crystallite size of the platinum. The structure sensitivity was explained by differences in the reactivity of the adsorbed oxygen on small and large Pt crystallites.

Within this work, the kinetics of the deep oxidation of dimethylamine (DMA) over Pt/Al<sub>2</sub>O<sub>3</sub> catalysts with different platinum mean crystallite size, small and large, was investigated. Reactions of DMA are an important commercial route for the production of several formulations of herbicides, which have wide-ranging applications as agrochemicals. The vapours of both the reactants and products are potentially hazardous for the environment. Consequently, the working objective of this study was to estimate the feasibility of employing a Pt/Al<sub>2</sub>O<sub>3</sub> catalyst for DMA removal. However, the products of the catalytic oxidation of DMA

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over a Pt/Al<sub>2</sub>O<sub>3</sub> catalyst include NO<sub>x</sub>, in addition to the benign products CO<sub>2</sub> and H<sub>2</sub>O, which certainly requires additional treatment; i.e., selective catalytic reduction, adequate NO<sub>x</sub> storage devices, etc.

## 2. Experimental

### 2.1. Catalysts preparation

The catalysts were synthesized by impregnation of a ( $\gamma + \theta$ ) Al<sub>2</sub>O<sub>3</sub> support (Rhône-Poulenc, Type 531A, in the form of spheres with a diameter of  $3.0 \pm 0.3$  mm) using an aqueous solution of hexachloroplatinic acid. Briefly, the support was dried for 4 h at 120 °C. An adequate amount of an aqueous solution of hexachloroplatinic acid was added to the support (about  $5 \text{ cm}^3 \text{ g}^{-1}$  support) by the incipient wetness method. The concentration of hexachloroplatinic acid in the impregnating solution was  $1 \times 10^{-2}$  mol/l. The duration of the impregnation of the support was 3 min. After adsorption of hexachloroplatinic acid, the catalyst was filtered, rinsed with distilled water to avoid the negative reaction of chloride ions and air-dried at 110 °C for 2 h. The catalyst was reduced in a dynamic hydrogen-nitrogen mixture. The temperature was increased to 500 °C at a programmed and maintained at this temperature for 5 h, whereby the catalyst was reduced. The platinum loading determined by chemical analysis was 0.12 wt.%. The catalysts had an egg-shell distribution, with almost all platinum content deposited in the outer shell of the support to a depth of 100  $\mu\text{m}$ . The surface area of the sample prepared by the above procedure was  $110 \text{ m}^2 \text{ g}^{-1}$ . In order to affect the Pt particle size, the catalyst synthesized in the previous procedure was calcinated in air at 700 °C for 48 h. The sintered sample was then reduced under the same conditions as the fresh sample. The sintered catalyst had a surface area of  $100 \text{ m}^2 \text{ g}^{-1}$ . Since the contribution of Pt to the overall specific surface area is negligible (less than  $1 \text{ m}^2 \text{ g}^{-1}$ ), the decrease in the specific surface area by about 10% should be ascribed solely to the support sintering. More specifically, this is the consequence of the partial disappearance of pores of size about 2–4 nm [22].

### 2.2. Catalysts characterization

The platinum dispersion measurements were performed by CO chemisorption at a temperature of  $24 \pm 0.2$  °C using a pulse gas chromatographic method, a self-made apparatus equipped with a TCD detector of a Varian Aerograph model 920 gas chromatograph. Before the chemisorption measurements, the catalyst samples were treated at 450 °C in a helium flow for 1 h. After cooling to room temperature, the CO was pulsed (pulse volume  $0.1 \text{ cm}^3$ ) into the helium stream ( $30 \text{ cm}^3/\text{min}$ ) through an adsorption cell. The catalyst adsorbed the CO pulses until saturation and the fraction of CO not adsorbed was detected by a thermal conductivity detector (TCD).

The specific surface area measurements were performed by nitrogen adsorption at  $-196$  °C, using the same apparatus as employed in the CO chemisorption measurements. Before the measurements, the samples were treated at 450 °C in a helium flow for 2 h. After that, a gas mixture of 27 vol.% of nitrogen in helium ( $30 \text{ cm}^3/\text{min}$ ) was passed over the sample and the sample cell was cooled by immersion in liquid nitrogen. The cooled sample adsorbs a certain amount of nitrogen from the gas stream and the adsorption equilibrium was established. When the liquid nitrogen bath was removed, the sample warmed and the adsorbed nitrogen was released, enriching the effluent which was monitored by a TCD detector. The specific surface areas of the samples were calculated by the “one point” BET method in a manner similar to that used in a standard volumetric BET method.

### 2.3. Kinetic measurements

The kinetics experiments of DMA oxidation were performed in a fixed bed catalytic reactor made of a stainless steel tube having 6 mm o.d., 4 mm i.d. and 115 mm in length. The catalytic reactor was situated within a Shimadzu 14-A gas chromatograph, in the oven that was designed for a commercial on-column OCI-14 injector. It was possible to temperature programme the reactor oven independently from the other heated sections of the gas chromatograph. The Pt/Al<sub>2</sub>O<sub>3</sub> catalysts were placed in the middle of reactor, housed on a quartz wool holder, with thermocouples on the top and bottom of the catalyst bed. The reactor was loaded with 0.1 g of granulated Pt/Al<sub>2</sub>O<sub>3</sub> catalysts, corresponding to a volume of  $0.135 \text{ cm}^3$ . In order to load the integral reactor, the whole catalysts spheres were completely homogeneously crushed down to 0.05 mm and pelletised. The tablets were ground and various granulations of catalyst were separated. The applied air flow rates through the catalyst bed corresponded to a space velocity of  $17,500 \text{ h}^{-1}$ . The investigated temperature range was between 110 and 140 °C. The temperatures were maintained with an accuracy of  $\pm 0.2$  °C. The kinetics measurements were performed under steady state conditions and at a conversion of DMA below 10%, to ensure the validity of the differential reactor assumption. Although, the range of conversion under 10% could be *a priori* accepted as kinetic, i.e., the region in which the surface reaction is the rate determining step of the overall process, the absence of an internal diffusion limitation was confirmed by using different granulations of catalyst. There were no significant differences between the conversions obtained with catalyst particles of mean diameter below 0.5 mm, in investigated temperature range. Based on these tests, the kinetic study was performed with catalysts particles of 0.25 mm mean diameter. The dependence of the reaction rate on the hydrocarbon concentration was measured by varying the concentration of DMA in the air (range from 50 to 2600 ppm). Measurements of the inlet and outlet concentrations of DMA were performed using an FID detector. The DMA concentrations were determined with an accuracy of  $\pm 2$  ppm. The reproducibility of the results was verified by performing each test several times. The reaction rates are expressed as the turnover frequency (TOF), defined as the number of the molecules reacting per second per one exposed Pt atom.

## 3. Results and discussion

Knowledge of the adsorption stoichiometry is necessary for the analysis of the CO chemisorption data and determination of the Pt mean crystallite size. It is well known that CO can form linear or bridged bonds with surface Pt atoms. The ratio of linear to bridged bonds depends on the size and structure of the Pt particles [23] and on the nature of the support. There are many studies that compare CO chemisorption with H<sub>2</sub> chemisorption and TEM results. There is general agreement that in the case of high Pt dispersion, the CO/Pt adsorption stoichiometry is 1 [24–27]. However, as the Pt dispersion decreased, the stoichiometry between adsorbed CO and Pt can be changed. With decreasing Pt dispersion below 30%, literature data show that the CO/Pt adsorption stoichiometry is in the range from 1 to 0.5 [26–31].

Therefore, a CO/Pt adsorption stoichiometry of 1 was adopted for the calculations of Pt crystallite size for the highly dispersed Pt catalyst. However, for the sintered catalyst, the CO chemisorption data were analysed using the two limiting values of the chemisorption stoichiometry: CO/Pt of 1 (CO adsorbs on Pt via linear bonds only) and CO/Pt of 0.5 (two surface Pt atoms are bonded to the same CO molecule). The mean crystallite size of Pt was calculated with the assumption that Pt crystallites were cubic-shaped with one face in contact with the alumina surface. The calculated size of the Pt crystallites was 1 nm for the catalyst with

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