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Combination of non-thermal plasma and heterogeneous catalysis for oxidation of volatile organic compounds
Part 2. Ozone decomposition and deactivation of γ-Al_2O_3

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Abstract

The role of ozone was studied for two different configurations combining non-thermal plasma (NTP) and heterogeneous catalysis, namely the use of a gas phase plasma with subsequent exposure of the effluent to a catalyst in a packed-bed reactor (post-plasma treatment) and the placement of the catalyst directly in the discharge zone (in-plasma catalysis). Non-porous and porous alumina and silica were deployed as model catalysts. The oxidation of immobilised hydrocarbons, toluene as a volatile organic compound and CO as an inorganic pollutant were studied in both operational modes.

While conversion and selectivity of hydrocarbon oxidation in the case of catalytic post-plasma treatment can be fully explained by the catalytic decomposition of O_3 on γ-Al_2O_3, the conversion processes for in-plasma catalysis are more complex and significant oxidation was also measured for the other three materials (α-Al_2O_3, quartz and silica gel). It became obvious that additional synergetic effects can be utilised in the case of in-plasma catalysis due to short-lived species formed in the NTP.

The capability of porous alumina for ozone decomposition was found to be correlated with its activity for oxidation of carbon-containing agents. It could be clearly shown that the reaction product CO_2 poisons the catalytic sites at the γ-Al_2O_3 surface. The catalytic activity for O_3 decomposition can be partially re-established by NTP treatment. However, for practical purposes the additional reaction pathways provided by in-plasma catalytic processes are essential for satisfactory conversion and selectivity.

Keywords: Non-thermal plasma; Post-plasma treatment; γ-Al_2O_3

1. Introduction

Electrical discharges provide a great potential for initiating chemical reactions in the gas phase due to the direct energy transfer by highly accelerated electrons. Thermal plasmas have been utilized to produce basic chemicals such as acetylene, carbon black and hydrogen from methane [1,2]. When the activation barrier of the desired reactions can be overcome under non-equilibrium conditions (with ‘hot’ electrons or other reactive species and ‘cold’ neutral gas molecules), the specific energy input can be minimised. Such non-thermal plasmas (NTP) have already been applied for the production of chemicals (e.g. methanol from methane [3,4] and other selective-oxidation reactions [5]), reforming [6,7] reduction of supported metal catalysts [8] and for the removal of hazardous compounds (e.g. nitrogen oxides and volatile organic compounds [VOCs]) from gas streams [7,9–11]. The specific thermodynamic conditions expressed by different temperature levels of the corresponding species can even lead to reduction processes in an air atmosphere. However, the variety of reactive species formed in an NTP (OH and O radicals, other atomic species, ions and activated molecules) results in a wide spectrum of reaction pathways and products. Unfortunately, on the basis of a large number of experimental results it has to be concluded that non-thermal plasma does not usually allow the simultaneous achievement

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of both a high conversion and a satisfactory selectivity with respect to the desired reactions.

To overcome this dilemma, the exploitation of catalytic effects has been considered. An excellent overview of recent research in the fields of plasma catalysis and plasma-supported catalyst preparation is provided in [12]. Applications of catalysts both in the plasma discharge zone and as an additional reactor bed in the off-gas of a gas phase discharge reactor have been studied. Plasma catalysis, i.e. the action of the catalyst directly within the discharge zone, holds the potential for a number of synergetic effects such as utilisation of short-lived plasma species, formation of new catalytically active centres, enhanced reactant concentrations due to adsorption, and in situ decomposition of ozone by appropriate packed-bed materials.

Meanwhile, in-plasma catalysis has been found to enhance the oxidation of various potential pollutants such as benzene (with TiO_2 catalysts [13] or alumina and zeolites [14,15]), toluene (also with TiO_2 [16,17]), 2-heptanone (using Pt supported on alumina [18]) and perfluorocarbons (using a commercial mixed oxide catalyst [19]). A detailed study by Kirkpatrick et al. [20] has shown that the extent of the synergetic effect due to plasma catalysis depends on the substance (toluene, NO_x, acetonitrile) to be removed. They employed Pt or Rh supported on vitreous carbon and compared the arrangement where the catalyst was in the plasma zone with a catalytic post-plasma treatment [20]. Under certain conditions, even a negative effect of the combination was observed. The interpretation of the phenomena correlated with plasma catalysis is rather difficult, especially when additionally taking into account the effects of the solid on the discharge characteristics [21]. In the case of titanium oxide photo-catalysis based on the ultraviolet radiation generated in NTP may play a substantial role. Therefore, further investigations are essential for clarifying the mechanisms of plasma catalysis in order to make it applicable for technical processes.

In Part 1 of this series [22], by studying the oxidation of various organic substances immobilised on non-porous and porous carriers we provided the first clear evidence that short-lived oxidising species formed in the NTP exist in the pore volume of porous materials. This finding is considered as a pre-requisite for the effective use of plasma catalysis exploiting its inherent synergetic potential [22,23].

One particularly important oxidising species formed by NTP treatment of oxygen-containing gas streams is ozone. Beside its direct reaction with hydrocarbons, the catalytic decomposition connected with the formation of an atomic O species according to

$$O_3 \rightarrow O_2 + O \qquad (1)$$

represents a major oxidation pathway. Due to the long lifetime of O_3, this process is relevant for in-plasma as well as post-plasma catalysis. It has been described for a number of catalysts [24–27] such as silica gel and porous alumina [27–29]. In this way, O_3 plays the role of a long-lived carrier of atomic oxygen. For γ-Al_2O_3, Lewis acid sites appear to play a major role in the catalytic process [27]. Sample pre-treatment (e.g. calcination temperature and residual water content) as well as the presence of additives and impurities influence the activity for O_3 decomposition. In our own previous studies using the same type of samples, the relevance of this catalytic process for the enhancement of selectivity to CO_2 formation was shown and the additional oxidation potential of externally produced O_3 was proved for the hydrocarbon/γ-Al_2O_3 system [22].

In this paper, the role of ozone in the oxidation of various organic compounds and CO using different operational modes will be considered. In particular, the catalytic decomposition, deactivation and various attempts at reactivation will be discussed. Finally, the experimental results are evaluated with respect to the potential for NTP-based removal of hydrocarbons, stability of operation and opportunities to enhance the performance of plasma reactors.

2. Experimental

2.1. Materials

Porous and non-porous alumina (α-Al_2O_3 [Aldrich] and γ-Al_2O_3 [Merck]) and silica (quartz powder [Merck] and silica gel [SilGel; Merck]) with specific surface areas of 0.26, 133, 0.4 and 372 m^2/g, respectively, and grain sizes in the 100 μm range were used as packing materials. Further details on the substances have been given elsewhere [22]. For reference tests, the non-porous ferroelectric perovskite $BaTiO_3$ with a dielectric constant of $\varepsilon_r \approx 3000$ (from Marco GmbH, Hermsdorf, Germany; grain size 1–1.6 mm, specific surface area below 0.1 m^2/g) was used [23].

The activity of γ-Al_2O_3 was found to depend markedly on the pre-treatment and the storage conditions (in air with the native CO_2 content). Where not otherwise stated, the alumina samples were calcined at 450 °C in air for at least 2 h before being applied in the experiments.

Three different non-volatile organic compounds were immobilised on the catalysts (SiO_2 and Al_2O_3): Carbowax (CW; poly(ethylene glycol), mean molecular weight = 400 g/mol, Varian Aerograph, p.a.), *n*-eicosane (Eic; Merck) and *p*-terphenyl (TPh; Merck). The preparation procedure, as described in detail in [22], resulted in multilayer coverages for α-Al_2O_3 and quartz and a sub-monolayer adsorption for the porous materials (γ-Al_2O_3 and silica gel). The distribution of the organic compounds was characterised by differential scanning calorimetry (DSC, using a DSC-50 calorimeter from Shimadzu) as shown in Fig. 1 for the two Eic/SiO_2 samples. The extent of the Eic coverage can be classified on the basis of the Eic melting peak, which is expected to occur for a multilayer coverage (on quartz) and to be absent for a sub-monolayer situation (on silica gel). Indeed, the experimental results confirm the