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On the quantitative aspects of hydrolysis of isocyanic acid on TiO_2

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Abstract

The selective catalytic reduction with aqueous solutions of urea is currently seen having the highest potential to reduce NO_x and particulate emissions for commercial diesel powered vehicles. Ammonia as the actual reduction medium is formed from urea in two consecutive reactions, i.e. via the thermolysis of urea to isocyanic acid and NH_3 and the catalyzed hydrolysis of HNCO over TiO_2 to NH_3 and CO_2. A kinetic model for the hydrolysis reaction was derived for a reaction scheme comprising a set of elementary steps. To minimize the number of unknown variables in the kinetic model for the overall rate, the equilibrium constants for both reactants (HNCO and H_2O) and products (NH_3 and CO_2) were determined from adsorption isotherms using Langmuir and multilayer adsorption models. A data set consisting of 49 data points for the rate determined at varying reactant concentrations was fitted with the kinetic model using a non-linear least mean squares regression analysis.

Keywords: Diesel emission; SCR; DeNO_x; Urea; Hydrolysis; Isocyanic acid; Adsorption; TiO_2; Anatase; Kinetic model; Rate

1. Introduction

Approximately 20% of the current global anthropogenic nitrogen oxide emissions originate from passenger cars and commercial vehicles [1], and it is foreseen that the increasingly rigid emission standards for NO_x being introduced by European and US legislation over the next years can only be fulfilled by exhaust gas after-treatment technology. Today, the selective catalytic reduction (SCR) with ammonia is considered as the most promising technique for reducing NO_x emissions from heavy-duty diesel engines [2–5]. However, the use of gaseous NH_3 requires elaborate safety precautions for handling and storage. Therefore, the European Automobile Manufacturers Association decided to recommend urea for the on-board production of the reducing agent NH_3 [6]. At present in most applications an aqueous urea solution (AdBlue®, i.e. a solution of 32.5% urea in H_2O) is injected into the exhaust gas stream.

Resulting from the typical spatial constraints of cars, the catalyst volume is aimed to be minimal. However, this is met with difficulties, as the dynamically varying loads of the engine drastically affect the reaction conditions for the catalyst [7]. To avoid overdosing and consequently the release of NH_3 under dynamic conditions a complex strategy is required. Several engineering design variants have been proposed suggesting urea decomposition reactors that are incorporated into the exhaust system or are built as separate units [8,9]. The most effective design introduced so far is an external monolithic hydrolysis catalyst heated by a partial stream of the exhaust gas. For a further optimization of the hydrolysis process a detailed knowledge of the kinetics of the (thermal and catalytic) transformation of urea into ammonia is essential [8].

The conversion of the aqueous urea solution to ammonia consists of two steps. In the first step, the aqueous urea solution is sprayed into the flue gas stream. After evaporation of H_2O, the remaining urea decomposes thermally into ammonia and isocyanic acid according to (1).

$$H_2N{-}CO{-}NH_2(s) \rightarrow NH_3(g) + HNCO(g) \quad (1)$$

In the second step, the isocyanic acid is hydrolyzed over an oxide catalyst yielding ammonia and carbon dioxide according to (2).

$$HNCO(g) + H_2O(g) \rightarrow NH_3(g) + CO_2(g) \quad (2)$$

It should be noted, however, that isocyanic acid can also undergo a series of condensation reactions leading to solid products ranging from cyanuric acid and biuret over ammelide and ammeline and melamine to polymeric forms of melamine [3,8,10]. These high molecular weight compounds have been

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reported [3] to deposit on the walls of the exhaust pipe and inside the monolith channels and are only slowly decomposed under the typical reaction conditions, which leads to severe catalyst deactivation. In order to minimize the formation of these polymeric species, the reaction conditions and the catalysts have to be optimized to maximize the rate of hydrolysis and to minimize condensation/oligomerization reactions of isocyanic acid.

The present work introduces a kinetic model for the overall rate of the HNCO hydrolysis on TiO_2 anatase, which is the well-established catalyst for hydrolysis reactions. Values for the adsorption equilibrium constants of the reactants HNCO and water as well as of the products ammonia and carbon dioxide were determined experimentally from sorption isotherms (by IR spectroscopy and gravimetry) and implemented into the kinetic model. Thus, the sensitivity of the model was enhanced by reducing the number of unknown variables being determined.

2. Experimental

2.1. Catalyst

The hydrolysis catalyst was TiO_2 in anatase form obtained from Süd-Chemie AG and coated onto a metal substrate obtained from Emitec. Textural promoters and/or binders (inorganic sol) were added to enhance the mechanical stability of the coating and to increase the adhesive strength to the metal foil, respectively. This catalyst is a typical formulation used in heavy-duty diesel trucks in the technical application. For studying the sorption of reactants and products by IR spectroscopy TiO_2 from the same source was used in powder form. TiO_2 was synthesized following the sulfate process in which titanium slag obtained by reduction of ilmenite $FeTiO_3$ with coke at around 1200 °C is treated with concentrated sulfuric acid at 100–180 °C [11]. The preparation process of TiO_2 is the origin of sulfate impurities observed by IR spectroscopy, which are discussed in the paper.

The specific surface area of the TiO_2 determined by the BET method was 80 m^2/g.

2.2. Preparation of isocyanic acid

The synthesis of isocyanic acid was carried out by the depolymerization of commercial cyanuric acid catalyzed by Al_2O_3 according to the method developed by Lercher and Zhan [12]. A heated quartz tubular reactor (18 mm i.d.) separated into three sections was used. The first section of the reactor was filled with quartz spheres to preheat the He carrier gas stream. The second section of the reactor contained 15 g of cyanuric acid (sublimation temperature 593–603 K), and the third section of the reactor held the Al_2O_3 catalyst used to depolymerize cyanuric acid. By using a catalyst, the decomposition temperature of the cyanuric acid could be lowered to $T = 643$ K compared to 753 K for thermal decomposition, which leads to a high purity of the product (less than 1 vol.% NH_3 and less than 1000 ppm CO_2). Downstream of the reactor, the gaseous HNCO was condensed in two serial cold traps at 193 K (isopropanol/dry ice). To obtain a CO_2 and NH_3 free product it is essential to bypass the cold traps during start-up of the reaction [13]. The depolymerization has to be performed in the absence of water, as Al_2O_3 not only catalyzes the depolymerization but also the hydrolysis of HNCO.

2.3. In situ infrared spectroscopy

Infrared spectra were measured with a Bruker IFS 88 FTIR spectrometer in a vacuum cell that allows to collect IR spectra *in situ* during activation and adsorption [14]. The spectra were recorded with a resolution of 4 cm^{-1} using a MCT detector. The catalyst samples were pressed into thin, self-supporting wafers ($\sim$5 mg cm^{-2}) and placed in a heatable sample-holder in the center of the IR cell equipped with CaF_2 windows. The samples were heated in vacuum ($p < 10^{-6}$ mbar) to 673 K (10 K min^{-1} increment). After reaching the activation temperature, O_2 with 1 mbar equilibrium pressure was introduced into the cell for 60 min in order to saturate the oxygen vacancies on the surface. The samples were subsequently cooled to 393 K in the O_2 atmosphere and evacuated. With this procedure the white color of the titania sample could be restored indicating the saturation of defect sites of TiO_2.

Ammonia, water, isocyanic acid and carbon dioxide were adsorbed at 393 K at equilibrium pressures between 10^{-4} and 10^{-1} mbar. For isocyanic acid the desorption was investigated by heating the sample from 393 to 673 K in vacuum (10 K min^{-1} increment). The surface coverage of the adsorbate was determined form the integral intensity of the characteristic IR bands.

2.4. Thermogravimetry

The sorption isotherm for water was additionally measured on a Setaram TG–DSC 111 thermoanalyzer. The sample ($\sim$20 mg) was activated at 673 K for 1 h (heating rate 10 K min^{-1}) under vacuum ($p < 10^{-7}$ mbar). Water was adsorbed at 393 K using stepwise pressure increments from 3×10^{-3} up to 16.1 mbar, and the weight increase was measured.

2.5. Kinetic measurements

The experimental set-up used for the kinetic experiments is shown in Fig. 1. The composition of the feed gas was chosen to present a typical diesel exhaust gas, containing 4% H_2O and 10% O_2 with N_2 being the balancing gas [5,15]. The gas flow rates were controlled using electronic mass flow controllers, and water was dosed through a fused silica capillary (0.1 mm i.d.) into the electrically heated heating block by means of a HPLC pump. HNCO was introduced into the system via an additional N_2 stream and a saturator, which was maintained at -30 °C; the standard concentration of HNCO was 500 ppm.

For the kinetic experiments aiming at the individual order of reaction, the concentration of the corresponding reactant or product, respectively, was varied over a reasonable range, and the rate was calculated.