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Materials for thermohydrolysis of urea in a fluidized bed

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ABSTRACT

The production of ammonia from urea was investigated in a fluidized bed reactor in order to avoid the formation of N_2O in the selective non-catalytic reduction (SNCR) process, which occurs when urea is directly injected into an SNCR reactor.

Among about 20 tested materials, γ-Al_2O_3 proved to be the best suited as a fluidized bed material due to its high catalytic activity as well as relatively good stability. Even better catalytic results were obtained with titanium oxide, which was, however, much less attrition resistant than the aluminum oxides. Silicon dioxide and silicates showed only a weak catalytic effect. The tested molecular sieves and zeolites showed catalytic results between those of silicates and alumina. The results of the catalytic tests are in accordance with a two-step mechanism: urea rapidly decomposes to ammonia and isocyanic acid initiated by simple heat transfer from the fluidized material, followed by the rate-determining catalytic hydrolysis of isocyanic acid.

The screening showed that a compromise had to be found for the catalytically active fluidized bed material, since good catalytic properties require high surface areas, which is in conflict with the desired high abrasion resistance of the material. Scale-up experiments in the pilot plant with γ-Al_2O_3 "CAT 250" as the best material among the screening experiments demonstrated that it is possible and straightforward to thermohydrolyze 10.6 kg/h of urea to 6 kg/h ammonia. Gas analyses of the product gas showed that urea was almost completely converted and that only minuscule amounts of isocyanic acid were formed.

1. Introduction

In the last decades, two processes to selectively reduce nitrogen oxide emissions in lean exhaust gases have gained in importance, i.e., selective catalytic reduction (SCR) at low and intermediate temperatures from 200 to 650 °C and selective non-catalytic reduction (SNCR) at high temperatures from 850 to 1100 °C [1–5]. Selective reduction requires a reducing agent that preferentially reacts with the nitrogen oxides in the exhaust gas but not with the residual oxygen. On the strength of past experience, nitrogen containing compounds are best suited for the selective reduction of nitrogen oxides, especially ammonia and ammonia releasing compounds, such as urea, ammonium formate, ammonium carbamate, methanamide, and guanidinium formate [6]. For a long time, ammonia was almost exclusively used as selective reducing agent. However, the high toxicity of this compound requires special safety measures for its storage and handling. While for large-scale plants, this expenditure is justified, for small-scale and vehicle applications, a 32.5% aqueous urea solution proved to be the best applicable reducing agent due to its virtual nontoxicity as well as simple storage and handling properties [7,8].

According to the current standard of knowledge, urea has to be decomposed to ammonia (NH_3) and isocyanic acid prior to the actual NO_x reduction reaction [7].

$$(NH_2)_2CO \rightarrow NH_3 + HNCO \qquad (1)$$

This reaction is endothermic, requiring a substantial heat supply of 185.5 kJ/mol under standard conditions to proceed [9]. Dry urea has a melting point of 132.7 °C. Already at 80 °C, the beginning of decomposition can be observed in the laboratory, but distinct decomposition is not observed below 132 °C.

Besides the main decomposition reaction, which results in ammonia and isocyanic acid, additional side products can be formed [7]. Many large-molecule side products are a direct consequence of the high reactivity of the isocyanic acid. For example, biuret is formed by the addition of HNCO to urea, and triuret, by the addition of HNCO to biuret.

$$(NH_2)_2CO + HNCO \rightarrow H_2N\text{–}CO\text{–}NH\text{–}CO\text{–}NH_2 \qquad (2)$$

$$H_2N\text{–}CO\text{–}NH\text{–}CO\text{–}NH_2 + HNCO \rightarrow H_2N\text{–}CO\text{–}NH\text{–}CO\text{–}NH\text{–}CO\text{–}NH_2 \qquad (3)$$

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A further possibility for isocyanic acid to react is its trimerization to cyanuric acid:

$$3HNCO \rightarrow (CHNO)_3 \tag{4}$$

Finally, cyanuric acid can react even further. By reaction with ammonia ammelide, ammeline and melamine are formed. Even larger molecules are melam and melem, but even these do not complete the list of possible reaction products. In principle, all of the above mentioned compounds decompose at a few hundred degrees Celsius. If their degradation is incomplete due to insufficiently high temperatures or insufficiently long reaction times, deposits might be formed in the exhaust gas system.

However, when urea solution is heated very rapidly, within 1 s, to over 280 °C, only ammonia and isocyanic acid are obtained [10,11]. Moreover, the formed isocyanic acid rapidly and selectively hydrolyses to ammonia and carbon dioxide in the presence of water on many different single and mixed metal oxides [12]:

$$HNCO + H_2O \rightarrow NH_3 + CO_2 \tag{5}$$

This reaction is exothermic with −95.9 kJ/mol under standard conditions; i.e., the hydrolysis of isocyanic acid produces considerable amounts of heat [9]. By addition of reactions (1) and (5), the well-known overall reaction is obtained:

$$(NH_2)_2CO + H_2O \rightarrow 2NH_3 + CO_2 \tag{6}$$

The standard enthalpy of this reaction is 185.5 − 95.9 kJ/mol = 89.6 kJ/mol. Since the thermohydrolysis is usually performed at 250–400 °C, additional energy is required to heat up the substances to this temperature. In the case of aqueous urea solution, excess water has to be vaporized and heated to the final temperature, as well.

In the SNCR process, ammonia is used to selectively reduce NO in a non-catalytic reaction at temperatures from 800 to 1100 °C to nitrogen. Instead of ammonia, urea may also be applied as a reducing agent. However, when using urea, increased concentrations of N_2O can be found, and CO appeared as new side-product [13,14]. A reason for this observation can be found in the radical reactions that are predominant in this temperature range. After the thermolysis of urea to isocyanic acid according to reaction (1), HNCO reacts in the following important radical reactions:

$$HNCO + H^\bullet \rightarrow {}^\bullet NH_2 + CO \tag{7}$$

$$HNCO + {}^\bullet OH \rightarrow {}^\bullet NCO + H_2O \tag{8}$$

The amidogen radical formed in reaction (7) reacts further with NO to elemental nitrogen. The NCO radical from reaction (8), however, results in the formation of N_2O:

$${}^\bullet NCO + {}^\bullet NO \rightarrow N_2O + CO \tag{9}$$

This side-product poses a problem for the SNCR process with urea. In fact, Muzio et al. found 7–25% of the NO converted to N_2O, whereas less than 4% conversion was found in the case of ammonia as the reducing agent [13,14]. The simplified reaction mechanisms of the SNCR process with ammonia and urea are depicted in Figs. 1 and 2, respectively, showing the additional reaction pathways to CO and N_2O for urea. For a comprehensive review of the SNCR process with both reducing agents, please refer to Javed et al. [15]. Proposed measures to reduce the N_2O formation when using urea are higher reaction temperatures, longer residence times [15], the use of microwave-plasma discharge [16], and the use of additives [17].

In this study, we tried a different approach to avoid the formation of N_2O, CO, or other side-products by converting urea upstream to pure ammonia of the actual SNCR reactor. It is known that urea solution may be quantitatively decomposed to ammonia without CO and N_2O formation below 200 °C over TiO_2 as hydrolysis catalyst [18,19]. However, a coated monolith as applied in the automotive sector or a fixed bed reactor is not suitable for larger scales, since the front part of the catalyst will cool down due to the evaporation of water and the endothermic decomposition of the urea. A way out of this problem is the application of a fluidized bed, by which rate limitations by heat and mass transfer are eliminated, even when urea solution is dosed on a large scale. According to concept, urea was decomposed with different catalytically active metal oxides in a fluidized bed reactor on the laboratory and pilot scale. The challenge with this reaction design was to find bed materials that are catalytically active for this reaction and at the same time resistant to the harsh abrasive conditions in the fluidized bed.

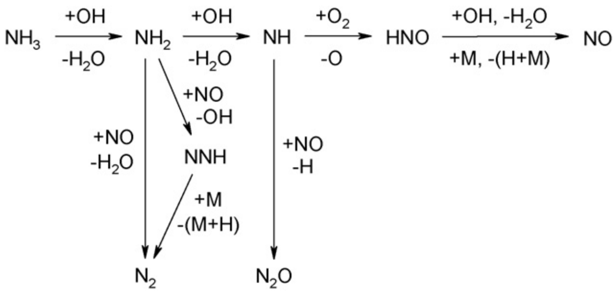

Fig. 1. Simplified reaction mechanism of the SNCR process with ammonia.

2. Experimental

The experimental setup for the thermohydrolysis of urea in fluidized bed reactors on the laboratory scale is shown in Fig. 3. For the screening experiments, four reactors with inner diameters of 20, 25, 50, and 80 mm were used, the most important parameters of which are summarized in Table 1. The concentration of the urea solution was chosen to be as high as possible in order to avoid unnecessary water vaporization; otherwise, the solubility of urea at room temperature allows maximum concentrations up to 50%. For solutions with higher concentrations, trace-heated pipe lines would be required. Therefore, a 50% urea solution was pumped from a storage tank to the reactor, in which the solution was dropped from

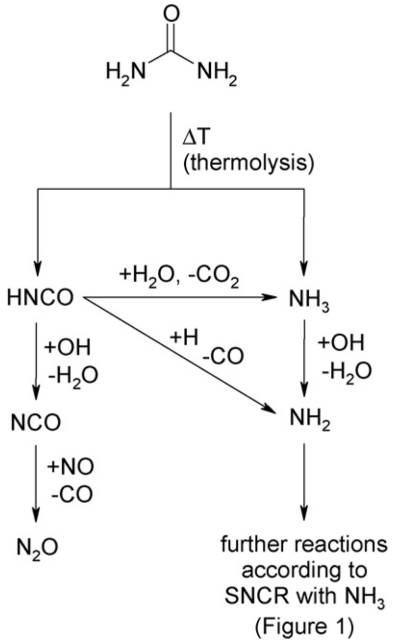

Fig. 2. Simplified reaction mechanism of the SNCR process with urea.

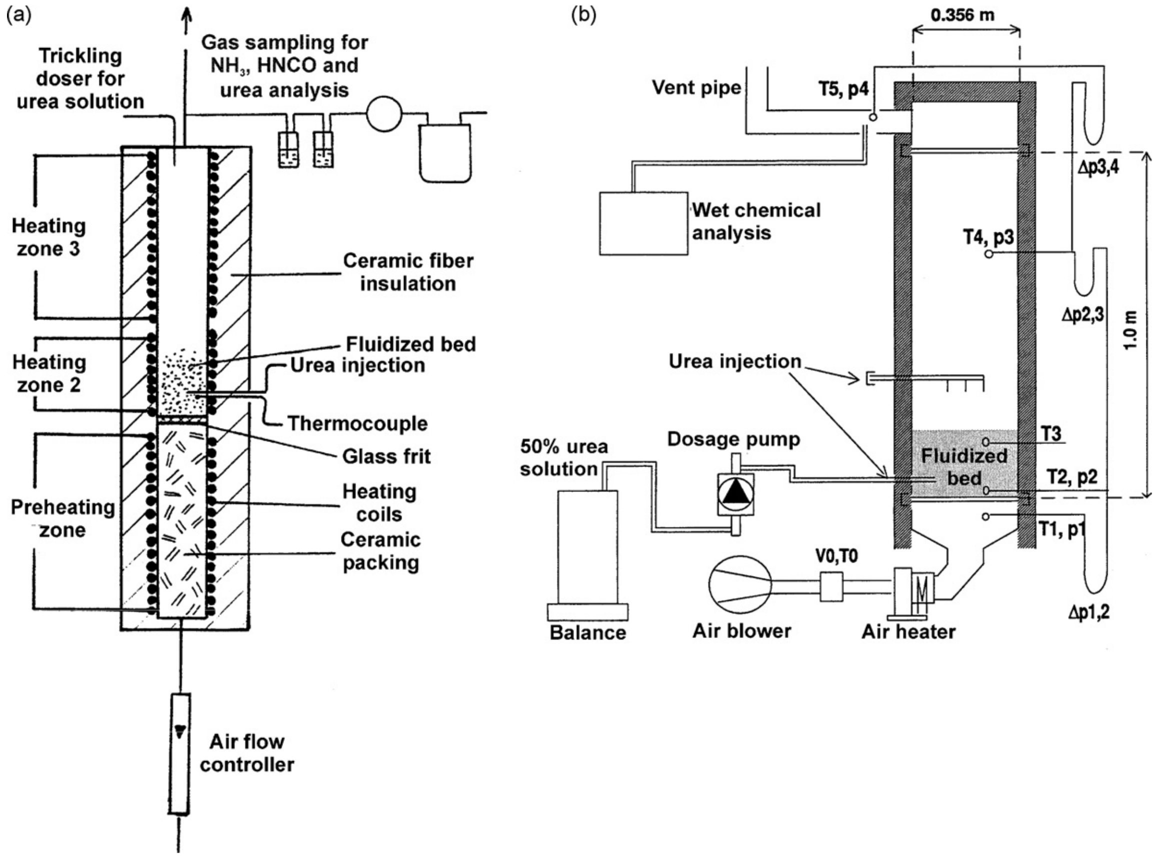

Fig. 3. Experimental setup of the fluidized bed reactor used in the (a) laboratory and (b) pilot plant for the decomposition of urea.

above onto the fluidized bed (Fig. 3a). The average droplet diameter was ca. 2 mm, which was large enough to prevent any entrainment by the fluidizing medium. The droplets were immediately incorporated by the fluidized bed without splashing, when hitting the upper end of the bed. The fluidizing medium, air, entered the reactor from the bottom with a temperature of 450–600 °C. Additional heat was provided by wall heaters, resulting in a bed temperature of 275–280 °C, which was measured slightly below the middle of the bed. The ammonia containing product gas left the reactor at the top.

Different bed materials were tested for the thermohydrolysis of urea in the fluidized bed. The investigated materials were mainly oxides or oxy-hydrates of aluminum, silicon, titanium, magnesium, or their mixtures, molecular sieves, and zeolites (Table 2). All materials except molochite possess large inner surface areas, as expected for these catalysts and support materials. The average grain sizes of the materials were between 0.2 and 2 mm.

The pilot scale experiments were performed in a fluidized bed reactor with a length of 1.0 m and an inner diameter of 356 mm. The reactor was heated to 200–350 °C by ca. 92 $m^3{}_N$/h of hot air, which entered the reactor at a temperature of maximum 590 °C and a speed of 0.21 m/s. The air flow was homogenized by a diffuser plate, which also supported the fluidized bed material. The urea solution could be injected either directly into the bed 100 mm above the air diffuser or from the top onto the fluidized bed 600 mm above the air diffuser. For the pilot experiments, γ-Al_2O_3 "CAT 250" from CU Chemie Uetikon was used, which was milled to a grain size of 0.5–1.0 mm with an average of 0.790 mm and a sphericity of 0.706. 11.44 kg of the resulting material was filled into the reactor as bed material, which had a height of 20 cm in the non-fluidized state.

The ammonia and isocyanic acid concentrations in the off-gas were measured by a wet chemistry method, using two wash bottles in series for the absorption. In the first wash bottle, 50 mL of water was used to absorb isocyanic acid, urea, and part of the ammonia

Table 1
Parameters of the fluidized bed reactors used for the laboratory experiments.

	Glass reactors			Steel reactor
Inner diameter [mm]	20	25	50	80
Length of pre-heater [mm]	150	150	250	400
Bed floor	Glass frit P0/P1	Disc with 1.2 mm holes		
Bed volume [mL]	15	15	60	250
Bed height resting [mm]	50	30	30	50
Bed height during operation [mm]	90	60–70	65–80	80–100
Smallest grain diameter [mm]	0.2–0.315	0.315–0.50	0.50–0.63	1.0–1.25
Largest grain diameter [mm]	ca. 2	1.0–1.25	ca. 2	1.0–1.25
Air flow [L_N/h]	150–640	150–190	1800–4700	6800–9400
Urea concentration [%]	5 or 50	50	50	50
Urea solution dosage [g/h]	5–190	50–190	190–350	800–2400
N_{in} [mol/h]	0.08–3.2	0.08–3.2	3.2–5.8	13.1–48

Table 2
Bed materials tested for the thermohydrolysis of urea in the fluidized bed.

Bed material	Trade name	Provider	S_{BET} [m^2/g]	Particle diameter [mm]
γ-Al_2O_3	Uetikon 1	CU Chemie Uetikon	300	2.0
γ-Al_2O_3	2035	Degussa		
α-AlOOH (boehmite)	Pural	Condea	200	0.2–0.315
γ-Al_2O_3	Puralox	Condea	194	0.2–0.315
γ-Al_2O_3	CAT 250	CU Chemie Uetikon	250	0.5–0.63
γ-Al_2O_3	Compalox			
γ-Al_2O_3		Condea	88	1.0–1.25
α-Al_2O_3	Spheralite 512 S	Rhone-Poulenc	8	1.6–2.0
γ-Al_2O_3	Spheralite 537	Rhone-Poulenc	190	1.6–2.0
TiO_2	Macrosorb T			0.2–0.315
TiO_2	7702	Degussa	40	0.50–0.63
V_2O_5/WO_3–TiO_2 (1% V_2O_5)	Commercial SCR catalyst	Argillon		0.315–0.5
SiO_2	Aerosil 200	Degussa	>160	0.5–0.63
$AlSiO_x$ (molochite)				0.315–0.5
$MgSiO_x$	Florisil	J.T. Baker	298	0.5–0.63
Molecular sieve 5 Å		Merck		0.2–0.315
Molecular sieve 13X		Fluka		0.5–0.63
H-MOR (module = 29.5)	KM-621	Degussa		Cylinder of 2·(2–4) mm
H-ZSM-5 (module = 45)	KM-622	Degussa		Cylinder of 2·(2–4) mm
Dealuminated Y (module > 200)	Wessalith DAY	Degussa		Cylinder of 2·(2–4) mm

from 20.0 L of exhaust gas. Quantitative absorption was achieved in the second wash bottle, containing 50 mL hydrochloric acid and bromophenol blue as indicator. The concentration of the hydrochloric acid was between 0.1 and 2 M, depending on the composition of the exhaust gas. The pH value had to be sufficiently low to quantitatively absorb the ammonia that was not captured in the first wash bottle but had to be higher than 5.0 after merging of the absorption solutions in order to prevent the hydrolysis of isocyanic acid. The joined solutions were replenished with water to a total volume of 200 mL, and the ammonia concentration was measured with an ammonia electrode. By the subsequent addition of hydrochloric acid to the solution the isocyanic acid was hydrolyzed and determined with the ammonia electrode as the sum of $NH_3 + HNCO$. In order to apply this method, ammonia and isocyanic acid had to be measured under exactly the same conditions, i.e., sample and calibration solution were adjusted to the same ionic concentration, the solutions were kept at the same temperature (±0.2 °C), and the concentrations of ammonia and isocyanic acid were measured without time-delay to prevent a drift of the electrode. The yields of the reaction products ammonia and isocyanic acid are referred to the molar nitrogen feed. The urea concentration was analyzed by absorption of a fixed volume of exhaust gas in 100 mL of water. The resulting solution of ammonia, isocyanic acid and urea was adjusted to pH 5.0 with 0.1 M hydrochloric acid by an automatic titrator. By addition of the enzyme urease (20 mg urease dissolved in 5 mL water, adjusted to pH 5.0), urea hydrolyzed to carbon dioxide and ammonia, which was neutralized by the automatic titrator within, typically, 40–60 min. The amount of hydrochloric acid needed for neutralization was converted to the amount of urea emitted from the reactor (1.00 mL 0.1 M HCl corresponds to 3.00 mg urea). With this method, urea amounts down to 0.3–0.5 mg could be detected in a 100-mL sample solution even in the presence of large ammonia concentrations (0.1 M, 100–200 mg/100 mL). A pH value of 5.0 was chosen for the measurement because the solution is only weakly buffered at this point, resulting in the highest possible pH change by the formation of ammonia.

3. Results and discussion

3.1. First tests with γ-Al_2O_3 "Uetikon 1" as fluidized bed material for the urea thermohydrolysis

First, aluminum oxide from Chemie Uetikon, denoted as γ-Al_2O_3 "Uetikon 1," with a particle diameter of 0.5–0.63 mm was tested in the 20 mm reactor at an air flow of 150 and 175 L_N/h (not included in Table 3). A diluted urea solution with only 5% urea was dosed directly into the fluidized bed. The experiments showed that it is possible to quantitatively decompose such a low-concentration solution in the temperature range from 135 to 250 °C. The HNCO yield was usually below 2%. When the urea concentration was increased from 5 to 50%, the lower temperature limit for total conversion increased to 225 °C for a dosage rate of 21 g/h of urea solution. Below this temperature, deposits were formed in the reactor, which partially blocked the fluidized bed. However, the deposits could be decomposed again when the reactor was heated to 350–400 °C. From HPLC analyses of deposits in urea SCR systems, it is known that these deposits mainly consist of cyanuric acid with smaller amounts of biuret [20]. Cyanuric acid decomposes quantitatively to isocyanic acid at temperatures above 350 °C [21], which is in accordance with the observed minimum reactor temperature to remove the deposits.

Higher dosage rates could not be achieved, as the bed material is locally cooled at the injection spot by the urea solution, which easily results in deposits. However, higher dosage rates could be applied by dropping the urea solution from the top onto the fluidized bed. The drops were always immediately incorporated into the bed type. No clustering or agglomeration of particles could be observed, even for short time, which indicates very fast heat transfer and material conversion for this type of dosage.

By using smaller particles of 0.2–0.315 mm, a larger active surface was generated, and, at the same time, the volume of the fluidized bed increased for the same air flow. Moreover, this measure also induced a higher degree of turbulence in the bed. Thereby, about 190 g/h of a 50% urea solution could be virtually completely converted to ammonia in the temperature range from 225 to 300 °C (Table 3). Downstream of the reactor, less than 0.5% of urea could be found to be undecomposed.

An important parameter for fluidized beds is the air flow rate. Therefore, in another experiment, with grains of the size 0.5–0.63 mm, the air flow was increased stepwise from 255 over 373 to 515 L_N/h (not included in Table 3). A higher air flow resulted in a lower residence time, which reduced the thermohydrolysis and increased urea emissions from 1.3% over 1.7–2.6%. The corresponding results for the HNCO yields were 6, 5, and 13%. One may ask if the HNCO emissions might be due to a water deficit in the system, since water was not dosed with the air flow. However, there should be more than enough water in the system to guarantee complete hydrolysis. The 50% urea solution used contains

Table 3
Test of fluidized bed materials for the thermohydrolysis of 50% urea solution.

Bed material	Particle diameter [mm]	Reactor diameter [mm]	Volume of bed material [mL]	Air flow [L_N/h]	Urea dosage type	Urea solution dosage [g/h]	Bed loading [g/(h·mL)]	Fluidized bed temperature [°C]	Y_{NH_3} [%]	Y_{HNCO} [%]	Urea slip [%]
γ-Al_2O_3 "Uetikon1"	0.2–0.315	20	15	150	From top	185	6.2	300	99	1	0.4
								275	99	1	0.4
								250	100	0	0.4
								225	102	0	0.5
								200	96	1	1.2
γ-Al_2O_3 "Uetikon1"	0.50–0.63	25	15	520	From top	185	6.2	300	97	4	1.2
								275	96	5	1.3
								250	84	12	2.6
								225	73	16	3.9
γ-Al_2O_3 "Compalox"	0.50–0.63	25	15	520	From top	185	6.2	300	96	0	1
								275	95	0	0.7
								250	96	1	0.9
								225	93	2	2.3
γ-Al_2O_3 "Puralox"	0.2–0.315	20	15	150	From top	185	6.2	300	96	5	0.4
								275	99	5	0.3
								250	96	4	0.4
								225	98	4	0.4
								200	99	4	0.9
γ-Al_2O_3 "CAT 250"	0.50–0.63	50	60	1860	From top	340	2.9	300	97	2	0.7
								275	98	3	0.6
								250	96	2	0.6
								225	97	3	0.6
								200	95	3	1.2
γ-Al_2O_3 "CAT 250"	1.0–1.25	50	60	3900	From top	350	2.9	300	96	0	1.9
								275	95	0	1.8
								250	94	1	1.6
								225	83	5	2.4
								200	66	15	5
γ-Al_2O_3 "CAT 250"	1.0–1.25	50	60	3900	Into bed	350	2.9	300	94	0	1.1
								275	94	1	1.2
								250	93	1	1.3
								225	89	6	2.3
γ-Al_2O_3 "CAT 250"	1.0–1.25	25	15	1109	From top	186	6.2	300	101	0	1.9
								275	100	2	1.7
								250	99	3	1.8
								225	84	12	3.2
γ-Al_2O_3 "Condea"	1.0–1.25	20	15	554	From top	185	6.2	300	89	5	5.8
								275	78	16	6.1
								250	69	23	6.3
γ-Al_2O_3 "SPERALITE 537"	1.0–1.25	50	60	3900	Into bed	350	2.9	300	94	3	1.9
								275	91	5	2.2
								250	85	7	3
								225	72	13	5
α-Al_2O_3 "SPERALITE 512 S"	1.6–2.0	50	60	4700	Into bed	290	2.4	300	47	31	9.1

Table 3 (*Continued*)

Bed material	Particle diameter [mm]	Reactor diameter [mm]	Volume of bed material [mL]	Air flow [L_N/h]	Urea dosage type	Urea solution dosage [g/h]	Bed loading [g/(h·mL)]	Fluidized bed temperature [°C]	Y_{NH_3} [%]	Y_{HNCO} [%]	Urea slip [%]
α-AlOOH (boehmite)	0.2–0.315	20	15	150	From top	185	6.2	300	99	3	0.8
								275	97	4	0.5
								250	96	3	0.8
								225	95	5	0.6
								200	96	5	0.7
SiO_2 “Aerosil”	0.50–0.63	25	15	410	From top	185	6.2	300	70	25	4.2
$AlSiO_x$ (molochite)	0.22–0.50	20	15	150	From top	4.5	0.02	400	61	25	n.d.
								350	55	34	n.d.
								300	38	33	n.d.
								250	24	20	n.d.
$MgSiO_x$ “Florisil”	0.50–0.63	25	15	400	From top	185	6.2	300	90	8	2.3
								275	86	7	2.1
								250	83	9	3
TiO_2 “Macrosorb T”	0.2–0.315	20	15	150	From top	185	6.2	300	104	1	0.7
								275	102	1	0.8
								250	95	4	2.7
								225	62	8	5.9
TiO_2 “7702”	0.50–0.63	25	15	520	From top	185	6.2	300	98	0	1.5
								275	99	0	1.2
								250	99	0	1
								225	99	1	1
								200	98	2	1.6
$V_2O_5/WO_3–TiO_2$	0.315–0.50	25	15	356	From top	185	6.2	300	96	1	0.6
								275	96	1	0.6
								250	90	6	1.1
								225	87	6	1.5
								200	82	6	2.9
Molsieve 5Å	0.2–0.315	20	15	150	From top	94	3.1	300	93	7	0.9
								275	58	21	7.2
Molsieve “13X”	0.50–0.63	25	15	410	From top	185	6.2	300	93	2	0.7
								275	76	13	1.2
								250	43	20	5.5
H-MOR	ca. 2·(2–4)	50	60	3900	From top	350	2.9	300	85	4	2.6
								275	83	6	2.8
H-ZSM-5	ca. 2·(2–4)	50	60	3900	From top	350	2.9	300	72	19	3.1
								275	66	25	3.6
Dealuminated Y	ca. 2·(2–4)	50	60	3900	From top	350	2.9	300	52	35	5
								275	51	36	5.6

3.3 times more water than the stoichiometric amount required for complete hydrolysis. Moreover, it is known from previous investigations that the surfaces of the applied metal oxides are easily hydrated in the presence of water. These hydrated particles will move in the fluidized bed and are able to rapidly hydrolyze the very reactive adsorbed isocyanate groups even at the lower end of the bed [12,22–24]. In a previous study we have shown that small water pulses are sufficient to hydrolyze isocyanate species adsorbed on TiO_2 anatase at a temperature of only 150 °C [22]. On the other side it is important to note that although HNCO is very easily hydrolyzed on the surface of metal oxides, it is also known to be quite stable in the gas phase in the presence of water [7]. Therefore, gaseous isocyanic acid, formed by thermolysis of urea in the upper part of the bed, may emit unchanged, if it does not adsorb on the particle surface.

3.2. Screening of potential bed materials for the thermohydrolysis of urea in the fluidized bed

After these first experiments with γ-Al_2O_3 “Uetikon 1,” a number of oxides or oxy-hydrates of aluminum, silicon, titanium, magnesium, or their mixtures, and molecular sieves were tested for their catalytic properties in thermohydrolysis of urea in the fluidized bed. All materials except molochite had large inner surface areas, as expected for these catalyst and support materials. The average grain sizes of the materials were between 0.2 and 2 mm, but particles with a diameter from 0.5 to 0.63 mm were preferred when available in order to make the results comparable. Table 3 shows the results of the different screening experiments of the various catalysts. It was found that the bed material must have catalytic properties to enhance the thermohydrolysis of urea, which requires a high surface area. This is only possible for porous materials, which are usually more fragile than smooth grains. As a consequence, there is a trade-off between high catalytic activity and high stability of the bed materials, for which a compromise had to be found.

α-AlOOH (boehmite), which was only available with a grain size below 0.5 mm, produced high ammonia yields and 3–5% isocyanic acid at a urea slip of $\leq$0.8% between 200 and 300 °C, which is slightly worse than for γ-Al_2O_3 “Uetikon 1.” The γ-Al_2O_3 “Puralox” material, which was also only available with a small grain size, showed comparable results as α-AlOOH (boehmite) at a somewhat smaller urea slip. From the producer of γ-Al_2O_3 “Uetikon 1,” we received a similar material, γ-Al_2O_3 “CAT 250,” which should be thermally more stable. Both materials showed good hydrolysis activities for a grain size of 0.5–0.63 mm, but the aluminum oxide “CAT 250” showed higher catalytic activities at temperatures below 250 °C. γ-Al_2O_3 “Compalox” cannot be used as fluidized bed material. The abrasion was so high that 50% of the material was decayed and blown out after 5 h of test duration. However, it had very good hydrolysis properties for urea decomposition. A test of the γ-Al_2O_3 “Condea” spheres with a diameter of 1.0–1.25 mm showed a markedly lower thermohydrolysis activity than “CAT 250” did. At 275 °C and at the same bed loading of 6.2 g/(h mL), 16% HNCO and 6.1% urea were found with the “Condea” spheres in the product gas, compared to 2% HNCO and 1.7% urea for “CAT 250.” α-Al_2O_3 “Spheralite 512 S” spheres with a diameter of 1.6–2.0 mm and a BET surface area of only 8 m^2/g showed very low thermohydrolysis activity. At 300 °C, the isocyanic acid yield was 31%, and the urea slip, 9%, for which reason we abstained from further experiments with this material. Slightly better results were obtained with γ-Al_2O_3 “Spheralite 537” spheres of the same diameter (not included in Table 3), but with a much higher BET surface area of 190 m^2/g. Since Spheralite spheres were not available with a diameter of 1.0–1.25 mm, a direct comparison with “CAT 250” was not feasible. Therefore, a fraction of 1.0–1.25 mm spheres was prepared by milling from the 1.6–2.0 mm spheres and tested as bed material. The results showed that the smaller grains indeed showed higher conversions as expected, but the activity was still clearly below that of “CAT 250.”

Titanium oxide was also tested as a promising material for the thermohydrolysis of urea. TiO_2 “Macrosorb T,” which was only available with a diameter of 0.2–0.315 mm, was remarkably active between 275 and 300 °C, comparable with γ-Al_2O_3 “Uetikon 1.” However, the isocyanic acid and urea emissions steeply increased at lower temperatures, and the material was not abrasion resistant. Another titania material from Degussa, TiO_2 “7702,” showed excellent thermohydrolysis activities, with values surpassing even those for γ-Al_2O_3 “Uetikon 1” below 250 °C. However, this material also suffered from high abrasion, making it not applicable as fluidized bed material.

Besides pure titanium dioxide, a titania-based SCR catalyst was also tested. An extruded V_2O_5/WO_3–TiO_2 catalyst with 1% V_2O_5 from Argillon was crushed and sieved, and the 0.315–0.5 mm fraction was used as bed material. The measured performance was comparable to that of γ-Al_2O_3 “Uetikon 1.” This result is not surprising in view of the high NO_x reduction activity of extruded V_2O_5/WO_3–TiO_2 catalysts in the SCR process, where urea aerosols hit the frontal area of the monolith [7]. Only very low amounts of ammonia and no isocyanic acid emissions are found downstream of the catalyst, which proves the excellent activity of vanadia-based SCR catalysts for urea decomposition.

With SiO_2 “Aerosil-200” as typical silica material, 25% isocyanic acid was still found in the product gas at 300 °C. At 275 °C and below, measurements were no longer possible because the fluidized bed was clogged by unhydrolyzed urea and collapsed. Besides pure silica with its low thermohydrolysis activity, aluminum and magnesium silicates were also tested. $AlSiO_x$ (molochite) is a typical fluidized bed material with low surface area, which is highly temperature stable. However, a fluidized bed with $AlSiO_x$ grains from 0.315 to 0.5 mm showed almost no activity for the isocyanic acid hydrolysis. The bed could only be weakly loaded with urea, and even at 400 °C, 25% HNCO was still found in the product gas. With $MgSiO_x$, much worse results were obtained than in the comparable experiments with CAT 250: at 250 °C, 9% HNCO and 3.0% urea were found, whereas with CAT 250, 2% HNCO and 0.6% urea were measured.

A variety of molecular sieves and zeolites were also tested. All these samples suffered from high abrasion, which prevents the application of this type of materials in the fluidized bed. With a 5-Å molecular sieve (grain size 0.2–0.315 mm), only 7% isocyanic acid and 0.9% urea were obtained in the product gas at 300 °C. However, at 275 °C, already 21% isocyanic acid and 7% urea were observed. Molecular sieve 13X showed similar results as the 5-Å molecular sieve. Again, the isocyanic acid yield and the urea emissions steeply increased at 275 °C and below. In the series H-MOR, H-ZSM-5, and dealuminated Y (DAY), the silica to alumina ratio (module) increases from 29.5 over 45 to >200. That means that the fraction of polar charged alumina centers decreases in this order, which makes the zeolite more hydrophobic. Although all zeolites were only available as large cylinders with dimensions of 2·(2–4) mm, H-MOR proved to be a highly active thermohydrolysis material for urea. At 300 °C, only 4% HNCO and 2.6% urea were found. With H-ZSM-5, 19% HNCO and 3.1% urea were found under comparable conditions. Finally, DAY showed only a small catalytic effect. At 275 and 300 °C, ca. 35% isocyanic acid and 5% urea were found downstream of the fluidized bed.

The results of the activity tests with the different bed materials are comparable to those of a model gas study on the isocyanic acid hydrolysis over different powdered single and mixed metal oxides. Piazzesi found that titanium oxide in the anatase modification was most active for the hydrolysis of HNCO (Fig. 4) [12]. Alumina was a less efficient catalyst for this reaction than titania, and silica showed only low activity. This order of activities was also found for the ther-

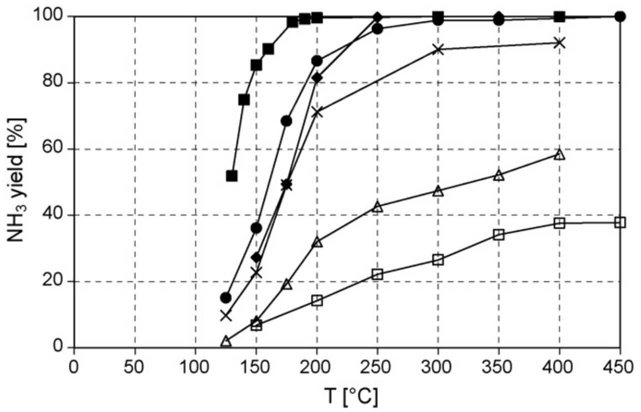

Fig. 4. Activity of different metal oxides for the hydrolysis of isocyanic acid in the plug flow reactor [11]. $m_{cat} = 150$ mg, flow rate = 200 L_N/h, inlet flow composition: 1000 ppm HNCO, 5% H_2O, 10% O_2, and N_2 balance. (♦) Al_2O_3, (□) SiO_2, (△) Al_2O_3/SiO_2 (15:85), (×) Al_2O_3/SiO_2 (24:76), (■) TiO_2 anatase, and (●) TiO_2 rutile.

Table 4

Test of the abrasion resistance of γ-Al_2O_3 "CAT 250" in the fluidized bed with and without water dosage. Volume of bed material = 300 mL. Weight of bed material after drying at 250 °C in air = 177.0 g. Air flow = 7400 L_N/h. Air temperature = 560–570 °C. Fluidized bed temperature = 270–280 °C. Water dosage (when applied) = 1030 g/h.

Time [h]	Catalyst weight		Abrasion		
	Start [g]	End [g]	[g]	%/24 h	mg/h
Water dosage					
3.0	177.0	174.8	2.2	10.0	740
12.0	174.8	173.2	1.6	2.4	174
25.0	173.2	171.1	2.1	2.2	160
37.0	171.1	169.7	1.4	1.6	116
Without water dosage					
55.0	169.7	165.8	3.9	3.1	217
77.0	165.8	165.4	0.4	0.3	18
99.0	165.4	164.8	0.6	0.4	29
339.0	164.8	16.1	4.7	0.3	19
Water dosage					
411.0	160.1	150.6	9.5	2.0	132

mohydrolysis of urea in the present study. TiO_2 "7702" was also found to be more active than alumina for the decomposition of urea, and silica was again the least active in this row. These similar results suggest that the hydrolysis of isocyanic acid might be the rate-determining step under the reaction conditions in the fluidized bed, and that the preceding thermolysis of urea to ammonia and isocyanic acid is indeed fast, as already claimed by Schmidt [10,11].

In another work, the excellent hydrolysis properties of H-ZSM-5 (module = 28) for isocyanic acid were described [25]. The H-ZSM-5 sample used in our investigation did not show such a high activity, which might be related to its high module of 45, i.e., the rather low alumina content. In this aspect, the H-MOR sample with a module of 29.5 seems to be better comparable. Both samples with almost the same module also showed similarly high activities for the hydrolysis of isocyanic acid and the thermohydrolysis of urea, respectively. When catalytic materials are screened for the application as fluidized bed material, besides the thermohydrolysis activity, the abrasion resistance is a decisive selection parameter. On this basis, aluminum oxide seems to be the best compromise due to its good catalytic activity as well as high stability.

3.3. Detailed test of γ-Al_2O_3 "CAT 250" as fluidized bed material for the urea thermohydrolysis

Due to the promising results with γ-Al_2O_3 "CAT 250," this catalyst was tested as bed material in more detail. First, the type of urea injection was varied between direct injection into the fluidized bed and injection from above onto the bed. The results in Table 3 show that the direct injection into the bed resulted in a higher conversion and a lower urea slip. However, the main problem with the direct injection was the required high injection speed in order to avoid deposits at the capillary tip. These deposits slowly grew and clogged the bed material, which finally collapsed. On the other hand, if the injection rate of the solution was too high, it reached the reactor wall, where the urea only partially decomposed and, as a consequence, again formed deposits.

A principal problem of fluidized beds is the loss of bed material due to attrition. Therefore, the abrasion resistance of γ-Al_2O_3 "CAT 250" was tested in a long term experiment with water dosage as a substitute for urea solution in the large laboratory reactor with 80 mm inner diameter. The comparison of the experiments with and without water dosage under otherwise equal conditions revealed that abrasion was more pronounced in the presence of water (Table 4). High fluctuations of the abrasion rate were found with values between 1.4 and 10%/d. An analogous experiment without water dosage showed abrasion rates between 0.3 and 3.1%/d. The long term experiments especially showed that the abrasion was more pronounced with water dosage than without. A possible explanation might be the thermal shock when the water ($T < 100$ °C) strikes the hot particles ($T > 250$ °C) or the weakening of the particle surface caused by structural changes through adsorption and desorption of water, i.e., the conversion of surface oxides to hydroxides and vice versa.

After the laboratory tests, the thermohydrolysis of urea was studied in the pilot scale in order to check if it is also possible to produce ammonia on a large scale without undesired side products, such as isocyanic acid. Table 5 summarizes the reaction conditions and the results of the pilot plant experiments with 11.44 kg (20 L) of γ-Al_2O_3 "CAT 250" as the bed material. In the first set of experiments, the reaction temperature was reduced stepwise from 300 to 230 °C. The analysis of the product gas showed that the urea emissions were very low and did not increase with lowering the exhaust gas temperature. The urea dosage was then increased to 21.2 kg/h 50% urea solution (10.6 kg/h of urea) at a constant bed temperature of only 251 °C. The most important result is that even this high amount could be converted to ammonia without an increase of the isocyanic acid or urea concentration in the product gas. It has to be stressed that this value was a result of the maximum dosage capacity of the urea pump and not due to a limit of the reaction design.

When the injection type was changed to urea injection from top onto the fluidized bed, similar low urea emissions were detected. On the basis of the gas analysis, this setup had no drawbacks compared to injection into the fluidized bed. However, small deposits of urea and bed material were found at the injection nozzle, which remained cold in this experimental setup and was not constantly cleaned by the moving bed material as it was for the in-bed injection.

After 68 h, the bed material was removed and investigated. The weight of the bed material was reduced to 9.6 kg, which corresponds to a loss of 16%. A sieve analysis of the fresh and the used material showed that the fractions with small particles were larger after 68 h of operation (Fig. 5). The finest fraction below 0.5 mm was markedly increased, whereas the large particle fraction (0.8–1.0 mm) was reduced by 12%.

Fig. 6 gives an indication for the loss of bed material. For that purpose, the pressure drop over the bed was plotted versus the operating time. The pressure drop is directly proportional to the weight of the bed material. The strong decrease after the start of operation is clearly visible, which can be explained by the abrasion of sharp corners and edges of the grains. With increasing operat-

Table 5
Pilot plant tests of the thermohydrolysis of 50% urea solution over γ-Al_2O_3 "CAT 250" as the fluidized bed material. Volume of bed material = 20 L. Weight of bed material = 11.44 kg.

Air flow [$m^3{}_N$/h]	Total gas flow [$m^3{}_N$/h][a]	Urea dosage type	Urea solution dosage [kg/h]	N_{in} [mol/h]	Bed loading [g/(h mL)]	T_{air} [°C]	T_{bed} [°C]	$\Delta p_{1,2}$ [mmWs]	$\Delta p_{2,3}$ [mmWs]	Y_{NH_3} [%]	Y_{HNCO} [%]	Urea slip [%]
91.6	108.1	Into bed	16.6	277	0.41	579	303	271	79	94	<1	0.2
91.3	107.6	Into bed	16.4	273	0.41	546	280	249	78	95	<1	0.2
92.2	108.6	Into bed	16.6	276	0.41	534	270	257	78	95	<1	0.2
92.2	108.6	Into bed	16.5	275	0.41	521	260	246	79	95	<1	0.3
92.6	109.2	Into bed	16.6	277	0.42	510	249	252	78	93	<1	0.4
93.0	109.6	Into bed	16.7	279	0.42	501	240	246	77	94	<1	0.3
93.0	109.7	Into bed	16.8	280	0.42	489	230	242	77	95	<1	0.3
93.6	111.1	Into bed	17.6	293	0.44	525	251	268	78	92	<1	0.4
93.4	112.4	Into bed	19.1	319	0.48	544	251	275	78	93	<1	0.5
93.4	114.4	Into bed	21.2	352	0.53	570	251	296	77	94	<1	0.3
93.6	114.7	From top	21.2	353	0.53	569	249	356	73	93	<1	0.3
93.3	114.4	From top	21.2	353	0.53	547	230	370	75	93	<1	0.3

[a] Total gas flow = air flow + thermohydrolysis gas flow.

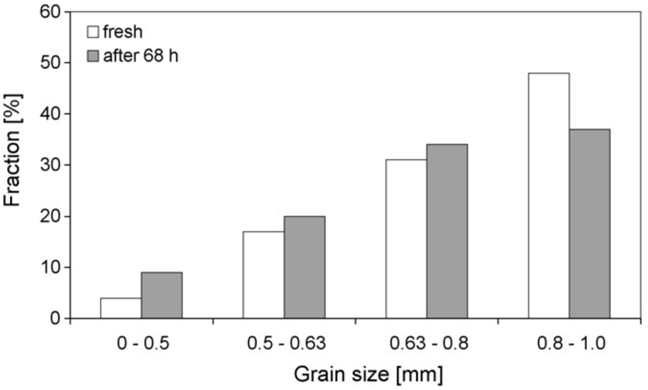

Fig. 5. Sieve analysis of γ-Al_2O_3 "CAT 250" in the fresh state and after 68 h of operation as a fluidized bed material for the thermohydrolysis of urea in the pilot plant.

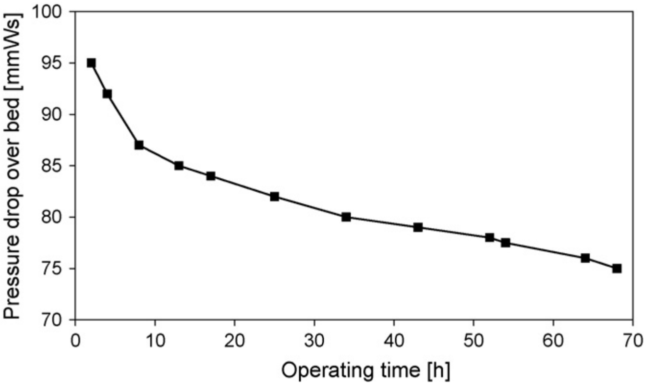

Fig. 6. Loss of bed material during operation of the pilot plant measured as pressure drop over the fluidized bed vs. time.

ing time, the curve plateaus and seems to stabilize at a loss rate of 0.2%/h.

4. Conclusions

The screening of different materials for the thermohydrolysis of urea in the fluidized bed laboratory reactors revealed that the bed material must be catalytically active for this reaction as well as highly stable to withstand the harsh mechanical stress within the fluidized bed. Aluminum oxides proved to best meet these requirements, especially the aluminum oxides "Uetikon1" and "CAT 250" in the γ-modification. For these two aluminum oxides, the urea emissions remained below 1.3% for almost all reaction conditions. Both γ-Al_2O_3 materials showed good hydrolysis activities, whereas the aluminum oxide "CAT 250" displayed better catalytic activities at temperatures below 250 °C. The lowest possible bed temperature with this material was around 230 °C, but at still lower bed temperatures, the ammonia yield decreased, the urea emissions increased, and the bed finally clogged. The highest possible temperature was mainly given by the start of ammonia oxidation around 450 °C.

The scale-up experiments in the pilot demonstrated that the urea thermohydrolysis can be performed in a fluidized bed of γ-Al_2O_3 without larger problems for the application in stationary SNCR processes. It was possible to quantitatively decompose 21.2 kg/h of a 50% urea solution at 230 °C to ca. 6 kg/h ammonia. For the tests, a 50% aqueous urea solution was used, which has a freezing point of 15.2 °C. It is reasonable to use a standard 32.5% urea solution in practice, which is commercialized under the trade name AdBlue for SCR applications in the vehicle, due to its much lower freezing point of −11 °C. While the catalytic properties of γ-Al_2O_3

"CAT 250" were satisfactory, the abrasion of the material and the involved changes of its properties (grain size distribution, average grain diameter, and others) were larger than expected. As a consequence, the loss of material due to blowing out of fine particles was too high at a rate of 0.2%/h. On the other hand, a small constant level of abrasion could help to clean the bed and to maintain its high catalytic activity.

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