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Urea Preparation by Oxidative Carbonylation of Ammonia

A.R. Elman and V.I. Smirnov

Rostkhim, Ltd., Moscow 105118, Russia

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Abstract: Effective one-stage method of urea preparation by catalytic oxidative carbonylation of ammonia in liquid phase is developed. The method allows to prepare urea with productivity of ~530 g/(L·h) in sufficiently mild conditions (total pressure ~30 bar, 45 °C). The process is characterized by high selectivity (near 100%) i.e. byproducts separation is not needed. Almost all CO is consumed during the process, this substantially diminishes the waste-gas purification costs and raises the process environmental characteristics; the only byproduct is water.

Key words: Urea, ammonia oxidative carbonylation, selenium, heat efficiency.

1. Introduction

More than fifty methods of urea preparation are known [1]. But not all of them are suitable for synthesis of small urea quantities. Such a small scale syntheses are needed, for example, for preparation of urea labelled with carbon or nitrogen isotopes. So, traditional industrial process of urea production based on CO_2 and NH_3 uses very drastic conditions (180-230 °C and 120-250 bar) [2]; at the same time equilibrium yield of product is not high (53% at 185 °C) and intermediate ammonia carbamate recycling is needed. So called “cyanide” methods of urea preparation [3] use very toxic compounds and also they are multistage and this leads to high losses of isotope label.

One of convenient urea synthesis methods is CO and ammonia interaction proceeding in the presence of elementary sulfur [4] (Eq. (1)). With the stoichiometric sulfur quantities the reaction proceeds at a temperature of 100-105 °C and pressure of 20-30 bar with the yield of 91%.

$$CO + 2NH_3 + S = CO(NH_2)_2 + H_2S \quad (1)$$

If selenium is used instead of sulfur the process proceeds at sufficient milder conditions: at room temperature and atmospheric pressure in tetrahydrofuran as a solvent the urea yield during 5.5 h achieves 94% [5]. The reduced Se^{2-} formed in the reaction is unable to carry out the process repeatedly after addition of starting reagents (CO and NH_3). The addition of oxygen in the presence of SeO_2 allows catalytic course of the reaction [6], but the catalyst activity is not high -52.7 h^{-1} (30 °C, 40 bar).

The purpose of our work was investigation of urea catalytic synthesis using CO and NH_3 in the presence of metal selenium powder and also increasing the process efficiency taking into account the influence of the reaction heat.

2. Materials and Methods

Tetrahydrofuran (THF) was purified from peroxides by boiling over Cu_2Cl_2 followed by distillation according to the known method [7]. Other reagents were used without additional purification.

The reaction was carried out in a glass reactor placed into diamagnetic stainless steel autoclave. Autoclave with a jacket was equipped with magnetic stirrer, vessel for dosing liquid ammonia and two calibrated

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Corresponding author: A.R. Elman, head of laboratory, Ph.D., main research fields: carbonylation reactions, catalysis, chemical technology. E-mail: elmanar@yandex.ru.

reservoirs for carbon monoxide and oxygen loading into the reactor (Fig. 1).

Certain quantity of selenium powder and solvent was loaded into the glass reactor and then the reactor was placed into the autoclave which was sealed and twice purged with nitrogen (5 bar). Further ammonia in required quantity was input into the reactor, and then we heated it up to required temperature, loaded carbon monoxide and added oxygen after 3 min. Pressure drop was observed during the reaction.

After reaction has stopped (ceasing of pressure drop) we switched off the stirrer, cooled the autoclave and discharged residual gas. If necessary methanol was added to dissolve urea obtained. Urea solution was separated from selenium by filtration and filtrate was additionally clarified by passing it through a column with activated carbon (15 × 1.1 cm, fraction 160-315 μm), then the solvent was evaporated under vacuum.

An isolated urea was identified by IR, NMR spectroscopy, electro spray ionization mass-spectrometry (ESI-MS) and by the melting point. IR spectra were registered using Nicolet 6700 FTIR spectrophotometer (Thermo Scientific, USA) in the range of 400-4000 cm^{-1} (KBr tablets). ^1H NMR spectra were registered using Bruker AM-360 instrument (Bruker, Germany), 300.16 MHz frequency (in DMSO-d_6 solution). ESI-MS spectra were written using Agilent 1100 MSD Ion trap DL LC/MS spectrometer (Agilent Technologies, Inc., USA) in the mode of positive ions; water solution of urea was injected into a column with C_{18} ODS sorbate (75 × 4.5 mm), distilled water was used as eluent. The melting point was determined using “Boecius” instrument (Germany); heating rate was 2 °C per minute.

Gas from the reactor was analyzed by adsorption gas chromatography (GC) using “Kristallux 4000M” chromatograph (“Meta-Khrom”, Ltd., Russia) equipped with thermo conductivity detector (TCD) and stainless steel column (3 m × 3 mm) with activated carbon (60-80 mesh, Shimadzu Seisakusho Ltd.). Column temperature program: 2 min. 30 °C, heating with rate 45 °C/min. up to 150 °C, 10 min. delay at 150 °C. TCD temperature 150 °C, current -70 mA, carrier gas (helium) flow 60 mL/min., sample volume 0.5 mL. Before analysis gas from reactor was passed through 50% water solution of H_2SO_4 for ammonia

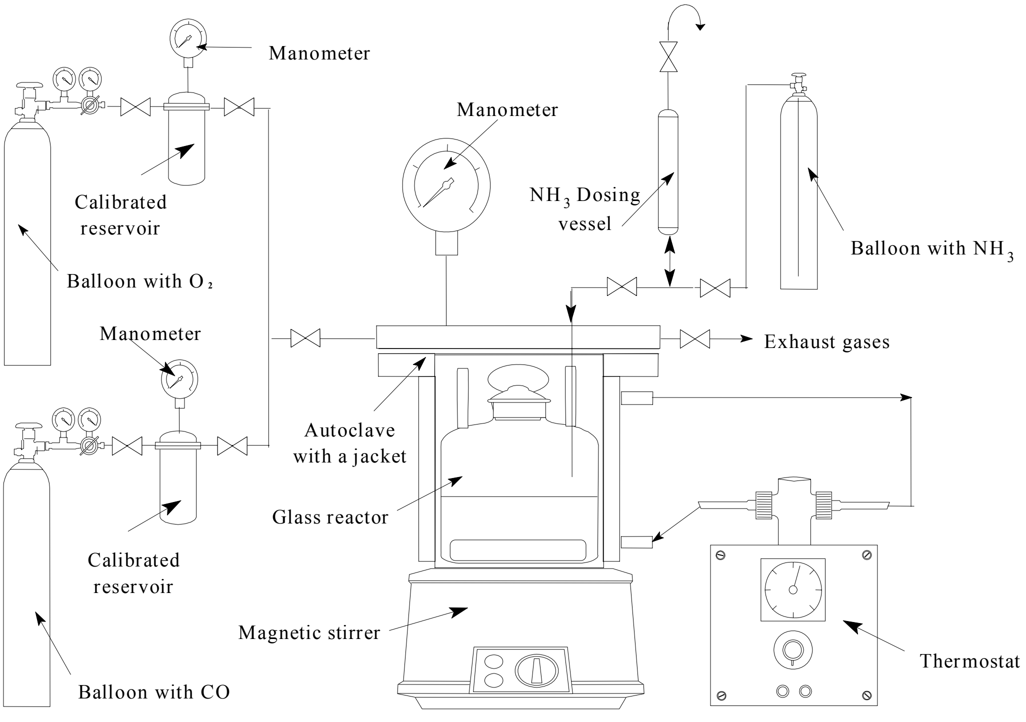


Fig. 1 Apparatus scheme.

absorption and then it was accumulated in gas burette over salt saturated water solution. CO and CO_2 content in the gas sample were determined by absolute calibration method.

3. Results and Discussion

3.1 Influence of Reaction Conditions on Process Characteristics

Mechanism of urea formation from CO and NH_3 in the presence of Se suppose that Se is reduced into Se^{2-} compounds such as COSe, H_2Se and others [8, 9]. In preliminary experiments [10, 11] it was shown that reduced forms of Se is not allowed carrying out further reaction: an addition of new CO and ammonia portions had not led to gas absorption. To provide a catalytic mode of the reaction and reoxidation of Se^{2-} into Se or higher valence forms of selenium oxygen was added into the reactor. For this purpose reaction gases were dropped periodically from the autoclave down to P = 1 bar after noticeable reaction braking and then new portions of NH_3, CO and O_2 were added (Fig. 2).

Fig. 2 shows that reagents (NH_3 and CO) and oxygen repeat loading is fully restore selenium activity after each gases adding. Using such manner ~20 g of urea was prepared during 5 cycles of gases loading (25 °C, P_{CO} = 14 bar); and total catalyst turnover number (TON) was 443 and its average activity (ratio TON to total time of process or turnover frequency) TOF was 307 h^{-1}. These results have shown an ability to carry out the process in catalytic manner.

Because of urea is not soluble in THF it precipitates during the reaction and retards the process when big product quantity forms. Therefore, we used THF-methanol mixture to homogenize the reaction mass (including selenium compounds dissolution) in the following experiments. Material balance was checked by the single loading all the components into the reactor (see section 2). Table 1 shows the obtained results.

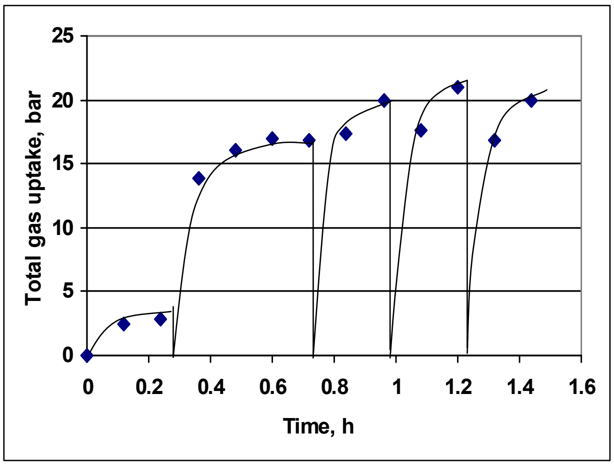


Fig. 2 Reaction gases consumption in urea preparation process; gas mixture was periodically loaded into the reactor. Reaction conditions: Se-0.76 mg-at.; THF-20 mL; after each autoclave dropping the gases loading was NH_3-0.18 mol; CO-14 bar; O_2-7.5 bar; t = 25 °C.

Table 1 shows quantity of urea formed is equal to quantity of CO loaded. Also it was especially shown that CO and oxygen are consumed almost fully and their residual part is not higher than 0.2% that was determined by GC-method after prior NH_3 absorption (see section 2). Electro spray ionization mass spectrometry (ESI-MS) analysis of the reaction mixture has shown that part of by-products is not higher than 1%. Carbon dioxide content in gas phase after process is equal to 0.6%. So, catalytic reaction equation may be represented as follows (Eq. (2)):

$$CO + 2NH_3 + 0.5O_2 \overset{Se}{=} CO(NH_2)_2 + H_2O \quad (2)$$

To study the process conditions influence on its characteristics we have conducted some experiment series with varying of selenium quantity, CO/O_2 ratio and solvent composition. All runs were carried out using near fourfold (mol.) excess of ammonia as compared to stoichiometric quantity.

On Fig. 3 one can see the dependences of formed urea quantity and TON *vs*. selenium quantity used.

These dependences show that even small selenium quantities provide full conversion of CO into urea (Fig. 3a); in spite of this maximal TON is about 270 (Fig. 3b) and TOF reaches 600 h^{-1} at chosen conditions.

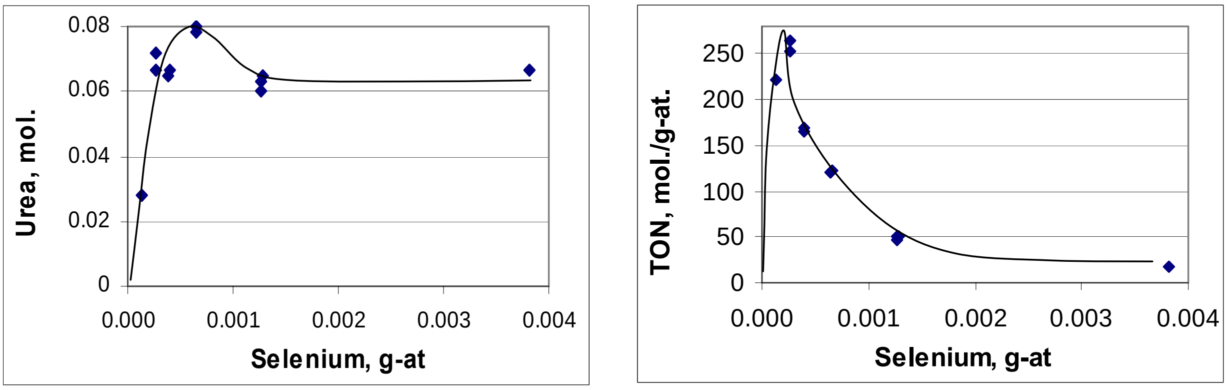
Fig. 4 shows influence of O_2: CO ratio in starting gas on the urea yield and reaction rate.

Both dependences (Fig. 4) have extreme character with a maximum at O_2: CO = 1:2 that corresponds to Eq. (2) stehiometry. Urea yield reduction at other

Table 1 Material balance of ammonia oxidative carbonylation.

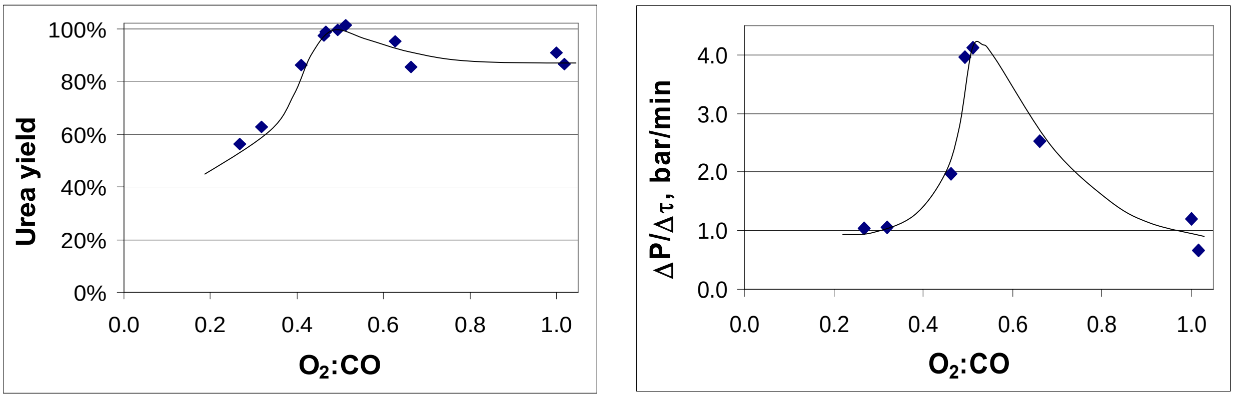
Run No.	Temp., °C	P_{total}, bar	Loading (mol)				Urea obtained, mol	Urea yield*, %	TON	TOF, h^{-1}
			Se	NH_3	CO	O_2				
1	45.0	28.5	6.40×10^{-4}	0.295	0.079	0.036	0.078	99.10	122.4	419.5
2	45.0	29.0	6.52×10^{-4}	0.598	0.079	0.040	0.080	101.21	122.5	459.5
3**	45.0	30.5	7.05×10^{-4}	0.330	0.077	0.038	0.077	99.30	108.6	635.5
4	23.0	21.0	0.10	0.208	0.097	0	0.091	94.64	0.9	4.1

* Urea yield based on CO loaded; ** Reaction was carried out in autoclave without glass reactor. TON: turnover number (mol urea/mol Se). TOF: average catalyst turnover frequency (TON/total reaction time).



(a) (b)

Fig. 3 Formed urea quantities (moles) (a) and TON (b) *vs.* selenium quantity used. Experimental conditions: NH_3-0.64 mol; CO-15 bar (0.08 mol); O_2-8 bar (0.04 mol); t = 45 °C; Se:CO ratio varied from 1:603 to 1:19.

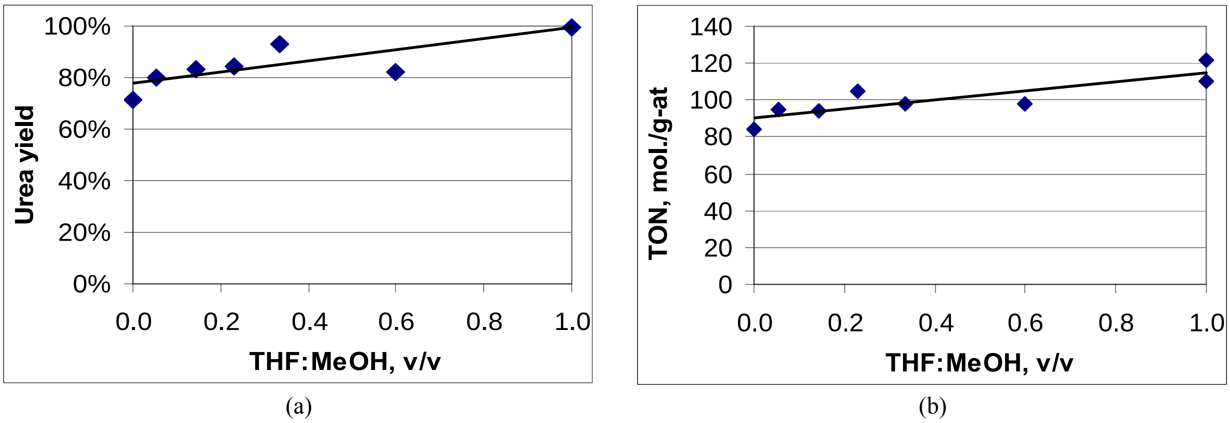


(a) (b)

Fig. 4 Influence of O_2:CO ratio in starting gas on the urea yield (a) and total gas consumption rate (b). Experimental conditions: NH_3-0.64 mol; CO-15 bar (0.08 mol); Se-0.65 mg-at; t = 45 °C.

O2:CO ratio may be explained either by impossibility to provide the greatest possible selenium turnover number in the chosen conditions (with oxygen deficiency) or by conversion of some selenium quantity into inactive forms with high degree of oxidation state (with oxygen excess). It is important to note that at stoichiometric ratio O2:CO = 1:2 urea yield calculated on loaded CO is close to 100% (Fig. 4a).

To prevent urea precipitation we used (as already mentioned) THF-methanol mixture as a solvent in oxidative carbonylation of ammonia. Variation of solvent composition (Fig. 5) has a small influence on the reaction. THF:methanol = 1:1 (vol.) provides maximal product yield (about 100%) at chosen conditions, and the yield decreases down to 71.2% with increasing of methanol content (until full exclusion of THF).



(a) (b)

Fig. 5 Urea yield (a) and TON (b) *vs.* volume ratio THF:methanol. Experimental conditions: NH_3-0.70 mol; CO-15 bar (0.08 mol); O_2-8.5 bar (0.04 mol); Se-0.65 mg-at; t = 45 °C.

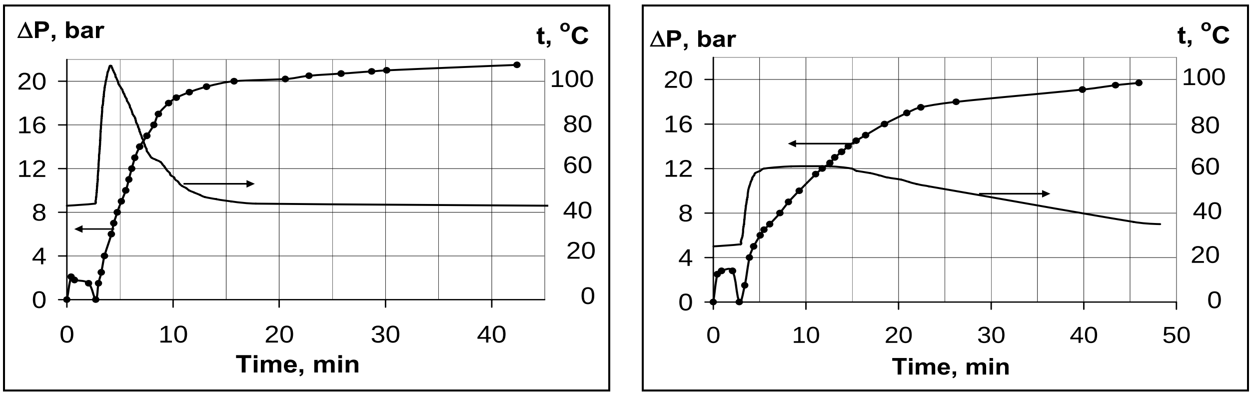
So stehiometry of ammonia oxidative carbonylation process catalyzed by selenium in the mixture of THF:methanol = 1:1 corresponds to Eq. (2) at chosen conditions and O_2:CO = 1:2; urea yield calculated on CO loaded is close to 100%.

After isolation the target product has the next characteristics: m.p. 132.7 °C (lit. data 131-133 °C [1, 2]); IR spectra (ν, cm^{-1}): 3443 v.s., 3347 v.s., 2804 w., 1678 v.w., 1624 v.w., 1464 s., 1153 m., 1002 m., 788 w., 574 s., 558 s., that corresponds to Ref. [12] and authentic sample spectra; admixtures content (^{1}H NMR in DMSO-d_6 solution) is about 0.1%.

3.2 Heat Efficiency of the Reaction

Considerable exothermic effect of urea formation reaction was discovered in special experiments. The reaction was carried out in glass reactor placed into the autoclave with a jacket in oven-control mode (heat carrier temperature was 45 °C) and without external heating (autoclave worked at room temperature ~25 °C). Reaction mixture temperature were measured by digital thermometer (thermocouple in a stainless steel cylinder equipped with digital temperature indicator); temperature values were recorded continuously by digital camera Canon SX-110 IS.

Fig. 6 shows that in the reaction initial period (before oxygen input, when only ammonia, CO and selenium are in the solvent) reaction mixture temperature is equal to heat-carrier temperature and not varies in the course of time. However, strong increase of reaction mass temperature is observed simultaneously with pressure drop during 1.5-2.0 minutes after oxygen was



(a) (b)

Fig. 6 Heat efficiency measurement of ammonia oxidative carbonylation reaction in the presence of Se catalyst in oven-control mode, t = 45 °C (a) and without external heating (b). Experimental conditions: CO-15 bar (0.08 mol); O_2-8.5 bar (0.04 mol); Se-0.66 mg-at.

added. In the heating-control mode temperature reached maximum of 107 °C and then decreased to the initial value of 45 °C in 15-17min. To this moment the reaction practically stops and total pressure drop is ~95% of the final value.

On the other hand without external heating (Fig. 6b) reaction mixture temperature after reaching the maximum not varies for a long time. Evidently this is due to rates equalization of heat emission due to reaction and heat removing into environment, the last is substantially lower than in the case of heat-carrier circulation.

Heat efficiency of non-catalytic reaction (stoichiometric Se quantity, absence of oxygen, heat-carrier temperature 45 °C) is substantially lower than in a case of catalytic reaction. Fig. 7 shows two runs carried out to check reproducibility.

Molar heats ΔH_r of the catalytic (Eq. (4)) and non-catalytic (Eq. (5)) carbonylation of ammonia in the presence of selenium were calculated based on Guess law equation (Eq. (3)) to calculate heat efficiencies of these reactions; heats of formation of reagents and products [13] are represented in Table 2:

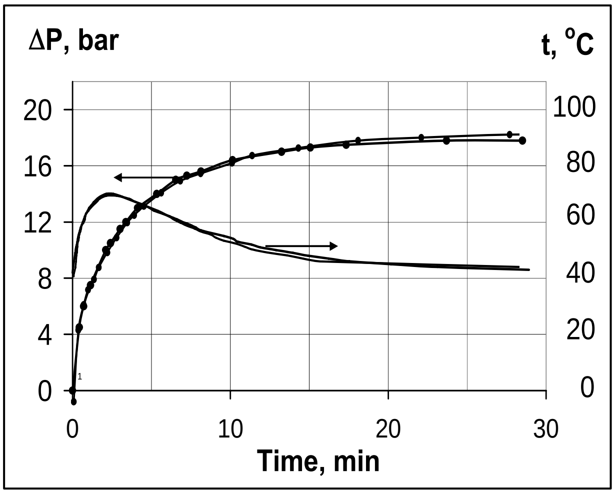


Fig. 7 Heat efficiency of non-catalytic ammonia carbonylation reaction in the presence of stoichiometric Se quantity. Experimental conditions: NH_3-0.77 mol; CO-15 bar (0.08 mol); Se-0.08 mg-at.; t = 45 °C.

$$\Delta H_r = \Sigma\Delta H_{PROD.FORM} - \Sigma\Delta H_{REAG.FORM.} \quad (3)$$

$$CO+2NH_3+0.5O_2=CO(NH_2)_2+H_2O–416.6\text{kJ/mol} \quad (4)$$

$$CO+2NH_3+Se=CO(NH_2)_2+H_2Se–101.1\text{ kJ/mol} \quad (5)$$

Taking into account urea quantity formed at the end of the above mentioned experiments the full heat efficiency calculated by Eq. (6) for catalytic process was -31.9 kJ and for non-catalytic process – -7.2 kJ.

$$\Delta Q_r = \Delta H_r \times \mu_U \quad (6)$$

where μ_U is number of urea moles formed at the end of reaction (0.077 moles for catalytic reaction and 0.071 moles for non-catalytic reaction).

Calculated ΔQ_r values show that heat efficiency of catalytic oxidative carbonylation of ammonia is over four times greater than heat efficiency of non-catalytic reaction and we have to take into account this fact to prevent spontaneous reaction mass heating and uncontrolled pressure rise when the process is carried out especially in large scale. However heat emission during the reaction not resulted in noticeable pressure rise at chosen conditions. In addition warming up of reaction mixture may be significantly diminished if to carry out the process at lower temperatures, *i.e.* owing to decreasing the reaction rate (Fig. 6).

4. Conclusions

The obtained results allowed developing effective one-stage method of urea preparation in the liquid phase by the catalytic oxidative carbonylation of ammonia [14]. In comparatively mild conditions (total pressure near 30 bar, 45 °C) the method provides productivity (urea quantity per reaction volume unit) ~530 g/(L·h^{-1}). The process is characterized by high selectivity (near 100%), that provides high quality of target urea. In addition almost full consumption of carbon monoxide takes place that is why significant costs on cleaning exhaust gas from CO is not required.

Important advantages of this process from the point

Table 2 Heats of formation of starting reagents and products for ΔH_r calculation.

Compound	Urea	Water (liq.)	CO	Ammonia	H_2Se
$\Delta H_{FORM.}$, kJ/mol	-333.1	-285.8	-110.5	-45.9	29.7

of view commercial application are environmental characteristics since water is the only byproduct.

Acknowledgements

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