Letter

A Facile Synthesis of Urea by the Carbonylation of NH_3

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Urea is obtained by the carbonylation of aqueous ammonia catalyzed by $K[Ru^{II}(EDTA-H)(CO)]$ at 30 atm CO and at 100 °C with a selectivity greater than 70%.

Urea, an important source of nitrogen fertilizer, is prepared on a commercial scale by the reaction of CO_2 with liquid ammonia at 246 atm pressure and 195 °C by the dehydration of ammonium carbamate [1]. Reactions are reported where CO is used along with hydrogen for the conversion of ammonia to methylamines, amides and nitriles [2 - 8]. However, there are no studies on the synthesis of urea by direct carbonylation of NH_3. The overall catalytic reaction between CO and NH_3 to give urea may be expressed as:

$$CO + 2NH_3 \xrightarrow{cat} CO(NH_2)_2 + H_2 \quad (1)$$

The above reaction is unique in two ways: the use of an easily available raw material, CO (synthesis gas/natural gas), which avoids the conversion of CO into CO_2 for use in the conventional urea synthesis and the low energy inputs of the reaction; 100 °C and 30 atm. In this work we report the activation of NH_3 involving CO insertion in the metal–nitrogen bond to give urea and simultaneously a molecule of hydrogen.

The carbonylation of ammonia was studied in aqueous solution in a 300 ml pressure reactor using $K[Ru^{II}(EDTA-H)(CO)]2H_2O$ catalyst at 30 atm CO and at 100 °C. The products were analysed by GC and TLC and characterised by the usual physicochemical techniques. The reaction gave urea (70% selectivity) with other side products such as hexamethylenetetramine (20%) and formamide (5%) and a viscous mass (5%). The turnover rate of urea obtained at 100 °C, 30 atm CO is 16 mol urea per mol catalyst per hour. This reaction has thus potential for industrial urea synthesis.

The mechanism suggested for the $K[Ru^{II}(EDTA-H)(CO)]2H_2O$ catalyzed carbonylation of aqueous ammonia to give urea is shown in Scheme 1, and involves the oxidative addition of NH_3 to $Ru^{II}(EDTA)(CO)$ complex 1 in a rate-determining step to give a hydrido-imide Ru(IV) intermediate 2. The insertion of CO in the $M-NH_2$ bond of 2 takes place in a fast step to

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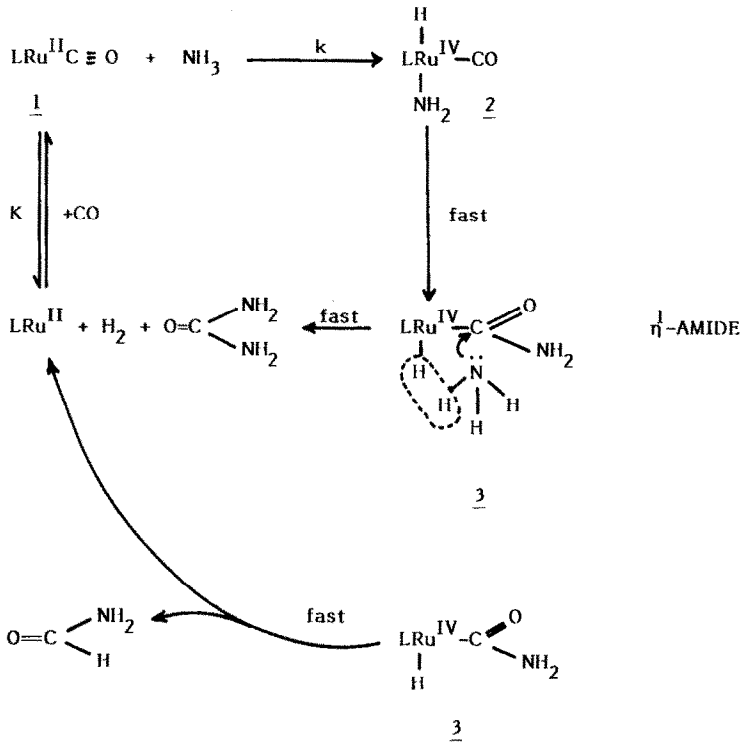

Side reactions

$$4NH_3 + 6HCHO \longrightarrow (CH_2)_6N_4 + 6H_2O$$
(hexamethylenetetramine)

urea + HCHO ⟶ urea–formaldehyde resin

Scheme 1.

give an η^1-amide 3. Nucleophilic attack of NH_3 on 3 gives urea and the LRu^{II} complex which reacts with CO to give back the active catalytic species 1. The value of k at 100 °C and 30 atm CO is computed as 4.1 M^{-1} h^{-1}.

In a side reaction, intramolecular nucleophilic attack of hydride in complex 3 on the carbon atoms of the η^1-amide gives formamide and Ru(II)–EDTA, which immediately reacts with CO in an equilibrium step to give the active catalyst 1 [9]. The formation of side products hexamethylenetetramine (20%) and viscous mass urea–formaldehyde resin (5%), shown in Scheme 1, result because of the formation of formaldehyde by the water–gas shift reaction under the reaction conditions [10]. The formation of formaldehyde via the water–gas shift reaction has been confirmed in our earlier studies [11].

In conclusion, the carbonylation of aqueous ammonia to urea has been achieved by a low pressure synthesis, with 70% selectivity to urea and a turnover rate of 16 mol urea per mol catalyst per hour. This is the first case of a facile synthesis of urea using a soluble metal complex catalyst.

References

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