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RAPID COMMUNICATION

Catalytic conversion of urea to biuret: A catalyst screening study

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Abstract−Biuret was synthesized from urea in a batch reactor using various homogeneous and heterogeneous catalysts, with the aim of searching for efficient catalyst in converting non-catalytic reaction to catalytic reaction. For this purpose, zeolite, heteropolyacid, organic acid and base, multicomponent bismuth molybdate, and multicomponent bismuth molybdate-alumina mixed catalysts were tested. It was revealed that the performance of catalytic reaction was better than that of non-catalytic reaction in the synthesis of biuret from urea. Among the homogeneous acid and base catalysts tested, thionyl chloride ($SOCl_2$) showed the best catalytic performance. Among the heterogeneous catalysts tested, on the other hand, a mixed catalyst comprising multicomponent bismuth molybdate ($Co_8Fe_3Bi_1Mo_{12}O_{50}$) and alumina showed the best catalytic performance.

Key words: Biuret, Catalytic Conversion of Urea, Catalyst Screening

INTRODUCTION

Biuret has attracted much attention as a parent compound of various organic substances [1]. Biuret has been widely used as a precursor for pharmaceuticals, herbicides, and analytical reagents. Biuret is typically produced from urea through a series of non-catalytic pyrolysis reactions at temperature above 130 °C (melting temperature of urea).

Biuret is formed through non-catalytic pyrolysis of urea according to the reaction mechanisms shown in Fig. 1 [1]. At high temperature above the melting point of urea, one molecule of urea decomposes into equimolar amount of ammonia and cyanic acid. Cyanic acid produced by the decomposition of urea then reacts with another urea to form biuret. Overall, two molecules of urea are converted into one molecule of biuret and one molecule of ammonia. As also shown in Fig. 1, however, a problem is that formation of by-products such as triuret and cyanuric acid increases with increasing the amount of biuret. Therefore, the ultimate goal of the reaction is to maximize the biuret formation by suppressing the side reactions. It is known that the commercial process for the synthesis of biuret from urea is conducted at 145 °C with residence time of 3 h in the absence of catalyst.

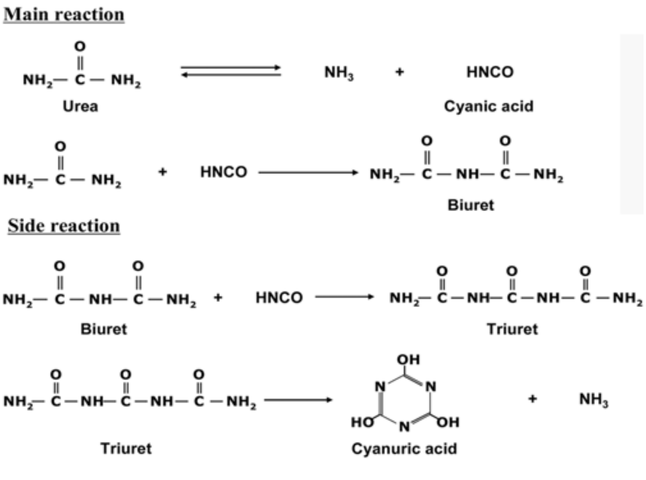

Fig. 1. Reaction mechanisms for producing biuret from urea.

Another problem in the synthesis of biuret through pyrolysis of urea is that yield of biuret is very low under mild reaction conditions [1]. Pyrolysis of urea at high temperature for long time can be a solution for this problem. However, reaction at high temperature for long time may yield an undesired by-product, cyanuric acid, as a main product. Although a few methods for increasing biuret formation were proposed [2-4], no significant increase of biuret formation was attained by the proposed methods. Nonetheless, no attempts have been made on the synthesis of biuret from urea using catalysts.

In this work, biuret was synthesized from urea in a batch reactor using various homogeneous and heterogeneous catalysts, with the aim of searching for efficient catalyst for the reaction. For this purpose, zeolite, heteropolyacid (HPA), organic acid and base, multicomponent bismuth molybdate, and multicomponent bismuth molybdate-alumina mixed catalysts were examined. Conventional non-catalytic synthesis of biuret from urea was also carried out in a batch reactor under the same reaction conditions for use as a reference. This is the first example reporting the catalytic conversion of urea to biuret.

EXPERIMENTAL

1. Catalysts

Commercially available zeolite (zeolite beta, mordenite, ZSM-5, and zeolite Y: Zeolist), organic acid (thionyl chloride ($SOCl_2$) and chlorosulfonic acid ($ClSO_2OH$): Sigma-Aldrich), organic base (imi-

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dazole and triethylamine: Sigma-Aldrich), and alumina (Degussa) catalysts were purchased.

Cation-exchanged heteropolyacid (HPA) catalysts were prepared as follows. $H_3PW_{12}O_{40}$ (Sigma-Aldrich) was thermally treated at 300 °C for 2 h for precise quantification. Cesium- and/or palladium-exchanged HPA ($Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and $Pd_{0.15}Cs_{2.5}H_{0.2}PW_{12}O_{40}$) catalysts were prepared by an ion-exchange method using $CsNO_3$ (Sigma-Aldrich) and $Pd(NO_3)_2$ (Sigma-Aldrich) as a cesium and a palladium precursor, respectively [5-7]. Cesium content in both HPA catalysts was fixed at 2.5, in order to take advantage of high surface area and large surface acidity of the catalysts [8-12]. The prepared cation-exchanged HPA catalysts were calcined at 300 °C for 2 h prior to use in the catalytic reaction.

A multicomponent bismuth molybdate ($Co_8Fe_3Bi_1Mo_{12}O_{50}$) catalyst was prepared by a co-precipitation method. 1.5 g of bismuth nitrate ($Bi(NO_3)_3\cdot 5H_2O$, Sigma-Aldrich) was dissolved in 10 ml of distilled water that had been acidified with 3 ml of concentrated nitric acid. The solution was then added into 100 ml of an aqueous solution containing 7.1 g of cobalt nitrate ($Co(NO_3)_2\cdot 6H_2O$, Sigma-Aldrich) and 3.7 g of ferric nitrate ($Fe(NO_3)_3\cdot 9H_2O$, Sigma-Aldrich) to obtain a mixed nitrate solution. The mixed nitrate solution was added dropwise into 50 ml of an aqueous solution containing 6.4 g of ammonium molybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, Sigma-Aldrich) under vigorous stirring. After the mixed solution was stirred vigorously at room temperature for 1 h, a solid product was obtained by evaporation. The solid product was dried overnight at 175 °C, and it was then calcined at 475 °C for 5 h in an air stream to yield $Co_8Fe_3Bi_1Mo_{12}O_{50}$ catalyst. Successful formation of $Co_8Fe_3Bi_1Mo_{12}O_{50}$ catalyst was confirmed by XRD (MAC Science, M18XHF-SRA) and ICP-AES (Shimadz, ICP-1000IV) measurements, as reported in the previous works [13-15].

2. Synthesis of Biuret from Urea

Synthesis of biuret from urea was carried out in a batch reactor (250 ml) in the absence or presence of catalyst. For the catalytic reaction, 10 g of urea was charged into a glass batch reactor with a reflux condenser. After urea was melted at 130 °C for 10 min, each catalyst (1 g for heterogeneous solid catalyst or 1 ml for homogeneous liquid catalyst) was charged into the batch reactor. The mixture of molten urea and catalyst was then heated to 145 °C with constant stirring. The catalytic reaction was carried out at 145 °C for 3 h under vigorous stirring (500 rpm). The reaction products were analyzed with a high performance liquid chromatograph (Younglin, ACME 9000). The reaction procedures for non-catalytic reaction were identical to those for catalytic reaction, except that no catalyst was introduced into the reactor.

RESULTS AND DISCUSSION

1. Effect of Reaction Time and Agitation Speed

Biuret was synthesized from urea in the absence of catalyst for use as a reference. In the non-catalytic reaction, conversion of urea and yield of biuret was found to be 24.0% and 22.7%, respectively. Yield of by-products including triuret and cyanuric acid was 1.6%.

Fig. 2 shows the catalytic performance of zeolite beta (H^+ form) in the synthesis of biuret from urea with time on stream at 145 °C. Conversion of urea continuously increased with increasing reaction time. On the other hand, yield of biuret was constant after 3 h-reaction. Therefore, all the reactions were carried out for 3 h in this work.

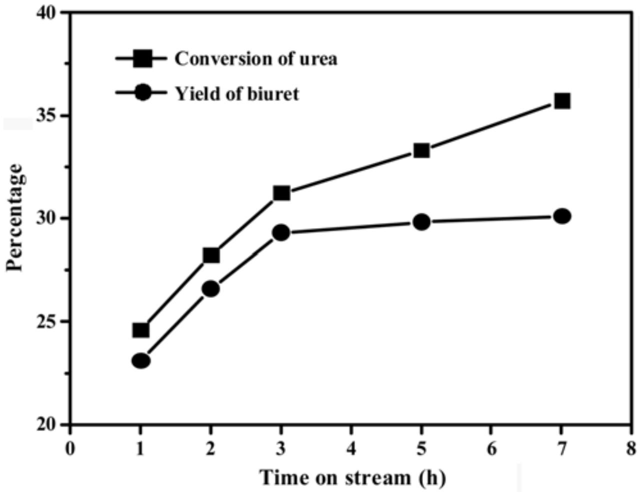

Fig. 2. Catalytic performance of zeolite beta (H^+ form) in the synthesis of biuret from urea with time on stream at 145 °C.

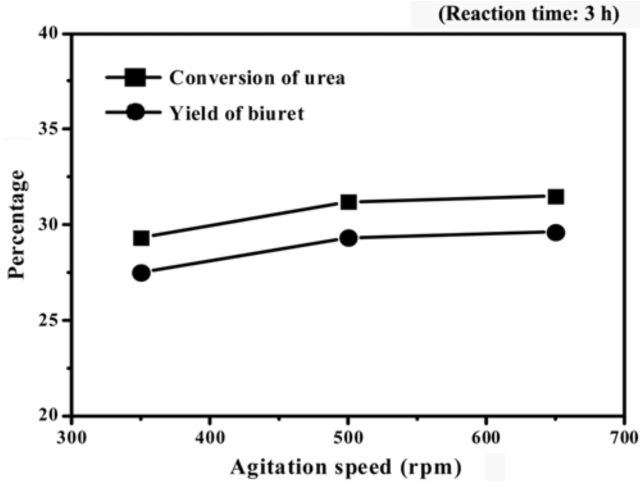

Fig. 3. Catalytic performance of zeolite beta (H^+ form) in the synthesis of biuret from urea with respect to agitation speed.

The effect of agitation speed on the catalytic performance of zeolite beta (H^+ form) in the synthesis of biuret from urea is shown in Fig. 3. Conversion of urea and yield of biuret were almost constant at agitation speed higher than 500 rpm. Therefore, all the reactions were conducted at agitation speed of 500 rpm in order to avoid mass transfer limitation.

2. Catalytic Performance of Heterogeneous Catalysts

Among various zeolite catalysts, zeolite beta, mordenite, ZSM-5, and zeolite Y were chosen as exemplary catalysts. All the zeolites tested in this work were H^+ form. Fig. 4 shows the catalytic performance of zeolite catalysts in the synthesis of biuret from urea. All the zeolite catalysts showed an enhanced catalytic performance compared to the non-catalytic reaction. Among the zeolite catalysts, zeolite beta showed the best catalytic performance.

Heteropolyacids (HPAs) were used as another solid acid catalyst in the synthesis of biuret from urea. One of the great advantages of

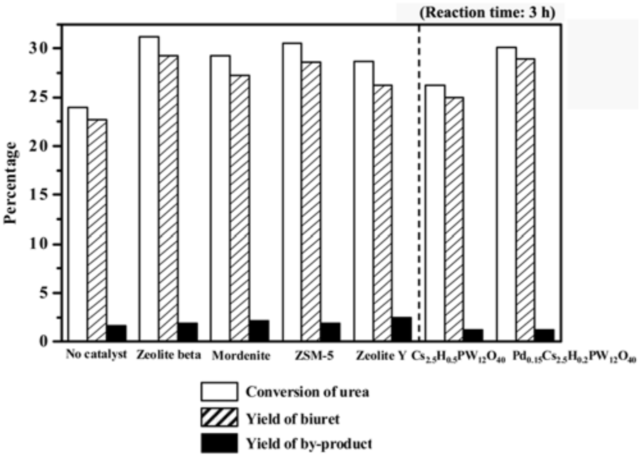

Fig. 4. Catalytic performance of heterogeneous catalysts (zeolite and cation-exchanged heteropolyacid catalysts) in the synthesis of biuret from urea.

HPA catalysts is that their catalytic properties can be controlled in a systematic way by changing the identity of constituent metal components [8-11,16,17]. Among various HPA catalysts, it was reported that cesium-exchanged HPA catalyst exhibited large surface acidity and retained insoluble nature in organics [10,11]. Therefore, cesium-and/or palladium-exchanged HPA ($Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and $Pd_{0.15}Cs_{2.5}H_{0.2}PW_{12}O_{40}$) catalysts were chosen as a model catalyst for use as a heterogeneous catalyst. Fig. 4 also shows the catalytic performance of cation-exchanged HPA catalysts in the synthesis of biuret from urea. Both HPA catalysts showed an enhanced catalytic performance compared to the non-catalytic reaction. Furthermore, $Pd_{0.15}Cs_{2.5}H_{0.2}PW_{12}O_{40}$ catalyst showed a better catalytic performance than $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ catalyst. This result indicates that acidic and noble metal-substituted HPA catalyst was efficient for the synthesis of biuret from urea.

3. Catalytic Performance of Homogeneous Catalysts

Organic acids were applied to the synthesis of biuret from urea as a homogenous catalyst. Thionyl chloride ($SOCl_2$) and chlorosulfonic acid ($ClSO_2OH$) were tested as an organic acid catalyst. Fig. 5 shows the catalytic performance of organic acid catalysts in the synthesis of biuret from urea. It was observed that both organic acids showed an excellent catalytic performance in the synthesis of biuret from urea. Although considerable amounts of by-products were also formed compared to the heterogeneous solid acid catalysts (Fig. 4), $SOCl_2$ showed the highest conversion of urea (51.7%) and the highest yield of biuret (46.9%) among the catalysts tested in this work. Catalytic performance of $ClSO_2OH$ was comparable to that of $SOCl_2$.

Organic bases were also tested as a homogeneous catalyst in the synthesis of biuret from urea. Imidazole and triethylamine were chosen as a model organic base catalyst. Fig. 5 also shows the catalytic performance of organic base catalysts in the synthesis of biuret from urea. Imidazole showed a better catalytic performance than triethylamine. However, these two base catalysts showed a lower catalytic performance than the organic acid catalysts, and they showed a comparable catalytic performance to the heterogeneous solid acid catalysts (Fig. 4).

4. Catalytic Performance of $Co_8Fe_3Bi_1Mo_{12}O_{50}$ and its Mixture with Alumina

Multicomponent bismuth molybdate ($Co_8Fe_3Bi_1Mo_{12}O_{50}$) catalyst was used in the synthesis of biuret from urea, with the aim of improving the desorption rate of ammonia from urea. $Co_8Fe_3Bi_1Mo_{12}O_{50}$ catalyst has been used for the production of acrylonitrile by ammoxidation of propylene. It is expected that $Co_8Fe_3Bi_1Mo_{12}O_{50}$ may serve as an efficient catalyst in the reaction involving ammonia.

Fig. 6 shows the catalytic performance of multicomponent bismuth molybdate ($Co_8Fe_3Bi_1Mo_{12}O_{50}$) and its mixture with alumina in the synthesis of biuret from urea. It was observed that conversion of urea and yield of biuret over $Co_8Fe_3Bi_1Mo_{12}O_{50}$ catalyst were 29.4% and 27.1%, respectively. It has been reported that cyanuric

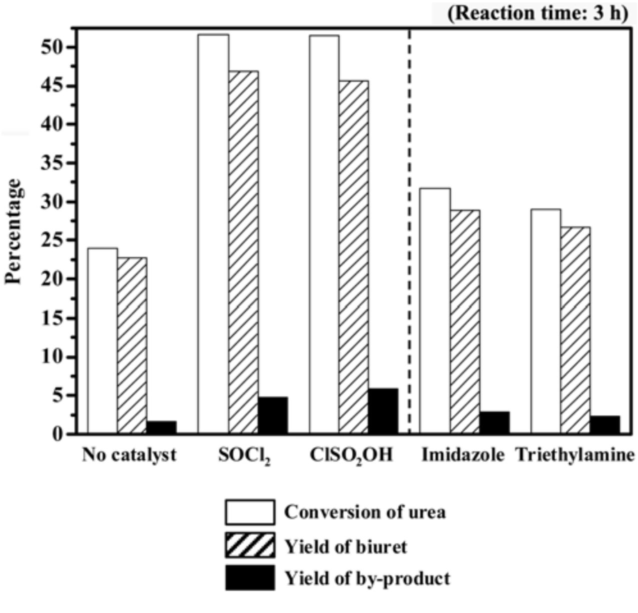

Fig. 5. Catalytic performance of homogeneous catalysts (organic acid and base catalysts) in the synthesis of biuret from urea.

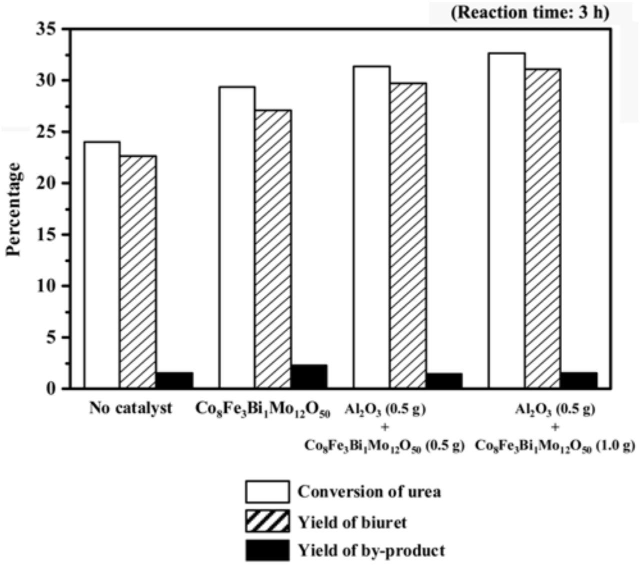

Fig. 6. Catalytic performance of multicomponent bismuth molybdate and its mixture with alumina in the synthesis of biuret from urea.

acid easily decomposes into cyanic acid over alumina catalyst [18]. Therefore, it is expected that cyanic acid formed through decomposition of cyanuric acid can be reused as a reactant in the synthesis of biuret (Fig. 1). For this reason, $Co_8Fe_3Bi_1Mo_{12}O_{50}$ mixed with alumina was used as a catalyst to achieve a synergistic effect of $Co_8Fe_3Bi_1Mo_{12}O_{50}$ (synthesis of biuret from urea) and alumina (decomposition of cyanuric acid to cyanic acid). As expected, the mixed catalyst showed an enhanced yield of biuret and a suppressed yield of by-products compared to the single $Co_8Fe_3Bi_1Mo_{12}O_{50}$ catalyst. Among the heterogeneous catalysts, $Co_8Fe_3Bi_1Mo_{12}O_{50}$-alumina mixed catalyst showed the best catalytic performance in the synthesis of biuret (Fig. 4 and Fig. 6). These results indicate that the mixed catalyst can serve as an efficient heterogeneous catalyst for the biuret synthesis from urea.

CONCLUSIONS

Synthesis of biuret from urea was carried out in a batch reactor using various homogeneous and heterogeneous catalysts for the first time, with the aim of searching for efficient catalyst in converting non-catalytic reaction to catalytic reaction. Zeolite (zeolite beta, mordenite, ZSM-5, and zeolite Y), cation-exchanged heteropolyacid ($Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and $Pd_{0.15}Cs_{2.5}H_{0.2}PW_{12}O_{40}$), organic acid ($SOCl_2$ and $ClSO_2OH$), organic base (imidazole and triethylamine), multi-component bismuth molybdate ($Co_8Fe_3Bi_1Mo_{12}O_{50}$), and $Co_8Fe_3Bi_1Mo_{12}O_{50}$-alumina mixed catalysts were examined. It was revealed that all the catalysts showed a better catalytic performance than the non-catalytic reaction. Among the homogeneous catalysts tested, $SOCl_2$ showed the best catalytic performance (51.7% of urea conversion and 46.9% of biuret yield). Among the heterogeneous catalysts tested, on the other hand, $Co_8Fe_3Bi_1Mo_{12}O_{50}$-alumina mixed catalyst showed the best catalytic performance.

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