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Synthesis of 3-Methylindole from Glycerol Cyclization with Aniline over CuCr/Al_2O_3 Catalysts Modified by Alkali Earth Oxides

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ABSTRACT: *In the present work, CuCr catalysts supported on γ-Al_2O_3 are prepared and modified with alkali earth elements by impregnation, characterized by N_2 adsorption–desorption, XRD, H_2-TPR (temperature-programmed reduction by H_2), CO_2-TPD and NH_3-TPD (temperature-programmed desorption of NH_3 or CO_2), and applied in the synthesis of 3-methylindole (3-MI) with a N-heterocycle from glycerol and aniline in the fixed-bed reactor. The results show that the introduction of alkali earth elements into the CuCr/Al_2O_3 catalyst can improve the yield of target 3-MI in the order of Mg $<$ Ca $<$ Sr $<$ Ba. CuCr-Ba/Al_2O_3 gives rise to a high 3-MI yield of 39.09% and 65.17% in N_2 as a carrier gas and 20%H_2–N_2 mixture gas, respectively. According to catalysts characterization and catalytic tests, the reaction pathway of glycerol cyclization with aniline is proposed, the formation of 3-MI and 3H-indol-3-yl methanol is hypothesized to be through the aniline cyclization with 2,3-hydroxypropanal from glycerol dehydrogenation over Cu^0 centers and basic sites. The acidic sites mainly play a role on activating aniline, which interacts with glycerol to form 3-MI or quinoline through cyclization and dehydration.* Heteroatom Chem 24:263–270, 2013; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.21090

INTRODUCTION

Indoles or alkylindoles are of considerable industrial interest and are applied as intermediates in the production of pharmaceuticals, herbicides, fungicides, dyes, etc. [1]. They are usually recovered from the biphenylindole fraction obtained after coal tar distillation; however, their production no longer meets the increasing market demand. Therefore, their chemical synthesis has attracted more and more interest. For instance, the Fisher synthesis has been widely applied in the preparation of indoles by reacting arylhydrazines with ketones or aldehydes as shown in Scheme 1 [2]. Campanati et al. [1, 3, 4] have reported that indoles can be formed from aniline (AN) cyclizaiton with 1,2-diols, which is hypothesized to mainly takes place between AN and intermediates (aldehyde or ketone) containing a carbonyl group formed from diols [1, 3].

As one of indoles, 3-methylindole (3-MI) has attracted considerable attention due to its potential application as perfume and synthesizing herbicides, antidiuretic, antihypertensive, muscular relaxant, respiratory inhibitor, and heart-stimulant medicaments, etc. [5]. As reported [1], 3-MI can be synthesized through AN cyclization with 1,2-propanediol

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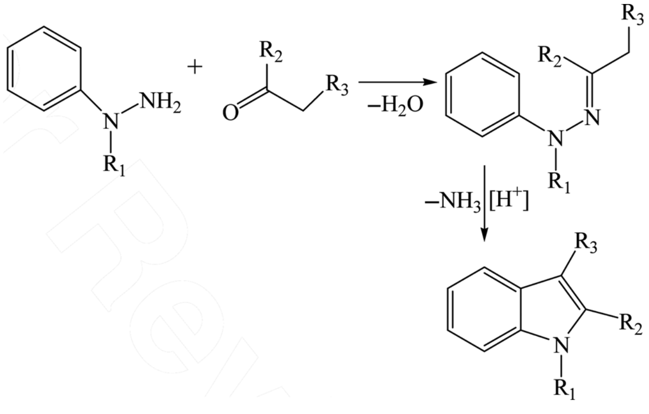
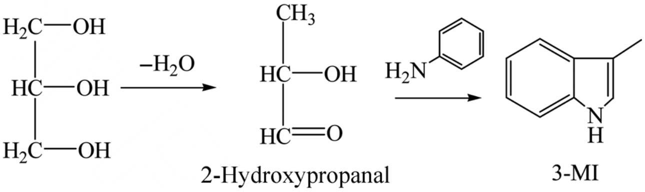


SCHEME 1

over ZrO_2/SiO_2 as a catalyst with a yield of 48.5%. Recently, Shi et al. [6–8] have found that glycerol (GL) can be used as a reactant to interact with AN to 3-MI through cyclization over Ag/SiO_2 and Cu-based catalysts. Both catalysts give rise to about 38% of 3-MI yield in N_2 as a carrier gas containing an amount of H_2. It is also hypothesized that the cyclization takes place between AN and an intermediate containing a carbonyl group from GL hydrodehydration over metal-active centers and acidic sites. If like this, the selection of catalytic-active species will play an important role in 3-MI synthesis from GL. According to our previous studies [9, 10], Cu^0 metallic centers exhibit an excellent catalytic activity for hydrodehydration of alcohols. In addition, Venugopal et al. [11] have discovered that the dichromate of transition metals can improve the GL cyclization with diamines to pyrazinyl compounds containing *N*-heterocycles. Therefore, the present work aims to prepare a kind of $CuCr/\gamma\text{-}Al_2O_3$ catalysts (CCA) by impregnation and uses them to catalyze GL cyclization with AN to 3-MI in the fixed-bed system.

During 3-MI synthesis from GL and AN, it is proposed by Shi et al. [7, 8] that 2-hydroxypropanal is an intermediate, which interacts with AN to 3-MI through cyclization and is produced by GL dehydration over the acidic sites. However, it is well known that the dehydration easily takes place between two adjacent —OH groups in the GL molecule to form 3-hydroxypropanal or hydroxyacetone. Therefore, it seems unreasonable that 3-MI formation is from the AN interaction with 2-hydroxypropanal as shown in Scheme 2. To investigate the reaction pathway for 3-MI synthesis from GL and AN, the present work introduces the basic species such as alkali earth metal elements into CCA (the obtained catalysts are denoted as M-CCA, where M refers to alkali earth metal elements) and investigates their effect on GL cyclization with AN. In addition, during GL cyclization with AN the obtained main product is 3-MI in a H_2-steam–N_2 mixture [7] and quinoline (QN) in air as the carrier gas [12], respectively. Therefore, the effect of carrier gas types and reaction temperature on yield toward target products and GL conversion in the cyclization is investigated and a new reaction mechanism is proposed according to the obtained results in the present work.



SCHEME 2

RESULTS AND DISCUSSION

Effect of Different Alkali Earth Metal

From Table 1, it is found that all CCA catalysts exhibit a smaller specific surface area and bigger average pore size than the support $\gamma\text{-}Al_2O_3$, indicating that the introduced oxide species of metals including Cu, Cr, and even alkali earth elements preferentially inhabit inside the micropore of support $\gamma\text{-}Al_2O_3$. No obvious decrease in the total pore volume shows that the introduced metal oxide species are able to produce some new pores.

The XRD patterns (Fig. 1) indicate that these catalysts mainly exhibit three obvious characteristic diffraction peaks of $\gamma\text{-}Al_2O_3$ (Pdf no. 1-1308) at $2\theta = 37.5^\circ, 45.9^\circ$, and 67°, respectively [13,14]. Moreover, CCA and those modified by alkali earth elements only exhibit some very weak characteristic peaks for CuO (Pdf no. 3-884) and $CuCr_2O_4$ (Pdf no. 26-509) besides $\gamma\text{-}Al_2O_3$, showing that most of introduced components are mainly dispersed in the form of the amorphous oxides phase.

Catalytic tests (Table 1) indicate that the cyclization products from GL and AN mainly include 3-MI, 3*H*-indol-3-yl methanol (3-IMol), and QN and the formed by-products are detected by GC include acrolein, *N*-propylaniline, *N*-methylaniline, *N*-ethylaniline, etc. The support $\gamma\text{-}Al_2O_3$ exhibits some catalytic activity in GL cyclization with AN to 3-MI with a yield of 12.37%, which, however, increases more than twice over Cu/Al_2O_3 (22.89%). Simultaneously, another two cyclization products such as QN and 3-IMol are also formed. It is obvious that 3-MI should be the product of 3-IMol hydrodehydration. It shows that Cu species should be

TABLE 1 Physiochemical and Catalytic Property of Different Catalysts in GL Cyclization with AN [a]

Catalyst	S_{BET} ($m^2 \cdot g$)	Pore Volume ($cm^3 \cdot g^{-1}$)	Pore Size (nm)	NH_3 Uptake ($\mu mol \cdot g^{-1}$)[b]	GL Conversion (%)[c]	Yield of Main Products (%)[c]		
						QN	3-MI	3-IMol
γ-Al_2O_3	210.2	0.51	9.6	575	57.12	1.73	12.37	3.39
Cr/Al_2O_3	189.5	0.48	10.5	398	7.24	1.61	3.09	0.41
Cu/Al_2O_3	197.4	0.50	10.2	380	48.54	0.94	22.89	–
CCA	181.7	0.51	11.1	353	64.09	10.64	26.03	6.02
Al-CCA	172.5	0.48	11.0	398	7.14	0.71	3.83	–
Mg-CCA	186.5	0.52	11.1	359	68.81	2.12	28.65	8.01
Ca-CCA	184.5	0.50	10.8	314	86.24	2.17	32.73	13.34
Sr-CCA	172.1	0.50	11.6	306	89.02	3.64	37.69	14.14
Ba-CCA	186.8	0.49	10.4	296	89.28	1.55	39.09	8.42

[a] Reaction conditions: temperature 260°C; feed rate of the liquid reactant mixture (AN/GL molar ratio = 3) 2.8 $mL \cdot h^{-1}$; catalyst 2 g; feed rate of N_2 as the carrier gas 60 $mL \cdot h^{-1}$.

[b] Data are calculated according to NH_3-TPD results.

[c] GL: glycerol, QN: quinoline, 3-MI: 3-methylindole, 3-IMol: 3*H*-indol-3-yl methanol.

catalytic active centers for GL cyclization with AN and 3-IMol hydrodehydration. From Table 1, it is discovered that the Cr catalyst supported on γ-Al_2O_3 gives a poor GL conversion and 3-MI yield; however, the CCA exhibits a higher 3-MI yield (26.03%) than Cu/Al_2O_3. It can be deduced that the Cr species act as a promoter and the simultaneous presence of Cu–Cr is helpful to GL cyclization with AN to 3-MI. Moreover, it is easily found that the introduction of alkali earth elements into CCA is able to further improve the yield of the target products including 3-MI and 3-IMol and, however, the introduction of acidic species alumina leads to the drastic decrease in GL conversion and yields of target products. Therefore, it is deduced that the acid–base property of CCA catalysts is probably an important factor that influences their catalytic activity in GL cyclization with AN.

From NH_3-TPD (temperature-programmed desorption of NH_3) results (Table 1), the introduction of Cu, Cr, and alkali earth elements decreases the NH_3 uptakes of catalysts; it means that the surface acidic sites are decreased. CO_2-TPD (temperature-programmed desorption of CO_2) curves of different catalysts (Fig. 2) indicate that γ-Al_2O_3 support gives a desorption peak below 100°C, which is weakened after introducing Cu, Cr, or alkali earth components. This peak is assigned to the strong physical adsorption in the pore of samples. The presence of Cu and Cr can lead to the production of weak or medium-strong basic sites; they give rise to CO_2 desorption

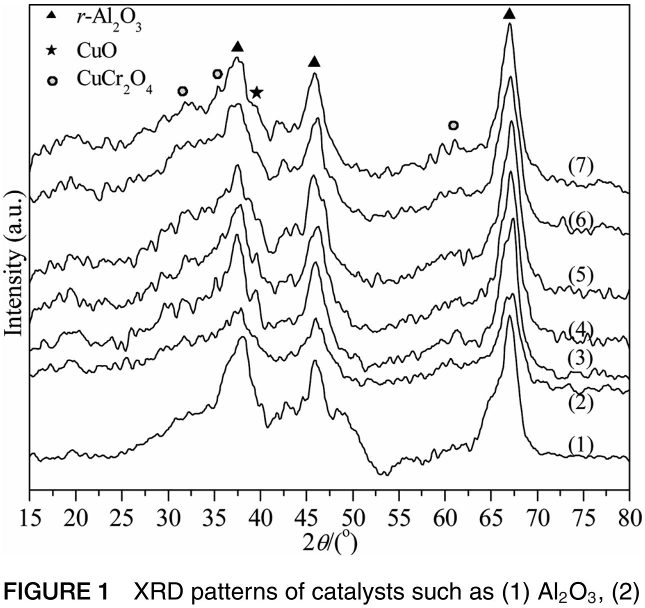


FIGURE 1 XRD patterns of catalysts such as (1) Al_2O_3, (2) CCA, (3) Al-CCA, (4) Mg-CCA, (5) Ca-CCA, (6) Sr-CCA, and (7) Ba-CCA.

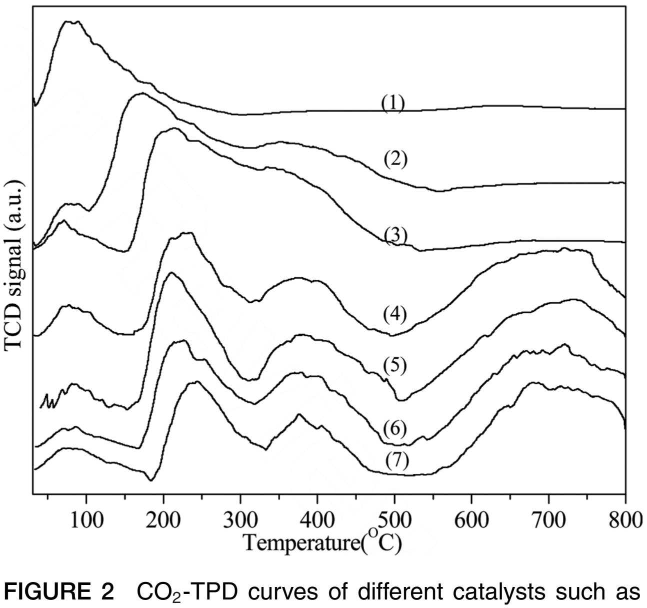


FIGURE 2 CO_2-TPD curves of different catalysts such as (1) Al_2O_3, (2) Al-CCA, (3) CCA, (4) Mg-CCA, (5) Ca-CCA, (6) Sr-CCA, and (7) Ba-CCA.

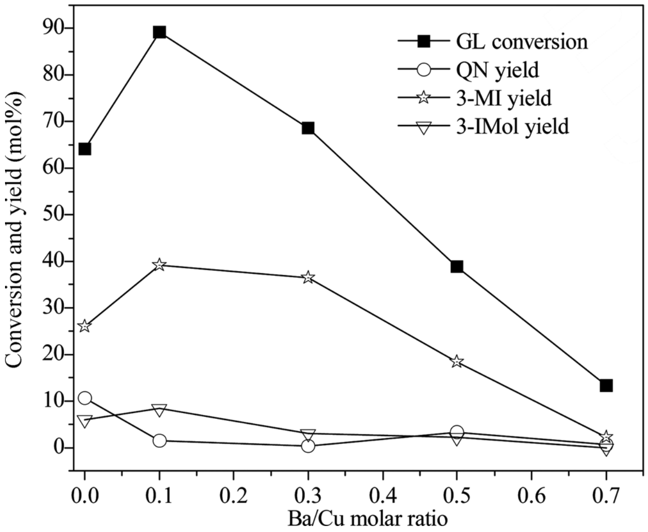


FIGURE 3 Effect of Ba loading on the catalytic property of Ba-CCA in GL cyclization with AN. Reaction conditions: temperature 260°C; feed rate of the liquid reactant mixture (AN/GL molar ratio 3) 2.8 mL·h^{-1}; catalyst 2 g; rate of N_2 as the carrier gas 60 mL·h^{-1}.

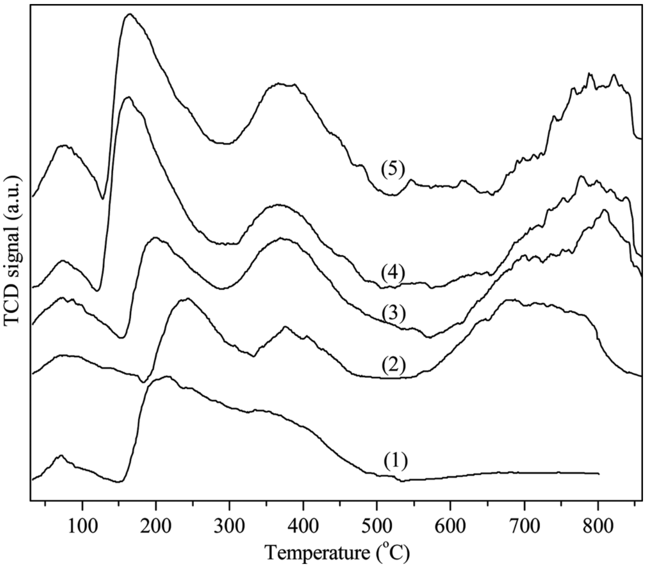


FIGURE 4 CO_2-TPD patterns of Ba-CCA catalysts with Ba/Cu molar ratio of (1) 0, (2) 0.1, (3) 0.3, (4) 0.5 and (5) 0.7.

peaks at about 200 and 380°C, respectively. The presence of alkali earth elements leads to the appearance of another desorption peak at 680°C, which is attributed to the strong basic sites. In addition, the introduction of alkali earth elements can also increase the amount of medium-strong basic sites and the basicity of weak basic sites whose desorption peak shifts to a higher temperature in the order of Mg < Ca < Sr < Ba, which is obviously coincident with the order of increase in the catalytic activity of corresponding catalysts. It indicates that the presence of basic sites is favorable to GL cyclization with AN.

Effect of Ba Loading

From above results, it can be concluded that the introduction of Ba plays an excellent function on improving 3-MI production. Therefore, the effect of Ba loading on catalytic properties of the Ba-CCA catalyst is further investigated in this work. From Fig. 3, Ba-CCA with a Ba/Cu molar ratio of 0.1 exhibits the highest GL conversion and 3-MI yield with 89.28% and 39.09%, respectively. With the further increase in Ba loading, both GL conversion and 3-MI yield are significantly declined. CO_2-TPD results (Fig. 4) indicate that the increase in Ba loading increases the amount of basic centers including weak, medium-strong, and strong basic sites. It is obvious that the effect of the Ba loading amount on the catalytic property of Ba-CCA seems to be contrary to the above -obtained results. To investigate this, the H_2-TPR (temperature-programmed reduction by H_2) technique is introduced to characterize the effect of Ba loading on the state of copper species.

From Fig. 5, it is clearly observed that a strong H_2-TPR peak at about 300°C, attributed to the reduction of Cu^{2+} to Cu^0 [9, 10], appears for $CuCr/Al_2O_3$ without Ba loading. In addition, the intensities of this peak are weakened and a new H_2-TPR band at a higher temperature range of 490–600°C comes forth after Ba loading. It is probably because that the presence of redundant Ba species will result in the

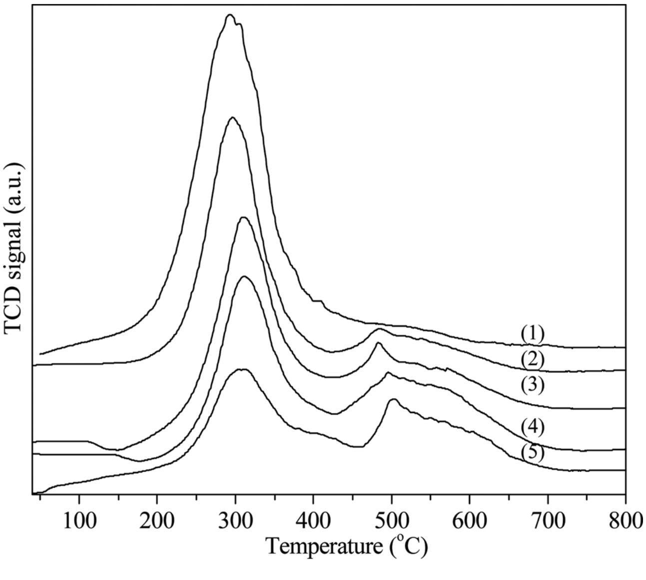


FIGURE 5 H_2-TPR profiles of Ba-CCA catalysts with a Ba/Cu molar ratio of (1) 0, (2) 0.1, (3) 0.3, (4) 0.5, and (5) 0.7.

occlusion of Cu^{2+} species, leading to the decrease in production of the surface Cu^0 species during the pretreatment with H_2. The results show that the Cu^0 species play an important role in GL cyclization with AN besides the basicity of Ba-CCA catalysts. The Cu^0 species probably promote the dehydrogenation or dehydration of GL to intermediates containing the carbonyl group, which can interact with the $—NH_2$ group in AN molecules to imines Schiff base (SB), and SB further cyclization to 3-MI, 3-Imol, and even QN easily takes place in the Cu^0-active species [1,3].

Effect of the Carrier Gas Composition

As mentioned above, GL dehydrogenation or dehydration to intermediates containing the carbonyl group is probably an important pathway for GL cyclization with AN. According to our previous studies [9,10], Cu^0 centers can exhibit a catalytic activity for hydrodehydration of alcohols with H_2. Therefore, the present work also investigates the GL cyclization with AN over the Ba-CCA catalyst in N_2 as the carrier gas by introducing a different amount of H_2 or O_2. The results (Fig. 6) indicate that the Ba-CCA catalyst gives a low GL conversion and yield toward 3-MI and 3-IMol; the product is mainly QN in oxidative carrier gases including air or $5\%O_2–N_2$ mixture, which is coincident with those results reported by Reddy and Ganesh [12] by using N_2 as the carrier gas; 3-MI with a yield of 39.09% is obtained as a main product. Moreover, 3-MI yield can be further improved by introducing an amount of H_2 into the carrier gas and reaches up to the highest value of 57.05% when using $20\%H_2–N_2$ as the carrier gas. Although the main product in GL cyclization with AN over Cu/SiO_2-Al_2O_3 and Ag/SiO_2 has been reported by Shi et al. [6–8] to be 3-MI in N_2 or a $N_2–H_2$ mixture gas; the obtained 3-MI yield over both catalysts is not too high (only 38%). It indicates that the present catalyst Ba-CCA with the Ba/Cu molar ratio of 0.1 exhibits a good catalytic activity in GL cyclization with AN to 3-MI.

Effect of Reaction Temperature

The effect of temperature on GL cyclization with AN over the Ba-CCA catalyst is investigated. As shown in Fig. 7, GL conversion increases when the temperature shifts from 220 to 300°C. A 3-MI yield of 41.36% is obtained at 220°C and reaches up to 65.17% when increasing the reaction temperature to 240°C. However, a higher temperature (>260 °C) will lead to a gradual decrease in the 3-MI yield. It indicates that a higher reaction temperature probably results in the side reaction from GL. From GC analysis of products mixture, the by-products involve *N*-methylaniline, *N*-ethylaniline, *N*-propylaniline, and acrolein. Anyway, it seems that 240°C is the optimum temperature for 3-MI synthesis from GL and AN over the Ba-CCA catalyst. It is obvious that the highest 3-MI yield obtained in the present work is much higher than that reported by Shi et al. [7,8].

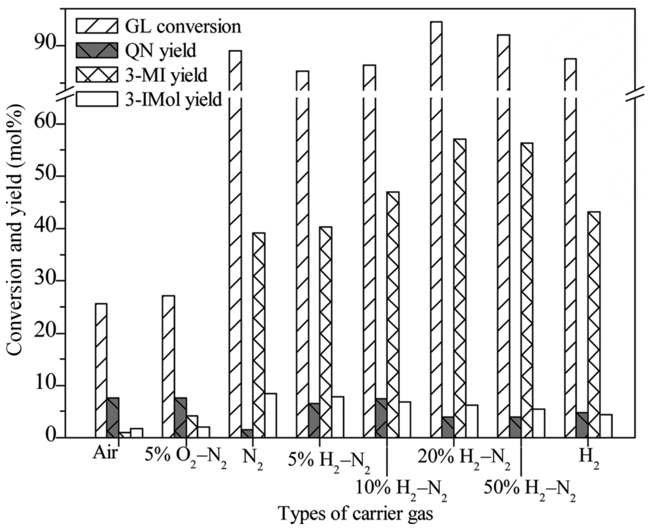


FIGURE 6 Effect of the carrier gas on the catalytic property of the Ba-CCA catalyst with Ba/Cu = 0.1. Reaction conditions: temperature 260°C; a feed rate of liquid reactant mixture (AN/GL molar ratio 3) 2.8 mL·h^{-1}; catalyst 2 g; rate of the carrier gas 60 mL·h^{-1}.

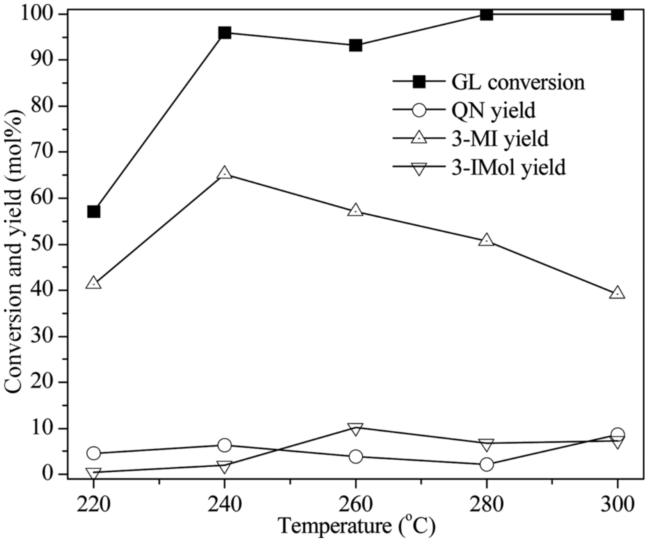


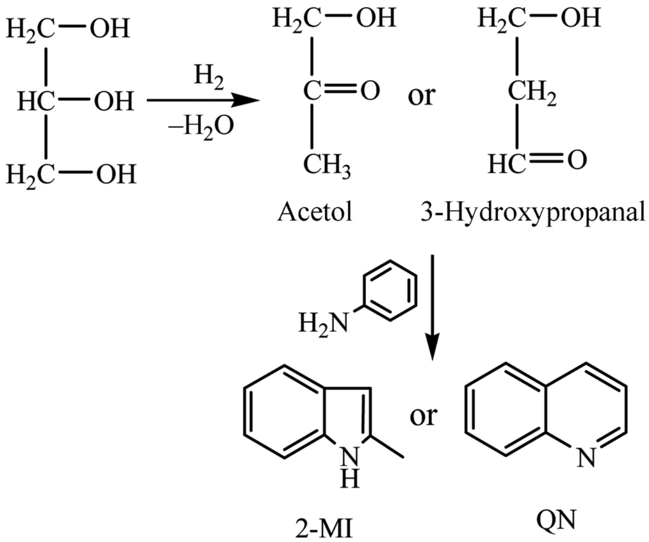
FIGURE 7 Effect of temperature on the cyclization over the Ba-CCA catalyst with Ba/Cu = 0.1. Reaction conditions: the feed rate of the liquid reactant mixture (AN/GL molar ratio 3) 2.8 mL·h^{-1}; catalyst 2 g, the rate of $20\%H_2–N_2$ as the carrier gas 60 mL·h^{-1}.

Proposed Cyclization Pathway

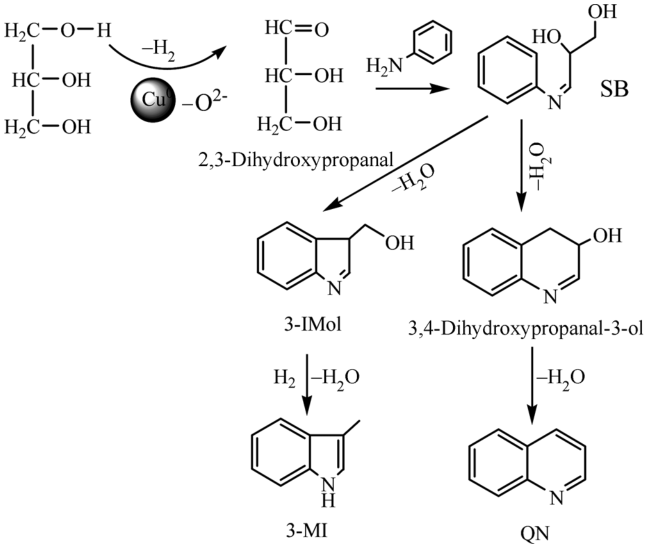
As proposed by Shi et al. [7, 8, 12], GL cyclization with AN takes place mainly through cyclization of SB, which is produced by *N*-alkylation of AN with carbonyl groups from dehydration of GL molecules. As well known, GL dehydration can produce two kinds of intermediates containing the carbonyl group such as 3-hydroxypropanal and acetol and is promoted by using Cu^0 as catalytic active centers in the presence of H_2. Thus, the cyclization of SB should lead to the easy formation of QN and 2-methylindole (2-MI) as shown in Scheme 3. It seems easy to illustrate the formation of by-products QN and acrolein through further dehydration of 3-hydroxypropanal. However, 2-MI as a cyclization product is not detected in our reaction system. In addition, it can not also explain that the formation of QN in N_2 as the carrier gas without H_2 and a higher yield of 3-MI has been obtained in N_2 or the H_2–N_2 mixture gas (Fig. 6). Therefore, the cyclization pathway as shown in Scheme 3 seems unreasonable for explaining the formation of 3-IMol and 3-MI.

From results of the above catalytic tests, it is observed that the introduction of Cu-active species and basic species improves 3-MI formation, and another cyclization product such as 3-IMol is also found to be formed. As reported [15–17], the basic sites are typical catalytic centers for dehydrogenation of alcohols to aldehydes. Therefore, it is proposed that the formation of SB is from AN and intermediate 2,3-dihydroxypropanal produced by the dehydrogenation of GL molecules [3] over Cu^0 particles or basic sites (Scheme 4). SB occurs intramolecular cyclization to 3,4-dihydroquinolin-3-ol and 3-IMol, which is probably a slow reaction step. The former easily forms QN through dehydration, and the latter produces 3-MI through the hydrodehydration. Moreover, both reactions should be a fast reaction, which can be improved by H_2 in the carrier gas. It indicates that the actual function of H_2 is not to promote GL hydrodehydration to intermediate, but to accelerate 3-IMol conversion to 3-MI. In addition, it seems contrary that a high 3-MI yield is obtained in N_2 as the carrier gas without H_2. In this case, H_2 as the raw material for 3-IMol hydrodehydration to 3-MI is mainly from GL dehydrogenation over Cu^0-active centers or basic sites (Scheme 4).

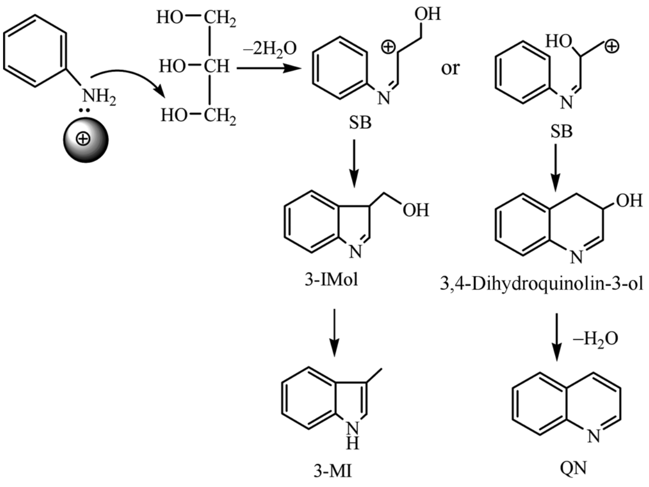
Obviously, the intramolecular cyclization of SB is an important step for the production of *N*-heterocycle products such as 3-IMol, 3-MI, or QN. As shown in Scheme 4, an achievement of this step and even production of the final products such as 3-MI and QN are through dehydration. It is proposed that dehydration mainly is carried out over the acidic sites, which has also been proved by NH_3-TPD (Table 1). In addition, there is still another fact that the acidic Al_2O_3, CCA and even other Cu-based catalysts such as Cu/SiO_2–Al_2O_3 reported by Shi et al. [7, 8] also lead to the 3-MI formation. It is probably because that acidic sites can activate AN molecules through chemical adsorption of —NH_2 groups, which can directly interact with —OH groups in GL molecules to SB as shown in Scheme 5. Certainly, the Cu^0-active species in acidic Cu-based catalysts also probably catalyze dehydrogenation of GL in the same way as shown in Scheme 4, which will also easily interact with the activated AN. Moreover, Cu^0-active species are also the catalytic centers



SCHEME 3



SCHEME 4



SCHEME 5

for 3,4-dihydroquinolin-3-ol dehydration to QN and 3-IMol hydrodehydration to 3-MI, respectively.

With the increase in reaction temperature (>240°C), SB as shown in Schemes 4 and 5 is easily converted to a by-product such as *N*-propylaniline through the fast hydrodehydration. Moreover, high temperature can also lead to the improvement on GL drastic dehydration to acrolein and even the C—C leakage of GL to aldehyde and formaldehyde ,which interact with AN to *N*-ethylaniline and *N*-methylaniline, respectively.

EXPERIMENTAL

Catalyst Preparation and Modification

Preparation and modification of CuCr/Al$_2$O$_3$ (CCA) catalysts were carried out by coimpregnation. Typically, 20 g of dried commercial γ-Al$_2$O$_3$ ($S_{\mathrm{BET}} = 210$ m^2·g^{-1}, particle size 0.8–1.2 mm) as support were crushed to the desired particles with a size of 0.45–0.85 mm and impregnated in the aqueous solution containing Cu(NO$_3$)$_2$, Cr(NO$_3$)$_3$, and/or nitrates of Al or alkali earth metals (such as Mg, Ca, Sr, and Ba) for 2 h at room temperature. Wherein, the molar ratio of Cu:Cr:M was 1:2:0.1 except those mentioned especially, the total weight percentare of Cu and Cr was controlled to 5 wt% in comparison with the support. The samples were dried at 80°C for 12 h, and then calcined at 550 °C for 7 h to obtain the M-CCA catalysts, wherein M referred to Al, Mg, Ca, Sr, or Ba.

Catalyst Characterization

BET surface areas (S_{BET}), pore volume, and pore size of the catalysts were measured by the N$_2$ adsorption-desorption isotherms at −196°C using an SSA-4200 analyzer (Builder Instrument Co., Beijing, China). Powder X-ray diffraction (XRD) analysis of catalysts was carried on a DX-2700 X-ray powder diffractometer (Fangyuan Instrument Co., Dandong, China) operated at 30 kV and 20 mA, using Cu Kα radiation. Temperature-programmed reduction by H$_2$ (H$_2$-TPR) and temperature-programmed desorption of NH$_3$ or CO$_2$ (NH$_3$-TPD or CO$_2$-TPD) were performed on a TP-5080 adsorption instrument (Xianquan Co., Tianjing, China) equipped with a thermal conductivity detector. In a typical H$_2$-TPR experiment, 20 mg of the sample placed in a quartz tube was first degassed under 30 mL·min^{-1} of N$_2$ at 300°C for 30 min and then cooled to room temperature. The TPR profiles were recorded from room temperature to 850°C with a heating rate of 10°C·min^{-1} under 30 mL·min^{-1} of 5% H$_2$–N$_2$ mixture. For TPD, 20 mg of catalysts were pretreated in N$_2$ at 300°C for 30 min. The adsorption of NH$_3$ or CO$_2$ was carried out by feeding 10 vol% NH$_3$ or CO$_2$ in 30 mL·min^{-1} of N$_2$ at room temperature. Samples were washed with dry N$_2$ for another 2 h to remove physisorbed molecules. The obtained samples were heated in He at a heating rate of 10°C·min^{-1} from 50 to 850°C for NH$_3$ or CO$_2$ desorption.

Catalytic Test

The catalytic tests were carried out in a fixed-bed quartz microreactor (i.d. 15 mm, length 40 cm) placed in an electronically controlled oven and operating at atmospheric pressure. Prior to activity test, 2 g catalysts were in situ pretreated in 40 mL·min^{-1} of H$_2$ at 300°C for 2 h. After 60 mL·min^{-1} of the given carrier gas was switched and temperature was decreased to a desired value (220–300°C), the liquid mixture containing GL and AN with a molar ratio of 1:3 was pumped into the reactor at a feed rate of 2.8 mL·h^{-1}. The tested period was 4 h, and the products liquid mixture was collected by an ice-salt cool trap and analyzed qualitatively and quantitatively on the SC-2000 gas chromatograph (GC; Chongqing Chuanyi Analyzer, China) equipped with an Agilent CAM capillary column (30 m × 0.32 mm × 0.25 μm film thickness) and a flame ionization detector. The residual reactants concluding GL and AN and products were ascertained according to the GC retention time of the corresponding standard substances; their amounts were calculated according to their GC peak area and the corresponding correction factors. Yields of target products were obtained based on GL conversion.

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