Chinese Chemical Letters 24 (2013) 751–754

Contents lists available at SciVerse ScienceDirect

Chinese Chemical Letters

journal homepage: www.elsevier.com/locate/cclet

Original article

Synthesis of pyrazinyl compounds from glycerol and 1,2-propanediamine over Cu–TiO_2 catalysts supported on γ-Al_2O_3

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ARTICLE INFO

Article history:
Received 26 February 2013
Received in revised form 2 April 2013
Accepted 3 April 2013
Available online 10 May 2013

Keywords:
Catalytic cyclization
Glycerol
Alkyl-substituted pyrazines
Steric effect

ABSTRACT

Cu–TiO_2 catalysts supported on γ-Al_2O_3 are prepared and used in glycerol cyclization with 1,2-propanediamine to produce pyrazinyl compounds including 6-hydroxymethyl-2-methylpyrazine, 5-hydroxymethyl-2-methylpyrazine, 2,6-dimethylpyrazine and 2,5-dimethylpyrazine in a fixed-bed system. It is found that glycerol cylclization with 1,2-propanediamine gave a high total yield of pyrazinyl compounds (>80%) over Cu–TiO_2/γ-Al_2O_3 catalyst, and cyclization was through the reactions between activated 1,2-propanediamine and the intermediates from glycerol dehydration and oxidation. In addition, the regioselectivity of the pyrazinyl compounds was mainly controlled by the steric hindrance of the substrates during the cyclization process.

1. Introduction

Pyrazinyl compounds such as pyrazine and alkyl-substituted pyrazines are widely used as intermediates for the production of perfumes, medicines and agricultural chemicals. 2-Methylpyrazine as a key intermediate for pyrazineamide, an effective antitubercular drug, has been successfully synthesized by a cyclization reaction between ethylenediamine (EDA) and propanediol [1–3]. Recently, it has been found that glycerol (GL) can also be used as a raw material providing two –OH groups to react with EDA through a cyclization reaction to form a 2-hydroxymethyl pyrazine intermediate, which is easily converted to 2-MP through a hydrodehydration reaction of one of the $-CH_2OH$ groups along with the production of H_2 [4,5]. Similarly, 1,2-propanediamine (PDA) containing two $-NH_2$ groups can also react with GL to form 6- or 5-hydroxymethyl-2-methylpyrazine (6-HMP or 5-HMP) and even 2,6- or 2,5-dimethylpyrazine (2,6-DMP or 2,5-DMP). Of course, it is important to choose a catalyst capable of activating both the $-NH_2$ group in PDA and the –OH group in GL simultaneously. Along this line of reasoning, the present work introduces Cu^0 and an acidic species TiO_2 to the γ-Al_2O_3 support to produce bifunctional catalysts that catalyze the GL vapor-phase cyclization reactions with PDA in a fixed-bed system.

2. Experimental

Cu–TiO_2/γ-Al_2O_3 (C_xT_yA, where x and y represented the weight content of the introduced TiO_2 and metal Cu relative to the γ-Al_2O_3 support, respectively) catalysts were prepared through fractional impregnation by using tetrabutyltitanate and $Cu(NO_3)_2{\cdot}3H_2O$ as precursors, respectively. After calcination at 400 °C in air, the obtained catalysts were characterized by X-ray powder diffraction (XRD) on a DX-2700 powder diffractometer with Cu Kα radiation, NH_3-temperature programmed desorption (NH_3-TPD) and H_2-temperature programmed reduction (H_2-TPR) on a TP-5080 adsorption instrument, respectively. GL cyclization with PDA was carried out at 380 °C with a feeding rate of liquid reactant with a GL:PDA:H_2O molar ratio of 1:1:8.84 being 1.5 h^{-1} in a fixed-bed quartz tubular reactor. Prior to catalyst testing, the catalysts were on-line pretreated by H_2. The collected liquid mixture were analyzed by a GC-2000 gas chromatograph (GC) equipped with a DB-WAXETR (50 m × 0.32 mm × 1.00 μm, Agilent, USA) capillary column and a flame ionization detector. The produced pyrazinyl compounds and unconverted raw materials were identified by the GC retention time of the corresponding standard reagents, and their contents were quantified using the corresponding GC peak areas and correction factors.

3. Results and discussion

From Table 1, it can be clearly observed that PDA cyclization with GL over typical catalysts certainly produces four important

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http://dx.doi.org/10.1016/j.cclet.2013.04.010

Table 1
Catalytic properties of typical catalysts in cyclization.[a]

Catalyst	Conversion (mol%)		Yield of target products (mol%)			
	PDA	GL	2,6-DMP	2,5-DMP	6-HMP	5-HMP
γ-Al_2O_3	96.4	94.1	21.4	10.5	6.2	8.4
T_7A	85.6	94.9	33.2	45.2	5.5	0.4
C_5A	87.5	92.1	34.5	44.2	4.6	1.2
C_5T_7A	86.9	94.8	37.6	41.3	4.5	1.4
$C_5T_{21}A$	83.1	93.5	31.8	39.8	8.8	1.2

[a] 20%H_2–N_2 mixture as carrier gas (SV 1200 h^{-1}).

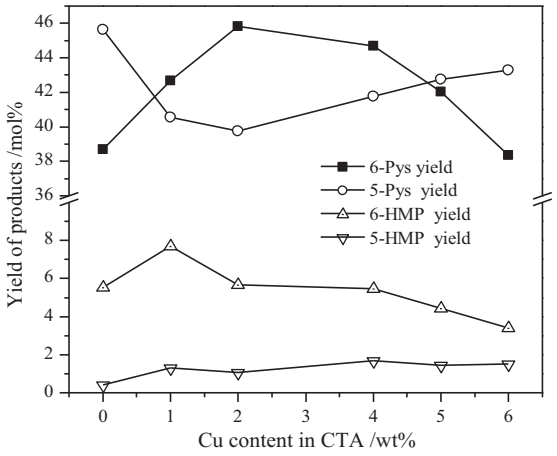
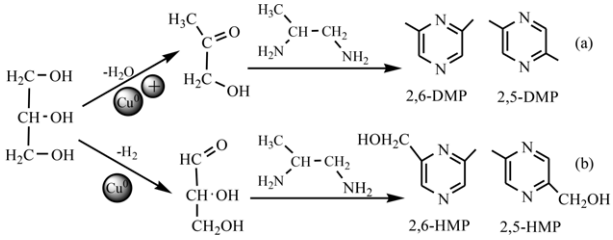


Fig. 1. Effect of Cu content on property of C_xT_7A catalysts in cyclization in 20%H_2–N_2 mixture. 6-Pys: 6-HMP and 2,6-DMP; 5-Pys: 5-HMP and 2,5-DMP.

pyrazinyl compounds, namely 2,6-DMP, 2,5-DMP, 6-HMP and 5-HMP. However, a low total yield for the four pyrazinyl compounds (only 46.5%) is obtained, although conversions of both GL and PDA are very high over γ-Al_2O_3.The total yield of the four products reaches up to 81.6% over Cu, TiO_2 or Cu–TiO_2 catalysts supported on γ-Al_2O_3. γ-Al_2O_3 gives some side-products, but the presence of Cu and/or TiO_2 species can improve the PDA cyclization with GL. Moreover, it can be found that the total yield of four products over four catalysts except γ-Al_2O_3 is near PDA conversion, indicating that the side reactions over these catalysts are mainly derived from GL molecules.

In order to investigate the role of Cu and TiO_2 species, the effect of Cu content on the catalytic properties of CTA catalysts (TiO_2 content = 7 wt%) in the cyclization reaction between GL and PDA is



Scheme 1. Formation of pyrazinyl compounds from GL and PDA.

studied first. The results show that all catalysts with a variety of different Cu contents (from 1 wt% to 6 wt%) give high PDA and GL conversions of about 85% and 95%, respectively. However, an increase of 6-Pys formation and a decrease of 5-Pys formation are found as shown in Fig. 1 when Cu content increases from 0 to 2 wt%, but a reverse trend is observed as the Cu content further increases. XRD patterns (Fig. 2) indicate that the supported Cu species are highly dispersed and TiO_2 is in the form of anatase phase. H_2-TPR results show that Cu species can be converted to Cu^0 during the catalyst pretreatment with H_2 at 420 °C. According to our previous studies [6], Cu^0 sites can catalyze the hydrodehydration reactions of alcohols. GL dehydration possibly leads to acetol formation [7], which can be improved by H_2 in carrier gas. Of course, the acidic sites are also known catalytic centers for the dehydration of alcohols [8]. Thus, GL cyclization with PDA is conceivably through the pathway as shown in Scheme 1(a).

The carbonyl group in acetol easily reacts with the terminal –NH_2 group in PDA to form selectively 2,5-DMP due to steric effect. But the terminal –NH_2 can be adsorbed on the acidic sites of catalysts, leading to a facile reaction between acetol and the 2-NH_2 group in PDA to form 2,6-DMP. The increase on Cu content will accelerate the acetol formation, which is helpful to the 2,6-DMP formation. However, increase of Cu species will reduce acidic sites (Fig. 3a), thus favors the 2,5-DMP formation. Clearly, GL can also be converted to dihydroxylpropanal (DHP) over Cu^0 or other active sites through dehydrogenation [9], which will result in the formation of 6- and 5-HMP as shown in Scheme 1(b). Incidentally, DMP can also be derived from HMP hydrodehydration.

The effects of TiO_2 content in the C_2T_yA catalyst (2 wt% Cu) on the condensation between GL and PDA (Fig. 4) to produce of 5- or 6-HMP are negligible, but the formation of 5- and 6-DMP strongly depends on the TiO_2 content. This is possibly a result ofthe production of more acid sites due to the presence of TiO_2 species, which is consistent with the NH_3-TPD results (Fig. 3b). Acidic sites provide catalytic centers for GL hydration to form acetol, also

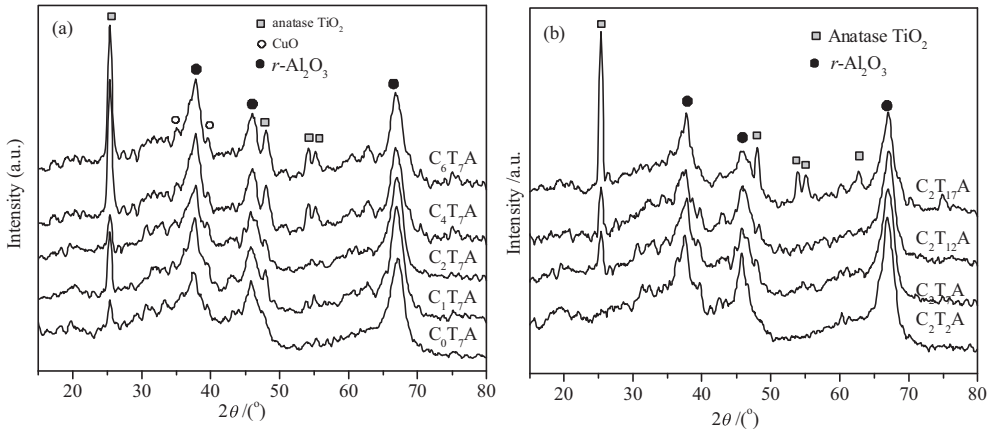


Fig. 2. XRD patterns of C_xT_7A catalysts (a) and C_2T_yA catalysts (b).