

Article

One-Pot Synthesis of *N,N'*-dialkylureas via Carbonylation of Amines with CO₂ Applying Y_{0.08}Zr_{0.92}O_{1.96} Mixed Oxide (YSZ-8) as a Heterogeneous Catalyst

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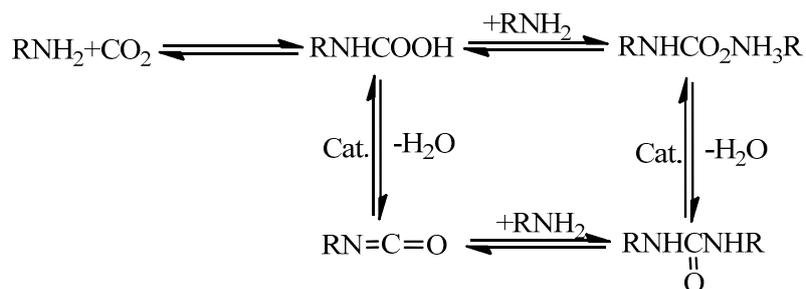
Abstract: One-pot synthesis of *N,N'*-dialkylureas were successfully achieved from catalytic carbonylation of aliphatic primary amines with CO₂ as the carbon source and Y_{0.08}Zr_{0.92}O_{1.96} mixed oxide (Yttria-stabilized zirconia, YSZ-8) as the heterogeneous catalyst. The yield of the target product was obtained up to 80.60% from a 48 h reaction with an aliphatic primary amine and 3.0 MPa CO₂ in *N*-methyl-2-pyrrolidinone at 160 °C. A multi-pronged mechanistic study was carried out where factors that might influence the reaction efficiency were studied, including catalyst structure, substrates basicity, CO₂ pressure, solvent polarity and reaction time. The presence of oxygen vacancies in YSZ-8 was found to be essential for the carbonylation process by creating additional reduction potential for the activation of CO₂ which would lead to the key intermediate species.

Keywords: Y_{0.08}Zr_{0.92}O_{1.96} mixed oxide; *N,N'*-dialkylurea; carbonylation; CO₂; heterogeneous catalysis

1. Introduction

N,N'-dialkylureas are widely used in the chemical industry, especially in the manufacture of pesticides, herbicides, pharmaceuticals, resin precursors and plant growth regulators [1]. Conventionally, they are prepared from highly toxic reagents depending on methods such as phosgene or isocyanates [2]. In the past few years, a number of safer and more environmentally benign synthetic routes were invented [3], including carbonylation of amines with various carbonyl derivatives such as carbonyldiamide [4], acetoacetanilide [5], carbonate [6], urea [7], carbamate [8] etc.; or with gaseous C₁ sources such as CO [9,10] or CO₂ [11]. Amongst them, direct carbonylation of amines by CO₂ is far more attractive from the standpoint of either environmental consideration or resource utilization [3].

For the preparation of *N,N'*-dialkylureas from catalytic carbonylation of amines with CO₂, the following steps are generally involved (Scheme 1):



Scheme 1. Reaction steps involved in the synthesis of *N,N'*-dialkylureas from amines and CO₂.

It is well-known that CO₂ readily combines with amines at room temperature and ambient pressure, forming the corresponding carbamic acids [12]. Thus, the key step in the aforementioned procedure is the equilibrium-limited dehydration of carbamic acids to ureas/or isocyanates [13]. Either harsh conditions (200 °C, and CO₂ pressures higher than 10 MPa) or the addition of stoichiometric amounts of dehydrating agents (such as dicyclohexylcarbodiimide, PCl₅, POCl₃, and so on) are usually needed to shift the equilibrium towards the desired product (Scheme 1) [14,15], which would inevitably lead to a series of side products. However, the adoption of a proper catalyst could be an ideal solution, such as Y₂(C₂O₄)₃ [9], K₃PO₄ [16], 1,5-diazabicyclo[4.3.0]non-5-ene (DBU) [17], guanidine [18], Cs₂CO₃ [19], CsOH/[bmim] OH [20], polymer-immobilized nanogold (Au@polymer) [21], KOH/polyethylene glycol [22], TBA₂[WO₄] (TBA = [(n-C₄H₉)₄N]⁺) [23], and cesium benzotriazolide [24]. It is of particular interest that the employment of Au@polymer as a heterogeneous catalyst resulted in an appreciable yield of *N,N'*-dialkylureas. However, the stability of Au@polymer catalyst is not promising, due to the relatively weak chemical bonding between gold nanoparticles and the self-unstable polymer support, particularly under extreme reaction conditions (5.0 MPa CO₂, 180 °C, 20 h, and alkaline reaction environment in the presence of amine as raw materials). Obviously, the exploration of more efficient catalysts, especially heterogeneous catalysts that can be easily recycled, is still highly desired for the catalytic carbonylation of amines by CO₂.

As a ceramic material with good thermal and chemical stability, Yttria-stabilized zirconia (YSZ) is also one of the most widely used heterogeneous catalysts/catalyst supports in the field of catalytic synthesis [25]. It was reported to catalyze reactions such as oxidation of hydrocarbons [26], hydrogenation of CO and CO₂ [27,28], electrochemically assisted NO_x storage-reduction [29], and so on. In this study, yttria-stabilized ZrO₂ (8 mol % Y, YSZ-8) was employed as a heterogeneous catalyst for the production of *N,N'*-dialkylureas via carbonylation of amines directly with CO₂. Factors influencing the reaction efficiency were studied systematically, where a possible reaction mechanism was also proposed.

2. Experimental

2.1. Synthesis of the YSZ-8 Catalyst

The YSZ-8 catalyst was synthesized using the co-precipitation method at room temperature as described in the literature [30]. The typical procedure is as follows: firstly, ZrOCl₂·10H₂O (>98.5% pure, Aladdin Chemicals) and Y(NO₃)₃·6H₂O (>99.5% pure, Aladdin Chemicals) were dissolved in de-ionized water and mixed according to a molar ratio of Zr/Y = 97:3 in a 250 mL three-neck flask equipped with a magnetic stirrer at room temperature to form a precursor solution. Then, the pH value of the precursor solution was adjusted to 8 with 0.1 M NH₃ solution (25 wt. % in water, Aladdin Chemicals), resulting in a cream-white suspension. The white precipitate was recovered by filtration, washed with ethanol, dried at 100 °C overnight, and calcinated in vacuum at 600 °C for 4 h.

As a comparison, pure Y₂O₃ and ZrO₂ catalysts were prepared following the same procedure as was used for YSZ-8, without zirconium or yttrium additives, respectively.

2.2. Characterization of Catalyst

X-ray diffraction (XRD) spectroscopy was performed on a Bruker D8 Advance diffractometer (Brukerstr., Beijing, China) with Cu K α 1 radiation. Scans were made over a range of $2\theta = 6\text{--}80^\circ$, at a rate of $1^\circ/\text{min}$.

X-ray photoelectron spectroscopy (XPS) was carried out on a Thermo Scientific/k-Alpha (Thermo Fisher Scientific, Shanghai, China) with Al K α radiation ($E = 1486.6\text{ eV}$). A C $_{1s}$ binding energy (BE) of 284.6 eV was used as a reference.

2.3. Carbonylation of Amine with CO $_2$

The carbonylation of amine with CO $_2$ (>99.9% pure, Jun Duo Gas Co., Guangzhou, China.) was performed using a 50 mL Teflon-lined stainless-steel autoclave equipped with a magnetic stirrer. In a typical procedure, 5×10^{-2} mol of amine, 30 mL of solvent and 4.5×10^{-4} mol of catalyst were firstly charged into the autoclave. Then, a flow of nitrogen was introduced to drive out the air contained in the autoclave, and a mixed gas of CO $_2$ /N $_2$ (2/1 in mole ratio) was introduced into the reactor at room temperature to meet a total pressure of 2.5 MPa, and then the gas inlet was shut off. After that, the temperature was slowly increased to 160 °C (caution: this would usually elevate the pressure to ca. 6.5 to 7.0 MPa), where the reaction mixture was remained for 6–48 h with stirring. When the reaction completed, the reactor was opened at room temperature, where the catalyst can be recovered simply by filtration, washed with deionized water and calcined under vacuum at 600 °C for 4 h. All these products were qualitatively and quantitatively analyzed over a QP2010 plus GC-MS instrument (Shimadzu, Shanghai, China) equipped with a RXiTM-5MS capillary column (30 m \times 0.25 mm). Both the conversion of amines and yields of various products were determined by comparing to an external standard and calculated following the equation $W_{sp} = W_{st} \cdot A_{sp} / A_{st} \times 100\%$, where *sp* and *st* refer respectively to specimen and standard. The reaction selectivity was calculated via area normalization method, based on the converted amine. As for the isolation of *N,N'*-dialkylurea, 100 mL of 1.0 mol % sodium carbonate aqueous solution was added to the previous filtrate, precipitating *N,N'*-dialkylurea as a white solid, which was then collected by filtration and dried at 80 °C for 24–48 h, and the filtrate was distilled to remove water for recovering the organic solvent. The solid was identified to be *N,N'*-dialkylurea via mass and IR spectroscopies. Based on the weight of solid, the isolated yield of *N,N'*-dialkylurea was obtained.

All the chemicals used above for the synthesis of *N,N'*-dialkylureas were purchased from Aladdin Chemical Co. (Shanghai, China), and dried prior to use to remove water.

3. Results and Discussion

3.1. Structural Characterization of the Catalysts

The XRD pattern of the YSZ-8 (Figure 1a) is totally consistent with that of the Y $_{0.08}$ Zr $_{0.92}$ O $_{1.96}$ mixed oxide (JCPDS No. 48-0224); no other crystalline nor amorphous phase was detected. It can be concluded that the YSZ-8 (Figure 1a) catalyst prepared in this work possesses exactly the structure of Y $_{0.08}$ Zr $_{0.92}$ O $_{1.96}$ mixed oxide. Nevertheless, the position of a few diffraction peaks at 2-theta angles of 30.2°, 55.3°, and 58.6° for YSZ-8 show a slight shift to high angle compared to the standard diffraction XRD card of Y $_{0.08}$ Zr $_{0.92}$ O $_{1.96}$ (JCPDS No. 48-0224). This could be ascribed to a homogeneous insertion of yttrium to the zirconia structure, which could result in sub-lattice zirconium defects in YSZ-8. When comparing the XRD pattern of pure Y $_2$ O $_3$ catalyst (Figure 1c) with that of YSZ-8 (Figure 1a), no distinguishable peak could be indexed to Y $_2$ O $_3$, further demonstrating the incorporation of Y into the zirconia framework. Meanwhile, the XRD intensity of YSZ-8 increased dramatically comparing to that of pure ZrO $_2$ (Figure 1b), indicating that the insertion of yttrium to the zirconia would result in a more perfect crystalline form.

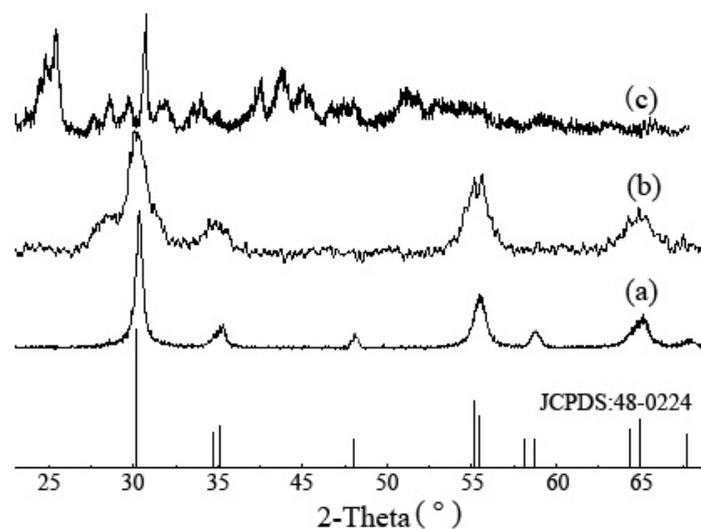


Figure 1. X-ray diffraction patterns of catalysts after thermal treatment at 600 °C. (a) 8 mol % yttria-stabilized zirconia (YSZ-8); (b) pure ZrO_2 ; (c) pure Y_2O_3 .

The chemical states of Y, Zr, and O atoms in YSZ-8 were investigated by XPS. As shown in Figure 2, the XPS spectra of Zr3d, Y3d and O1s in YSZ-8 powder are consistent with the reported characteristics of yttrium and zirconium atoms in yttria-stabilized zirconia [31–35]. The elemental ratio of Y/Zr on the surface of YSZ-8 obtained by XPS is 0.09:1, which is in good agreement with XRD analysis. The BE of $Zr3d_{5/2}$ in YSZ-8 was found to be 181.9 eV (Figure 2a)—slightly lower than pure ZrO_2 (182.5 eV [32])—while that of $Y3d_{5/2}$ was 156.9 eV (Figure 2b)—slightly higher than pure Y_2O_3 (156.2 eV [33]). The significant chemical shift observed on both Zr3d and Y3d core level peaks might probably be due to the insertion of yttrium into the zirconia framework, leading to highly mobile oxygen vacancies in the catalyst, as observed from the XRD pattern of the YSZ-8 catalyst. Afterwards, electrons from yttrium could be further transferred to these vacancies, where a similar charge transfer from the vacancies to zirconium could also happen, ultimately leading to peaks of Zr3d shifting toward lower BE and those of Y3d toward higher BE.

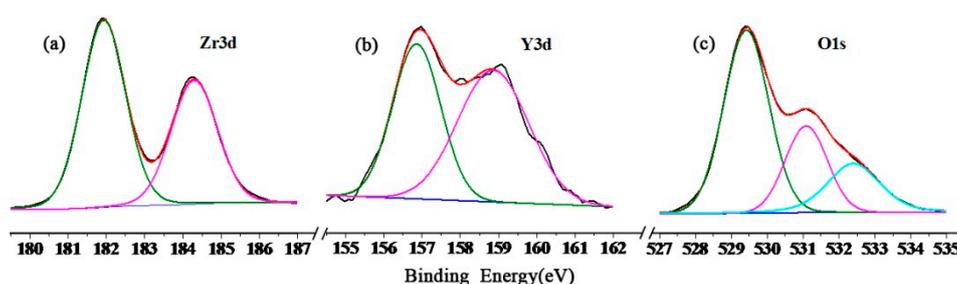


Figure 2. Zr3d (a), Y3d (b) and O1s (c) of the synthesized YSZ-8 catalyst.

The former hypothesis is further supported by the O1s spectra (Figure 2c), which revealed the existence of three oxygen ions: lattice oxygen O^I (BE = 529.4 eV), chemisorbed oxygen O^{II} (BE = 531.1 eV), and oxygen related to vacancy sites O^{III} (BE = 532.4 eV). This perfectly matched that of yttria-stabilized zirconia as reported in the literature [31,34,35], except that the relative intensities of the three oxygen components in the synthesized YSZ-8 changed comparing with the YSZ-8 reported in *Ref.* 31. More specifically, the ratio of their relative intensities for the synthesized and reported YSZ-8 are $O^I:O^{II}:O^{III} = 56:24:20$ and $74:20:6$, respectively, displaying an increase in the O^{III} peak of the synthesized YSZ-8. The increase of the relative intensity of the O^{III} peak in the synthesized YSZ-8 could

be resulted from an increase of oxygen vacancy sites and/or an increase of the sub-lattice zirconium defects sites.

3.2. Carbonylation of 1-Butanamine by CO₂

Various catalysts and solvents were tested for the carbonylation of 1-butanamine (1a) by CO₂ and the results were listed in Table 1. In the absence of a catalyst (entry 1), the conversion is only 4.17% and the selectivity in *N,N'*-dibutylurea (2a) is 94.03% after 24 h. Unsurprisingly, the employment of a catalyst resulted in a large increase in conversion (entries 2~11) and, in most cases, an increase in selectivity of 2a.

Table 1. Results for carbonylation of 1-butanamine (1a) to the corresponding *N,N'*-dibutylurea (2a) with CO₂ ^a.

Reaction scheme: 2 molecules of 1-butanamine (1a) react with CO₂ (20 atm) and N₂ (10 atm) in a solvent at 160 °C for 24 h to produce *N,N'*-dibutylurea (2a) and H₂O.

Entry	Catalyst	Solvent	Con ^b . (%)	Sel ^c . (%)			Yields ^d (%)
				2a	Main by-Products		
1 [11]	-	NMP	4.17	94.03	-	5.97	3.92
2	Y ₂ O ₃	NMP	44.25	96.14	-	3.86	42.54
3	ZrO ₂	NMP	35.79	95.25	-	4.75	34.09
4	YSZ-8	NMP	64.32	90.13	7.96	2.01	57.97
5 ^e	YSZ-8	NMP	72.32	90.78	7.63	1.59	65.65
6 ^{e,f}	YSZ-8	NMP	83.95	91.01	7.74	1.25	76.40
7 ^g	YSZ-8	NMP	63.92	89.68	7.80	2.52	57.32
8	YSZ-8	DMI	60.17	89.59	8.43	1.98	53.91
9	YSZ-8	DMA	50.02	90.41	7.38	2.21	45.22
10	YSZ-8	DEDM	35.19	90.33	7.52	2.15	31.79
11	YSZ-8	BuOH	8.95	69.71	12.09	0.56 + 17.64 ^h	6.24

^a Unless otherwise mentioned, all reactions were carried out under conditions as follows: 5×10^{-2} mol of amine, 30 mL of solvent, 2.5×10^{-3} mol of catalyst, 2.5 MPa total pressure of a mixed gas CO₂/N₂ (2/1 in mole) at 25 °C, 160 °C, 24 h; ^{b,c} Conversion of amine and selectivity to various products, obtained via area normalization method based on GC determined data; ^d GC yield (isolated yield); ^e 0.5 g 4 A zeolite as the dehydrating agent was added; ^f Reaction time = 48 h; ^g Reaction was conducted by using the recovered catalyst after the reaction in entry 4. This catalyst was reused for the tenth time; ^h Selectivity to n-butyl isocyanate was 0.56% and the rest number for other byproducts, including mainly *N*-butyl carbamate, butyl butylate and dibutyl carbonate. NMP: *N*-methyl-2-pyrrolidinone; DMI: dimethylimidazolidinone; DMA: *N,N'*-dimethylacetamide; DEDM: 2-methoxyethyl ether.

The conversion of 1a increased most when catalyzed by YSZ-8, where conversions above 64.32% (entries 4–7) and selectivity up to 90.13% were achieved. It can be easily seen that both the conversion of 1a and the yield of 2a for the catalysts involved in this work have an order of YSZ-8 > Y₂O₃ > ZrO₂. Undoubtedly, YSZ-8 possesses the best catalytic activity amongst all these tested catalysts. Based on the structural characterizations based on XRD and XPS patterns of YSZ-8 in Section 3.1, such an activity can be ascribed to the interfacial structure of YSZ-8 catalyst which would be more favorable for adsorption and activation of CO₂ due to an increase in oxygen vacancies with the yttrium insertion into zirconia. This can be further validated from the literature: as was pointed out by Ge, de Leitenburg and co-workers [36], CO₂ preferred to adsorb on negatively charged defects in the lattice of catalyst through a bent configuration, resulting in the activation of the adsorbed CO₂; while, based on a comparison of YSZ-8, Y₂O₃, and ZrO₂ upon CO₂ adsorption by Penner and co-workers [37], their CO₂ adsorptive capacity displayed an order of YSZ-8 > Y₂O₃ > ZrO₂, and the relative fraction of CO₂ adsorption on the oxygen vacancies sites with YSZ-8 is much higher than with the others.

Notably, when a recovered YSZ-8 catalyst was employed under the same conditions of entry 4, almost the same result as that of entry 4 was obtained (entry 7); clearly stating the reusability of the YSZ-8 catalyst in the carbonylation of amines by CO₂ to the corresponding *N,N'*-dialkylureas.

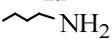
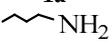
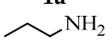
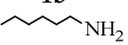
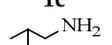
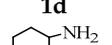
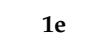
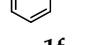
Meanwhile, the employment of a dehydrating agent (4A zeolite, entry 5), or prolonging of the reaction time (from 24 h to 48 h, entry 6), based on the YSZ-8 catalyst, led to the formation 2a, especially in the latter case, and a selectivity as high as 91.01% along with 76.40% GC yield was achieved (entry 6).

Solvents were also found to affect the results obviously (*cf.* entries 2, 8–11): the conversion of 1a in a protic solvent such as BuOH was practically low (entry 11), while higher conversions were acquired in aprotic polar solvents including *N*-methyl-2-pyrrolidinone (NMP), 1,3-dimethylimidazolidinone (DMI), *N,N'*-dimethylacetamide (DMA), and 2-methoxyethyl ether (DEDM), where the conversion increased with the polarity increase of the aprotic solvent. Two reasons can be ascribed here: Firstly, the basicity of amines would be reduced in protic solvents with respect to aprotic ones [38]. As a consequence, the carbonylation process tends to be retarded in BuOH but not in aprotic solvents such as NMP, DMI, DMA, and DEDM. Secondly, the stimulation of the conversion by aprotic solvents displayed an order of NMP > DMI > DMA > DEDM, coinciding with the order of their polarity increase [39]. This result could be ascribed to the stronger inductive effect on CO₂ with aprotic solvents of higher polarity. For instance, NMP is an excellent choice for such a combined physical and chemical trapping of CO₂, as it not only absorbs CO₂, but also stabilizes the ionic intermediates of the chemisorptions [40].

What is also notable is that *N,N'*-dibutylloxamide (3a) was identified as one of the main byproducts in the synthesis of *N,N'*-dialkylurea only when catalyzed by YSZ-8 rather than by ZrO₂ and/or Y₂O₃. This closely correlated to the presence of oxygen vacancy sites and/or sub-lattice zirconium defects sites in YSZ-8, which does not exist in ZrO₂ and/or Y₂O₃ catalysts. In fact, it is reported that the presence of oxygen vacancies in the Rh/CeO₂ and CeO₂-promoted Rh/SiO₂ catalysts could also lead to the reduction of CO₂ by creating additional reduction potential, on the basis of adsorption and activation of CO₂ to surface carbonaceous species [41]. Also reported is that *N,N'*-dialkylloxamides can be prepared from direct oxidative double-carbonylation of amines with CO and O₂ catalyzed either by homogeneous Pd or Ni complexes or by heterogeneous supported gold nanoparticles (Au NPs) [9]. Furthermore, it must be noted that butyl butylate formed from oxidation of *n*-butanol was also detected from the reaction of 1-butanamine and CO₂ catalyzed by YSZ-8 in *n*-butanol, which further evidenced that CO₂ could be partially dissociated into CO and oxygen in the presence of YSZ-8 catalyst. Summarizing, these results clearly revealed that the couple of YSZ-8 catalyst/NMP solvent possessed a unique and significantly superior activity for the carbonylation of amines to the corresponding ureas with CO₂.

Under the optimized conditions (Table 1, entry 5: with YSZ-8 as the catalyst, NMP as the solvent and 4A zeolite as the dehydrating agent), the substrate scope of amines was investigated (Table 2). Aliphatic primary amines were converted to the corresponding *N,N'*-dialkylureas with moderate to high yields (entries 1–7). Specifically, for linear amines, the selectivity of 2 slightly changed with the increasing of C number or chain length of the attached alkyl, while the total conversion of the substrate amine increased rapidly. This may be due to that, on the one hand, starting amines with longer chains possess higher basicity which are more favored by the reaction, as in good agree with the reactivity difference between aprotic solvents and protic ones; on the other hand, the high steric hindrance had a positive effect on the formation of the carbamoyl species from which 2 was generated via reductive elimination. This was further confirmed by a highly hindered branched amine, iso-butylamine 1d, with an 81.38% conversion of 1d and a 96.89% GC selectivity of 2d at 160 °C in 24 h (entry 6). This works perfectly with cyclic aliphatic primary amines such as cyclohexylamine 1e, *N,N'*-dicyclohexylureas (2e), which was obtained with excellent yield (72.11% isolated) and quite high conversion (up to 85.89%) under the same condition (entry 7). Besides the more favored high steric hindrance, the particularly high reactivity of 1e could be ascribed to the greater nucleophilicity and basicity of the N atom compared with the rest amines including 1a/b/c/d/f.

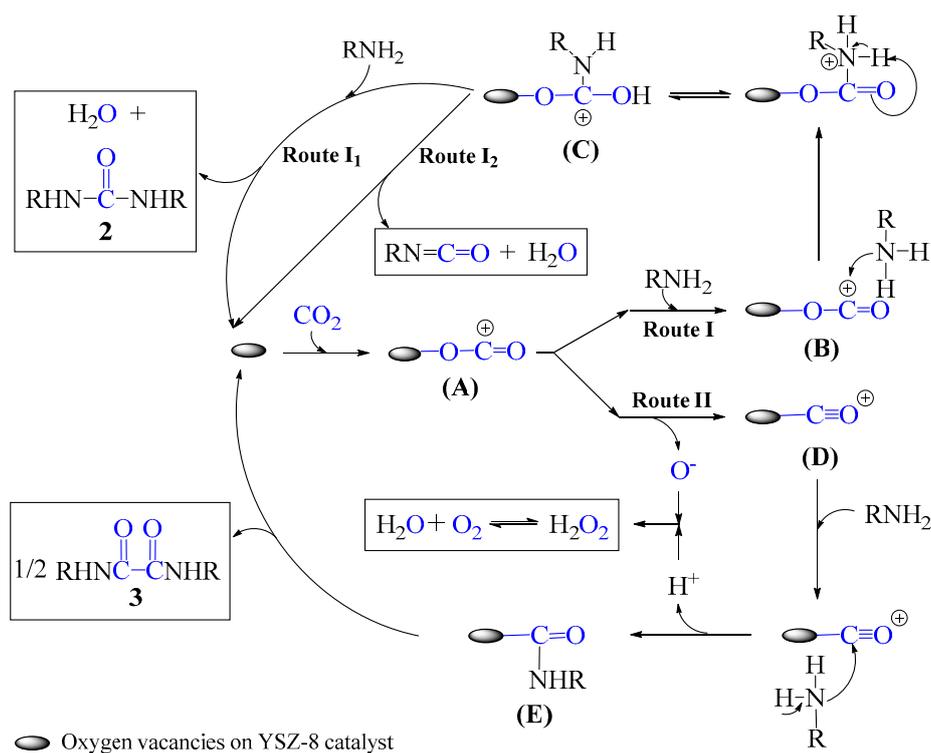
Table 2. Results for carbonylation of various amines (**1**) to the corresponding *N,N'*-dialkylureas (**2**) with CO₂ ^a.

$2 \text{ R-NH}_2 \xrightarrow[\text{NMP, 160}^\circ\text{C, rt.}]{\text{YSZ-8, CO}_2(20\text{atm}), \text{N}_2(10\text{atm})} \text{R-NH-CO-NH-R} + \text{H}_2\text{O}$							
		1		2			
Entry	1	Time (h)	Con ^b . (%)	Sel ^b . (%)		Yields of 2 ^c (%)	
				2	By-Products		
				RHN-CO-NHR		R-N=C=O	
1		12	50.12	94.10	2.81	3.09	47.16
	1a						
2		24	72.32	90.78	7.63	1.59	65.65
	1a						
3 ^d		24	80.23	95.84	2.89	1.27	76.89
	1a						
4		24	71.23	94.87	3.05	2.08	67.58
	1b						
5		24	82.74	96.27	2.41	1.32	79.65
	1c						
6		24	81.38	96.89	2.03	1.08	78.85
	1d						
7		24	85.89	93.84	2.15	4.01	80.60
	1e						
8		24	3.07	-	-	-	-
	1f						
9		24	-	-	-	-	-
	1g						

^a Unless otherwise noted, all reactions were carried out under the following conditions: YSZ-8 (0.313 g), 4 A zeolite (0.500 g), amine (0.05 mol), NMP (30 mL), total pressure of a 2/1 mixture of CO₂/N₂ (2.5 MPa at 25 °C), 160 °C; ^b Determined by GC using an external standard method and calculated using the area normalization method; ^c GC yield based on **1**; ^d The reaction was carried out under 30 atm (at 25 °C) of a 2/1 mixture of CO₂/N₂.

Consistently with the results reported in the literature [19], aromatic primary amines such as aniline **1f** showed very low reactivity towards the carbonylation reaction, with only 3.07% conversion and a negligible GC yield of **2f**, where quiazoline and 1-isocyanatobenzene were detected as the main by-products (entry 8). This could be rooted in the weak nucleophilicity and basicity of anilines [39]. Nevertheless, *N*-dibutylamine **1g**, as a secondary primary amine, could hardly be converted to the corresponding 1,3-di-*N,N*-dibutyl-2-urea via carbonylation with CO₂ (entry 9). Apparently, such a striking difference in reactivity between primary and secondary amines cannot be simply attributed to basicity, nucleophilicity, or steric hindrance between them. Still, it is notable that *N,N'*-dialkylureas were obtained as the main byproduct in the synthesis of isocyanates from monoamides of oxalic acid with peroxydisulfate [42]. In fact, small amounts of isocyanates were also detected by GC-MS in the reaction mixtures of primary amines with CO₂, in especial at early stages. Therefore, it is clear that the reactivity difference between the two types of amines depends on their ability to generate an isocyanate, which is formed in situ via the dehydrolysis of carbamic acids originated from CO₂ and primary amines (Scheme 1). Not surprisingly, the reaction runs faster at higher reaction pressure (compare with entries 2 and 3).

It is well-known that CO₂ easily combines with amines to afford the corresponding carbamic acids at room temperature under atmospheric pressure [12]. However, further transformations of carbamic acids to ureas were much more difficult, except in the presence of a catalyst or stoichiometric amounts of bases [13], which is also in accordance with our experimental results as shown in Table 1. Besides, no reaction was observed to occur between secondary amine and CO₂ in the presence of catalyst YSZ-8 (see Table 2, entry 9). Mechanistic studies in literature showed that the presence of oxygen vacancies in catalysts (such as ceria oxide and rhodium oxide) played a key role in the adsorption and activation of CO₂ on the catalyst surface by creating additional reduction potential for the transformation of CO₂ to CO and/or surface carbonaceous species [41,43]. Meanwhile, XRD and XPS analysis revealed that oxygen vacancy sites and/or sub-lattice zirconium defects sites were formed on the surface of our YSZ-8 catalyst, as discussed in Section 3.1. Based on the combined experimental and literature study, a plausible reaction mechanism is proposed (Scheme 2): initially, a CO₂ molecule is adsorbed to an oxygen vacancy site on YSZ-8, generating complex A which would result in the activation of a carbon-oxygen double bond in the CO₂ molecule. Then, the carbon atom of CO₂ undergoes a nucleophilic attack by an amine, forming complex B as the key active intermediate species. A subsequent proton transfer from amine to the carbonyl oxygen in complex B would result in complex C, which is then nucleophilically attacked by another amine, forming the desired product *N,N'*-dialkylurea (2) with H₂O as a co-product with the catalyst being regenerated (Route I₁). Elimination of complex C could also afford the byproduct isocyanate (Route I₂). Elimination of complex C could also afford the byproduct isocyanate (Route I₂). Elimination of complex C could also afford the byproduct isocyanate (Route I₂).



Scheme 2. Plausible mechanism for the preparation of *N,N'*-dialkylurea from amine and CO₂ over YSZ-8 catalyst.

Meanwhile, an electron transfer from the oxygen vacancy site of YSZ-8 to the adsorbed CO₂ in complex A could result in the formation of both CO species (D) and O⁻ by creating additional reduction potential [22,43]. Afterwards, a nucleophilic attack of the freshly-formed CO by an amine occurs, generating H⁺ and complex E. Subsequent C-C coupling of complex E would yield the byproduct *N,N'*-dialkyloxamide (3), accompanied by the catalyst regeneration (Route II). In general, the reduction of CO₂ to CO and oxygen is much more difficult than that of CO₂ with amines. Consequently, route I

is relatively easier to process than route II, which is consistent with our experimental results where the selectivity of the byproduct *N,N'*-dialkyloxamide (3) is much lower than that of the desired product *N,N'*-dialkylurea (2) (see Tables 1 and 2).

4. Conclusions

The YSZ-8 material prepared in this work was identified as being totally consistent with the compositions of nanosized $Y_{0.08}Zr_{0.92}O_{1.96}$. XRD and XPS patterns of YSZ-8 indicated that the yttrium moiety was incorporated into the zirconia framework, resulting in an increase of oxygen vacancy sites. As a heterogeneous catalyst, YSZ-8 exhibits very high activity and selectivity toward the carbonylation of aliphatic primary amines with CO_2 , forming *N,N'*-dialkylurea under relatively mild conditions. The yield of *N,N'*-dialkylurea was obtained up to 80.60% after 48 h at 160 °C under 3.0 MPa, with YSZ-8 as the catalyst, *N*-methyl-2-pyrrolidinone as the solvent and 4 Å zeolite as the dehydrant. Mechanistic studies revealed that the presence of oxygen vacancies in the YSZ-8 catalyst played a key role in the adsorption and activation of CO_2 by creating additional reduction potential for the reduction of CO_2 to CO and/or surface carbonaceous species. This would result in the coordination of a carbonyl oxygen of CO_2 to an oxygen vacancy site, which is the key intermediate species to the activation of CO_2 . Then, a reaction intermediate formed from a nucleophilic attack of the amino group towards the carbonyl carbon, which would end up in the final carbonylation product.

Author Contributions: Dalei Sun and Xianghua Yang conceived and designed the experiments; Kaihong Xie performed the experiments; Dalei Sun and Yanxiong Fang analyzed the data; Yanxiong Fang contributed reagents/materials/analysis tools; Dalei Sun wrote the paper.

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