# Environmentally benign alcoholysis of urea and disubstituted urea to alkyl carbamates over alkali-treated zeolites

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## ABSTRACT

Alkali-treated zeolite material was prepared by using 0.1–0.4 mol/L NaOH aqueous solution, as characterized by XRD, SEM, $N_2$ adsorption-desorption technique and ammonia-temperature programmed desorption ($NH_3$-TPD). The as-prepared zeolite was found to be an effective catalyst for alcoholysis of urea and disubstituted urea to produce alkyl carbamate, getting 91.8–100% conversion of urea and substituted urea with >98.0% selectivity to alkyl carbamates. The results indicated that the high reactivity of the zeolites for alcoholysis of urea and N-substituted urea could be mainly ascribed to the enhanced specific area and balance between acidic and basic sites on the HZSM-5 surface caused by the alkali-treatment. This catalyst can be easily recovered and reused.

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## 1. Introduction

Carbamic esters are commercially important class of organic compounds. They are widely used as intermediates in the synthesis of a variety of organic chemicals, such as polymer (e.g. polyurethane), microbicides, agricultural pesticides, herbicides and pharmaceutical agents [1]. They are also served as protective groups for amines as well as excellent templates for the formation of C–C bonds [2]. As the most simple carbamate, methyl carbamate (MC) is a crude material for the synthesis of dimethyl carbonate [3] that is not only used as an environmentally benign substitute for highly toxic phosgene and dimethyl sulfate in carbonylation and methylation, but also as a promising octane booster, reducing particulate emission and the cost of fuel due to its high oxygen content [4]. Traditionally, carbamate has been synthesized by alcoholysis of isocyanate, which is produced by a primary amine and phosgene, or aminolysis of chloroformate. The major drawbacks of the former are that the phosgene is highly toxic and corrosive. Analogously, massive waste salt was produced in the chloroformate process. Alternatively, phosgene-free methods for synthesizing carbamates have been recently developed, including

reductive carbonylation of nitro aromatics and oxidative carbonylation of amines [5,6]. However, the reductive carbonylation route using platinum group metal catalysts is economically not viable; only one-third of CO could be effectively utilized and the separation of CO from $CO_2$ increases the operation cost. Recently, the synthesis of carbamates utilizing $CO_2$ as carbonylation reagent has been widely focused [7]. But this process requires strict reaction conditions due to the thermodynamic inertness of $CO_2$, as well as alkyl halide using as alkylation reagent [8], or dehydration reagent [9]. Otherwise, low yield was achieved in the synthesis of carbamates from $CO_2$, amines and alcohols in the absence of dehydration reagent. Acidic catalysts such as polyphosphoric acid [10], $BF_3$ [11] and cupric acetate [12] have been used for the reaction of urea with methanol to generate MC. However, the yield of carbamate is low in these cases; furthermore, additional process steps for separation of the catalysts or the byproduct from the methanol/MC solution are required when using these homogeneous catalysts. In order to enhance the yield of carbamate, a semicontinuous process for the synthesis of methyl carbamate in the absence of catalyst has been investigated. A higher yield of MC was obtained at the optimal reaction conditions with a long reaction time and high temperature [13]. Besides, alcoholysis of disubstituted ureas to N-substituted carbamates over $TiO_2/SiO_2$ has been reported with good catalytic activity [14]. Therefore, the effective synthesis of carbamates are now depending on the way to transfer carbonyl group from urea or

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disubstituted urea into carbamates or N-substituted carbamates using highly efficient and environmentally-friendly heterogeneous catalyst. In this work, alkali-treated zeolites with different concentrations of NaOH aqueous solution were prepared and characterized by XRD, SEM, $N_2$-adsorption-desorption and $NH_3$-TPD technique. Among the catalysts screened, the zeolite treated with 0.2 mol/L NaOH aqueous solution exhibited high catalytic activity in alcoholysis of urea and disubstituted urea [dicyclohexyl urea (DCU)] with low-molecular-mass alcohols such as methanol, ethanol, propanol, iso-propanol, butanol, iso-amyl alcohol, octanol and benzyl alcohol, getting ca. 100% conversion and >99% selectivity to MC and methyl N-cyclohexyl carbamate (MCC) for methanolysis of urea and disubstituted urea.

## 2. Experimental section

### 2.1. Preparation and characterization of the catalyst

Before the alkali-treatment, the zeolite HZSM-5 (Si/Al = 38, Tianjin Chemist scientific Ltd. Co.) was calcined at 550 °C for 6 h in an oven. After cooling down, 2.0 g of HZSM-5 was added to 40 mL of various concentrations (0.1, 0.2, 0.3 and 0.4 mol/L) of NaOH aqueous solution. The mixture was heated to 80 °C in a water bath and stirred at this temperature for 2 h. The alkali-treated zeolites were obtained by filtration, and then washed with distilled water until neutral washing water was achieved. The zeolites were dried at 120 °C for 12 h after washing and denoted as HZSM-5-x, where x represented the concentration of NaOH solution (x = 0.1, 0.2, 0.3, 0.4).

X-ray powder diffraction (XRD) of the samples was performed on a Bruker-D8 Advance X-ray diffractometer with Cu Kα radiation (40 kV and 36 mA) at scan rate of 0.3°/step and wavelength of radiation source 0.154056 nm. The $N_2$ adsorption/desorption isotherms were measured using a quantachrome NOVA2000E instrument. Before the measurement, the sample was treated to remove the gasses adsorbed on the surface at vacuum and 300 °C for 3 h. The $N_2$ adsorption/desorption isotherms were measured at temperature of 77 K (−196 °C).

$NH_3$ temperature-programmed desorption (TPD) were conducted using a home-made device with a TCD detector of GC (GC-14C, SHIMADZU). 100 mg sample was pretreated in argon flow at 500 °C for 1 h and cooling to room temperature before TPD run. The adsorption of $NH_3$ on the catalyst was performed with feeding anhydrous $NH_3$ gas for about 10 min at room temperature, and then the catalyst was sufficiently purged by argon stream to remove the excessive adsorbate. The TPD was conducted by heating the sample in argon (80 mL/min) from 50 °C to 600 °C with a heating rate of 10 °C/min.

The morphology of the catalysts was observed by a Hitachi S-4800 scanning electron microscopy (SEM). The preparation procedure of the samples: conductive adhesive was daubed on the SEM stage, and then powder samples were uniformly sprayed by syringe on the stage, followed by shaking the stage to disperse the samples and smoothing the aggregated powder by syringe needle. The ratios of Si to Al and Na (or K) content in the zeolites were determined by 7500CE ICP-OES (P-E Company).

### 2.2. Catalytic tests

The catalytic reaction was conducted in a stainless steel 250 mL autoclave with a magnetic stirrer in an oil bath. In a typical procedure, 40 mL (1.0 mol) or 20 mL (0.5 mol) of anhydrate methanol, 1.5 g (0.025 mol) of urea or 1.2 g (5.41 mmol) of dicyclohexyl urea (DCU) and 0.3 g or 0.2 g of the catalyst (HZSM-5-0.2) were charged into the reactor in turns. After purging three times with $N_2$ gas, the

reactor was heated to 180 °C with a speedy stirring and the reaction was carried out at this temperature for 8 h, the reaction formula was shown in Scheme 1. At the end of the reaction, the mixture solution was filtered to remove the catalyst and the filtrate was analyzed by GC (Agilent 7820), GC-MS (Agilent 7890-5975C) with FID detector (GC) and HP-5 column (30 m × 0.32 mm × 0.25 μm) for synthesis of MC and HPLC (Waters class) with UV-detector at wavelength of 210 nm, $C_{18}$ column and the mixture solution of acetonitrile/$H_2O$ (1:1 v/v) as mobile phase for synthesis of MCC. The temperature program for GC measurement was shown as following: the column temperature box was heated from the initial temperature 50 °C–70 °C at heating rate of 10 °C/min, followed by continuously heated to 230 °C at heating rate of 20 °C/min; and then it remained at this temperature for 1 min. The gas and liquid chromatograms for MC and MCC synthesis were shown in Figs. SI1 and SI2 in supporting information.

## 3. Results and discussion

### 3.1. Characterization of the alkali-treated zeolites

The XRD patterns of as-received and alkali-treated zeolites were depicted in Fig. 1. It was clear that these alkali-treated samples basically preserved the specific MFI structure and no input phase was found after treated with alkaline solution. HZSM-5-0.1, HZSM-5-0.2, HZSM-5-0.3 and HZSM-5-0.4 exhibited almost the same XRD patterns as that of parent HZSM-5 although obvious decrease in relative crystallinity could be observed, especially for the higher concentration alkali-treated samples HZSM-5-0.3 and HZSM-5-0.4, the diffraction peaks around 45° were too weak to be observed due to the NaOH solution severer dissolving Si or Al atoms from the zeolite framework. Besides, significant changes were also found in the Si/Al ratio, specific surface area and morphology for the alkali-treated zeolites. As shown in Table 1, the Si/Al ratio was basically decreased as increasing in the NaOH concentration for treating these zeolites, implying that the alkaline solution mainly dissolved Si from the framework. However, SEM was used to view the morphology of the alkali-treated samples as shown in Fig. 2. It was seen from the images that the parent HZSM-5 exhibited regular rectangular crystals (Fig. 2a) and the surface of the alkali-treated samples looks like rough, some irregular crystalline grains and defects on the surface were observed for ZSM-5-0.1 and HZSM-5-0.2 (Fig. 2b and c), which certainly caused the increase in their specific surface areas as compared with the parent HZSM-5 (Table 1). Furthermore, the SEM images (Fig. 2d and e) exhibited that more irregular crystalline grains were aggregated together after treatment with 0.3 and 0.4 mol/L NaOH solutions, inevitably causing remarkable decrease in their specific surface areas (Table 1). Especially for HZSM-5-0.4 sample, much closer aggregate and more irregular crystalline grains were observed as shown in Fig. 2e.

### 3.2. Catalytic activities of alkali-treated zeolites

Alkali-treated zeolites with various concentration of NaOH aqueous solution were employed as catalysts for the alcoholysis of urea or disubstituted urea. Their catalytic activity was listed in Fig. 3. The HZSM-5-0.1 and HZSM-5-0.2 represented higher activity than the parent HZSM-5. Evidently, HZSM-5-0.2 exhibited ca. 100% conversion of urea and 98.0% selectivity to MC. On the contrary, the alkali-treated HZSM-5 zeolites under severe condition gave relatively low conversions, exhibiting 90.4% for HZSM-5-0.3 and 77.8% conversion for HZSM-5-0.4, respectively. In these cases, the selectivity to MC was basically unchanged, being over 98.0%. Differently, the conversion of DCU was increased as the NaOH concentration