



Cu-doped zeolites for catalytic oxidative carbonylation: The role of Brønsted acids

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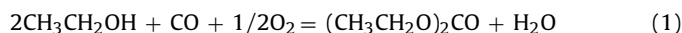
ABSTRACT

The aim of this work was to establish the role of Brønsted acidic sites in Cu-doped zeolites for the oxidative carbonylation of ethanol to diethyl carbonate (DEC). In order to eliminate the influences of other factors such as channel structure, faujasite (FAU) with different SiO₂/Al₂O₃ ratios and Beta before and after passivation were investigated. Fourier Transform infrared spectroscopy (FTIR) of pyridine adsorption indicated that all of Brønsted acidic sites were exchanged with CuCl to form effective active sites for oxidative carbonylation. Characterization data showed that passivation on Beta zeolites has little effect on surface area and pore volume distribution except Brønsted acidic sites. The relationship between Brønsted acidic sites and catalyst activity was built on different types of zeolite supports. Diffuse reflectance infrared Fourier transform spectroscopy (DIRFTS) of CO adsorption revealed that the location of Cu active sites was related to the distribution of Brønsted acidic sites, which also influenced catalytic performance of oxidative carbonylation.

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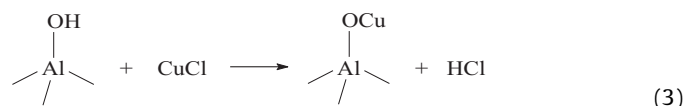
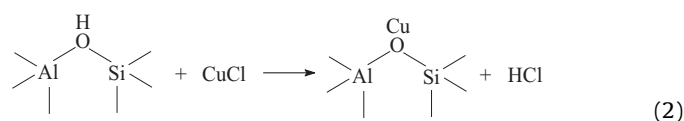
1. Introduction

The rapid evolution of green chemistry has spurred tremendous interests on clean and safe synthetic routes and thus development of new catalysts. Production and applications of organic carbonates (e.g., dialkyl carbonates) are directly concerned within the frame of this principle. They are environmentally benign compounds with versatile applications in chemical synthesis [1]. Due to their low toxicity and bio-accumulation, they have been widely used as solvents [2] and oxygen-containing fuel additives. Oxidative carbonylation has been considered as one of most promising approaches to replace the conventional phosgene method to produce dialkyl carbonates (e.g., dimethyl carbonate (DMC) [3–7] and diethyl carbonate (DEC) [8–10]). Recently, DEC has been proposed as an attractive oxygen-containing fuel additive to replace methyl tert-butyl ether (MTBE) because of its high oxygen content (40.6 wt%) and favorable gasoline/water distribution coefficients, which are superior to alternatives such as DMC and ethanol. Thus, it has attracted increased attention to develop a gas-phase process for producing DEC (Eq. (1)).



Zeolites have been extensively employed as catalytic materials for synthesis of a variety of chemicals due to their unique structural properties and tunable acidity [11]. Bridging hydroxyl groups (e.g., Al–OH–Si) on zeolites that function as Brønsted acidic sites play

an important role in catalysis, ion exchange, adsorption, and other practical processes [12–14]. Recently, Cu-doped zeolites prepared by solid-state ion exchange (SSIE) with CuCl have received considerable interests in catalysis, particularly for oxidative carbonylation [15]. Since Cu-doped zeolites via a conventional ion exchange with aqueous solutions of cupric ions usually contain coexistence of copper ions in different aggregation and oxidation states, it is difficult to elucidate the structural properties of Cu active sites. By contrast, catalysts prepared via the SSIE have been considered as model solids, containing only isolated copper species in a single oxidation state [16]. Additionally, high exchange degree can be achieved in a single step via SSIE, and Cu ions can enter narrow pores and anchor at cavities more easily relative to exchange in aqueous solution. It has been generally recognized that the Brønsted acidic sites on zeolite can be exchanged by Cu⁺ ions during the SSIE process (Eqs. (2) and (3)) [17–19]. The formed surface-bound Cu⁺ was proposed to be active species for the carbonylation reaction.



Therefore, the nature of Brønsted acidic sites in zeolites, which depends on the bond angle of Si–O–Al [13], composition of the framework (e.g., SiO₂/Al₂O₃ ratio), and degree of dispersion of the Al ions [20], could influence the exchange degree and local

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