



Effect of Cu and Zn ion-exchange locations on mordenite performance in dimethyl ether carbonylation

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ABSTRACT

Cu^{2+} and Zn^{2+} ion-exchange locations in mordenite (MOR) were evaluated using infrared spectroscopy, pore-size distribution, and temperature-programmed reduction. Isolated copper ions were the most abundant ion-exchanged species, as detected by UV-vis spectroscopy, in addition to oxide nanoparticles, with no presence of binuclear species, which was assigned to a low copper loading of 0.3 Cu/Al. The characterization revealed that only zinc could exchange in 8-membered rings. Hartree-Fock modeling confirmed copper exchange into 12-membered rings involving at least one T1 atom, and zinc exchange in T4 sites and in 8-membered structures, including T3 sites. Copper ion exchange did not offer improvement in the dimethyl ether carbonylation rate or selectivity over acidic mordenite. Zinc ion exchange led to the selectivity and stability improvement with some loss of activity. This work contributes to the understanding of acid and metal site contribution to DME carbonylation and contributes to the understanding for Cu^{2+} and Zn^{2+} ion-exchange locations in MOR with a low metal/Al loading (< 0.2).

1. Introduction

In their pioneering work in 1984, Fujimoto et al. [1] discovered that zeolites can catalyze halogen-free carbonylation of methanol and dimethyl ether (DME) and confirmed earlier results by Ono et al. [2], who noted that activated methyl groups form on solid acid sites. Later, the groups of E. Iglesia, A. Corma, and BP Chemicals performed kinetic and modeling studies of mordenite-catalyzed DME carbonylation [3–7]. Active T3 sites located in 8-membered rings (8-MR) of mordenite (MOR) were suggested as unique selective sites [5,6] that are also present in carbonylation-active ferrierite with 8-MR [8]. Substantial research on the use of MOR for DME carbonylation has shown repeatedly that it is unstable and subject to deactivation. Most groups accept that the deactivation happens by coking of 12-membered rings (12-MR) of MOR [6,9] though water produced through the reaction mechanism could also be a source of deactivation [5,6].

With the goal to improve the catalyst's performance for potential commercialization, the effect of the addition of various metals has been addressed. BP Chemicals patented MOR's ion exchange with Cu, Ag, Au, Ni, Ir, Rh, Pt, Pd, or Co, with preference given to Cu and Ag [10,11]. Zhang et al. [12] investigated the activity of a variety of Cu/MORs and

found that DME conversion above 90% after 2 h of reaction was achieved compared to 42% for MOR (Si/Al ratio of 10). However, all catalysts showed rapid deactivation after only 3 h in reaction, with selectivity to MeOAc decreasing to less than 70% after 10 h of reaction time. Wang et al. [13] ion exchanged Cu, Ni, Co, Zn, and Ag onto MOR (Si/Al of 9) and compared DME conversions and MeOAc selectivities at steady state (which lasted 1.5 h for MOR and 2.5 h for Cu/MOR). The Cu and Zn catalysts showed about 1.3-fold improvement in the activities over MOR. The 10-h stability was evaluated only for the Cu/MOR catalyst: MeOAc selectivity dropped to 65% for MOR, while it remained close to 100% between 5 and 10 h in the presence of Cu [13].

In early works [14], the use of copper-exchanged MOR for methanol carbonylation was suggested to be beneficial because the limiting step of the reaction was proposed to be the CO attack on the methyl group and copper is known to activate CO. The recent findings indicated that CO adsorbed on Cu^+ /MOR is not an active species to produce methyl acetate [15] and that the reaction intermediate undergoing carbonylation in Cu/MOR is a methoxy species on a Brønsted acid site (BAS) [16]. Lewis acid-site activated CO is also known to be inactive in DME carbonylation [4]. Our recent communication [17] showed almost negligible Cu influence on the MOR performance in DME carbonylation

Abbreviations: BAS, Brønsted acid site; DRIFTS, diffuse reflectance infrared Fourier transform spectroscopy; HF, Hartree-Fock; HK, Horvath-Kawazoe (pore-size distribution); IR, infrared (spectroscopy); 5-, 6-, 8-, 12-MR, 5-, 6-, 8-, 12-membered rings of a zeolite; MAS, magic angle spinning (in NMR); MeOAc, methyl acetate (product of DME carbonylation); MOR, mordenite; NMR, nuclear magnetic resonance; T1, T2, T3 and T4, active sites in various locations of a mordenite as per; TEM, transmission electron microscopy; TPD, temperature-programmed desorption; TPR, temperature-programmed reduction; UV-vis, ultraviolet-visible (spectroscopy)

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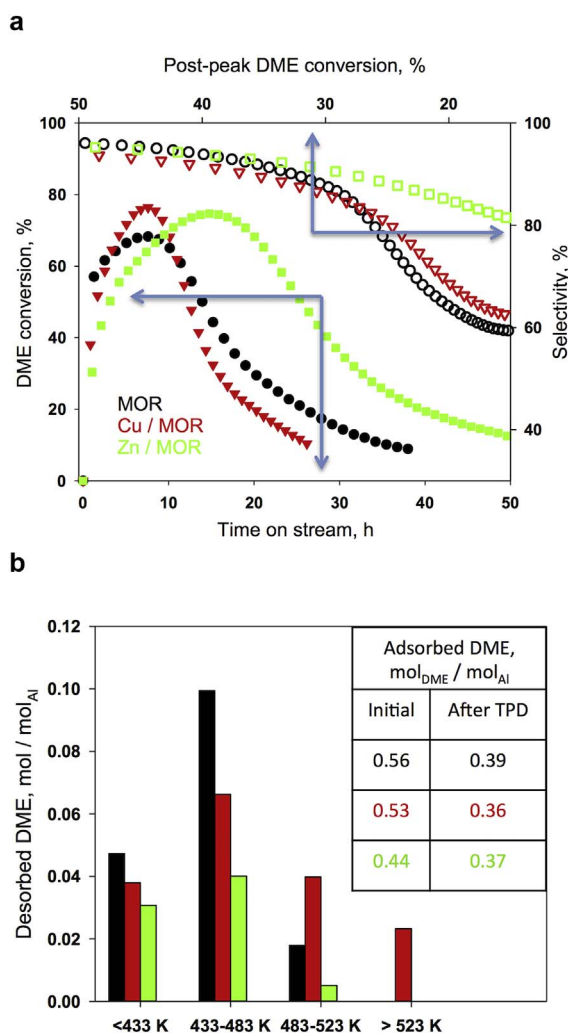


Fig. 1. (a) DME conversion versus time on stream (closed symbols), and selectivity to methyl acetate versus post-peak DME conversion (open symbols) at 483 K, 1 MPa CO, 48 kPa DME; (b) DME titration and TPD. The experimental details and complete selectivity-conversion plots can be found elsewhere [17].

regardless of its ability to activate CO, while Zn/MOR demonstrated a significant difference in terms of deactivation behavior and maintained $> 80\%$ + MeOAc selectivity upon deactivation versus approximately 60% for the MOR and Cu/MOR catalysts (Fig. 1a) [17]. The Zn/MOR catalyst lifetime and cumulative MeOAc produced over the reaction time were doubled. The DME adsorption and temperature-programmed desorption (TPD) evidenced that the metal presence affected the materials' adsorption capacity and fractions of desorbed DME at different temperatures (Fig. 1b). The selective methyl acetate formation is known to occur only on T3 sites in 8-MR [5,6] that comprise only 33% of BAS in MOR (T1:T2:T3:T4 = 36:20:43:29 [18]), implying that it is possible that the ion-exchanged metals at metal/Al ratio of 0.3 and lower do not occupy active T3 sites but only other unselective T1, T2, and/or T4 sites. Given a similar catalytic behavior of MOR and Cu/MOR but a slightly lower pre-peak activity and improved deactivation resistance of Zn/MOR, it is thus possible that Zn affects mostly the unselective sites and a fraction of carbonylation-active T3 sites.

Interestingly, our recent study of hierarchical MORs with different Si/Al ratios revealed that a similar selectivity improvement upon deactivation occurred with the progressive coupled removal of T3+T4 sites located in the 8-MR and 12-MR of MOR, while the ultimate activity loss was ascribed to T1 and T2 sites [19]. Given the analogy of the catalytic behavior between the selectively dealuminated samples and Zn/MOR, it is now interesting to see if Zn presence affects the same sites

as those removed in the hierarchical samples. From a practical viewpoint, if a metal is found that can inhibit side reactions at unselective sites, the DME carbonylation might become a more industrially enticing process. Therefore, comparison of the locations of relatively efficient zinc ions and indifferent but frequently reported copper ions as promoters in DME carbonylation over mordenite is desired.

The nature of copper species and their location in mordenite has presented a challenge to researchers for over three decades. A plethora of species was detected through experimental characterizations and simulations, such as isolated ion-exchanged copper cations [20–25], hydrated isolated species or clusters [26–30], Cu_n clusters [31], copper oxide nanoparticles [32] and a variety of oxo-copper cores [23,27,28,33–43]. The existing data indicate that the nature and prevalence of one species over another or their co-existence, as well as their location, depend largely on copper loading, and its precursor, the sample preparation and activation method. The formation of oxo-copper clusters was reported mostly for high copper-exchange levels with a threshold of > 0.2 Cu/Al [16,34,35]. As shown by Narsimhan et al. [16], the oxo-copper clusters, that are active in methane oxidation to methanol, are inactive in carbonylation. The co-existence of various copper species for 100–150% ion-exchanged Cu on MOR was shown using computer simulation and static lattice methodologies [26]. Sayle et al. [26] identified that 48% of copper likely existed as isolated species, specifically with coordination numbers of 3 and 4, while 52% existed in Cu_x(OH)_n clusters (CuOCu or CuOOCu were not simulated). For a sample with Cu/Al ratio of 0.43, Vanelderden et al. [25] observed the formation of two monomeric Cu²⁺ species and binuclear species. As expected and as will be shown below in the current work, with the used Cu/Al ratio of 0.3, the majority of detected ion-exchanged copper species were isolated copper cations, in addition to copper oxide nanoparticles. The copper oxide nanoparticles are inactive in DME carbonylation, as we confirmed for a conventional impregnated Cu/Al₂O₃ catalyst that did not show any DME conversion. The present work, thus, focuses on the nature and location of favorable ion-exchanged Cu²⁺ cations on a low-exchanged mordenite.

Almost every possible Cu²⁺ ion-exchange location has had some evidence presented for it in the literature. Based on ¹H MAS NMR, IR-spectroscopy, and NH₃ titrations, Xue et al. [44] concluded that copper cations almost equally exchanged both in 8- and 12-MR of MOR. X-ray diffraction data [45] suggested that Cu²⁺ preferred to ion exchange in the 8-MR, coordinated to 6 framework O atoms and 2 water molecules. Following this, the Cu²⁺ ion exchanged between T1 and T2 Al atoms in 12-MR, coordinated to 4 framework O atoms. A final location was determined to be between T2 and T4 Al atoms, where Cu²⁺ binds to 3 O atoms [45]. In other works, Cu²⁺ was suggested to be coordinated in a square planar or square pyramidal coordination [20]. Further characterization showed that Cu²⁺ only occupies the 8-MR in MOR at low Cu loadings and coordinates with 6 framework O atoms. At higher loadings, Cu²⁺ binds to 4 framework O atoms between the T1 and T2 Al atoms in the 12-MR [21,46]. Contrary to these findings, a DFT modeling study determined that at low loadings, Cu²⁺ coordinates to the 6-MR with 2 Al atoms in the 12-MR (the 6-MR consists of T1 and T2 Al atoms). At higher loadings, it was determined that Cu(OH)⁺ binds to 6-MR or 5-MR with only 1 Al atom. Calculations also seemed to indicate that the 8-MR was not occupied by Cu²⁺ [24].

By comparison with Cu²⁺, there are very limited studies on Zn²⁺ ion exchange on MOR. Zn²⁺ could ion exchange in the smaller 5-MR and 6-MR that contain 2 Al atoms [47,48]. Zn(II) cation was most stable when it was surrounded by two nearby Al-O-Si centers [49]. The formed species are also dependent on the loading, with ion exchange occurring at two framework Al atoms at lower exchange levels (below 30% as determined for zeolite BEA) [50]. From DFT calculations [48], T2 and T3 sites were thought to be more favorable as ion-exchange locations compared to T1 and T4. The ion-exchange behavior might be expected to be different with different Si/Al ratios, with the next nearest neighbors affecting the acidity of any given site [51].

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