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Promoting Effect of Copper Loading and Mesoporosity on Cu-MOR in the Carbonylation of Dimethyl Ether to Methyl Acetate

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Abstract: Cu-mordenite (Cu-MOR) catalysts with different copper loadings were prepared, characterized and examined in continuous, gas-flow synthesis of methyl acetate (MA) by dimethyl ether (DME) carbonylation. Improved activity and selectivity were observed for Cu-MOR catalysts with up to 1 wt% Cu and X-ray photoelectron spectroscopy (XPS), electron paramagnetic resonance (EPR) spectroscopy and temperature-programmed reduction with hydrogen (H2-TPR) were used to elucidate the state of copper in the catalysts. Moreover, mesoporous MOR catalysts (RHM) were prepared by mild stepwise recrystallization with X-ray powder diffraction (XRPD) and ammonia temperature-programmed desorption (NH3-TPD) demonstrating the retained MOR structure and the acid property of the catalysts, respectively. The RHM catalysts showed improved lifetime compared to pristine MOR giving a yield up to 78% MA with 93% selectivity after 5 h on stream (GHSV = 6711 h⁻¹). Under identical reaction conditions, 1 wt% Cu-RHM catalysts had an even higher catalytic activity and durability resulting in a MA yield of 90% with 97% selectivity for 7–8 h of operation as well as a lower coke formation.

Keywords: carbonylation; dimethyl ether; methyl acetate; Cu-Mordenite; recrystallization

1. Introduction

Methyl acetate (MA) finds extensive use as a solvent, particularly in pharmaceutical and dye industries, and is applied for the manufacture of acetic anhydride (alkylation reagent) as well as for production of bio-ethanol (gasoline additive or fuel substitute) [1,2]. MA production typically involves carbonylation of methanol with CO to form acetic acid followed by esterification using halides and expensive Rh-complex catalysts in a liquid, homogeneous process [3]. The process is generally hampered by complicated handling, harsh reaction conditions and severe corrosion, thus making it desired to develop a more benign and eco-friendly reaction system. An alternative, two-stage gas-phase MA production route was recently devised wherein dimethyl ether (DME), which can be formed efficiently and selectively from petro- or biomass-derived syngas via methanol, are carbonylated with CO using solid acid catalysts [4–6]. Optionally, MA can in a subsequent step be hydrogenated to (bio)ethanol with recycling of excess syngas and a byproduct of methanol (Scheme 1). However, an important challenge that needs to be addressed before this method potentially can find an industrial application is to increase the activity and stability of the solid catalyst for the DME carbonylation.

Solid acid zeolites (MFI, FER, FAU, CHA and MOR) as well as heteropoly acids, have been examined for MA synthesis by DME carbonylation [7–10]. Among these catalysts, the MOR framework type zeolites appears most promising [11–14] although CHA-type zeolites (SSZ-13s) have also recently shown good potential [10]. The MOR structure consists
of two types of cavities: 12-member-ring (12-MR) main channels as well as 8-member-ring (8-MR) side pockets where the active sites for carbonylation are located [12]. The carbonylation process is initiated by a surface reaction between DME and acidic hydroxy groups (Si-OH-Al) to form surface methoxy and methanol. The latter, on the other hand, can also react with hydroxy groups to yield surface methoxy groups and water. The surface methoxy groups then undergo CO insertion into the methoxy group to form surface acetyl species, which is the rate-determining step [11]. Afterwards, the obtained acetyl species react with another DME molecule to produce MA and regenerate the surface methoxy groups for another catalytic cycle. The intermediate surface active acetyl species could only be identified in 8-MR side pockets by in-situ solid-state nuclear magnetic resonance (NMR) spectroscopy studies [15,16], and their formation was recently predicted from density functional theory (DFT) calculations and verified experimentally to proceed partly via initial ketene formation [17].

![Scheme 1. Carbonylation of dimethyl ether (DME) derived from syngas via methanol to yield methyl acetate (MA) followed by hydrogenation to ethanol and methanol, which can be recycled.](image)

Despite the promising performance, unmodified MOR suffers from severe deactivation due to the deposition of carbonaceous species during the course of the reaction. For instance, the surface methoxy groups in the 12-MR channels react more rapidly with DME to form trimethyl oxonium cation (TMO⁺), which can further aggregate into aliphatic olefins and/or aromatics [18]. Accordingly, suppressing coke formation in the 12-MR channels by intra- or extra-framework modifications have also been examined. Hence, coke formation was shown to be reduced by improving the diffusion processes efficiently by reducing the MOR crystallite size from the typical micrometer scale to the nanometer level [19], resulting in significantly enhanced DME carbonylation efficiency [20]. Moreover, significant improvement in catalyst performance was reported by pre-adsorption of pyridine and other organic amines [21–23], dealumination of MOR [24] or selective ion-exchange with tetramethylammonium ions [25].

Transition metal introduction into the framework or extra-framework is an established route for changing the physicochemical properties of zeolites and thus improving their performance in reactions. For DME carbonylation, ion exchange of Cu(I) or Ag(I) ions in the framework has in particular been reported to be beneficial under moderate reaction conditions [14,26,27], since Cu incorporation can prompt the overall reaction efficiency and eliminate coke accumulation. According to Fourier-transform infrared spectroscopy (FTIR) and solid-state NMR studies, Cu-MOR has two neighboring sites that could contribute to the formation of MA, such as bridged hydroxyl and neighboring Cu⁺ sites. NMR studies with ¹³CO adsorbed on Cu⁺ revealed the formation of hydrocarbons instead of MA, indicating that Cu⁺ did not participate in the carbonylation reaction but rather stabilized DME and suppressed the formation of hydrocarbons [28]. Alternatively, the yield of MA has recently been found to correlate positively with the amount of Cu⁰ and negatively to the content of Cu⁺ over a series of Cu-MOR catalysts with different amounts of Cu, suggesting Cu⁰ to be responsible for the promotional effect in DME carbonylation [29].

In-situ IR and DFT calculations corroborated a synergetic working model of Cu⁰ and the neighboring acid site where DME adsorption and dissociation resulted in the formation of methyl-Cu⁰, which after co-adsorption of CO gave an acetyl-Cu⁰ intermediate that reacted further with methanol adsorbed on the acid site to produce MA [30]. The promoting role of Cu⁰ was further supported by DFT calculations (on Cu-ZSM5), predicting a strong electrostatic interaction between nucleophilic methyl⁺-CO intermediates and electrophilic Cu⁰ sites [31].
Although apparent relationships between MOR and Cu-MOR have been noted in the prior DME carbonylation studies reported above, no comprehensive evaluation on the effect of Cu loading in combination with MOR recrystallization has, to the best of our knowledge, been performed. Thus, here we report the results obtained from DME carbonylation with Cu-MOR catalysts with different copper loadings and the influence of recrystallization to modify the pore structure of MOR and Cu-MOR.

2. Results and Discussion

2.1. Characterization of Fresh Cu-MOR Catalysts

The prepared Cu-MOR catalysts were characterized using X-ray powder diffraction (XRPD), nitrogen physisorption, temperature-programmed desorption of ammonia (NH₃-TPD), temperature-programmed reduction with hydrogen (H₂-TPR) and Raman spectroscopy. Selected catalysts were further characterized using X-ray photoelectron spectroscopy (XPS), temperature-programmed oxidation (TPO), electron paramagnetic resonance (EPR) spectroscopy and transmission electron microscopy (TEM).

The XRPD patterns of the prepared Cu-MOR catalysts (Figure S1) all demonstrated highly crystalline MOR [32], validating that the MOR structure was preserved irrespective of the copper loading. All catalysts with copper loadings of 0.5–10 wt% exhibited crystalline copper oxide with diffraction lines at 2θ of 35.5 and 38.7° (CuO, tenorite, PDF-Nr. 48–1548: 2θ (relative intensity) = 35.4° (37), 35.5° (100), 38.7° (99), 38.9° (21), 48.7° (30)). Moreover, there was no indication of the presence of metallic copper in the catalysts, which would give intense diffraction lines at 43.0° {111} and 50.5° {200} (PDF 04-0836), but relatively low intensity lines corresponding to Cu₂O were seen at about 2θ = 36° for all copper loadings [33]. The line widths of the XRPD peaks were rather broad for all samples, indicating that the crystal sizes were quite small.

Nitrogen physisorption isotherms (Figure S2) attributed to type IV with minor hysteresis confirmed that pristine mordenite (HMOR) and Cu-MOR catalysts contained both micro- and mesopores, and the corresponding specific surface areas remained almost unchanged up to copper loadings of 1 wt%, as shown in Table 1. At higher copper loadings of 2.5–10 wt%, both surface areas and micropore volumes decreased significantly due to blockage of the micropores by larger copper particles, resulting in up to 26–27% loss of micropore surface area and micropore volume.

Table 1. Textural properties of HMOR and Cu-MOR catalysts.

| Catalyst           | Specific Surface Area ¹ | External Surface Area ² | Micropore Surface Area | Micropore Volume ³ | Mesopore Volume ³ | Total Pore Volume ⁴ |
|--------------------|-------------------------|-------------------------|------------------------|-------------------|------------------|---------------------|
| HMOR               | 447                     | 51                      | 396                    | 0.185             | 0.088            | 0.273               |
| 0.5 wt% Cu-MOR     | 449                     | 52                      | 397                    | 0.185             | 0.089            | 0.274               |
| 1 wt% Cu-MOR       | 451                     | 53                      | 399                    | 0.184             | 0.1              | 0.284               |
| 2.5 wt% Cu-MOR     | 433                     | 55                      | 378                    | 0.176             | 0.12             | 0.296               |
| 5 wt% Cu-MOR       | 401                     | 54                      | 347                    | 0.162             | 0.11             | 0.272               |
| 10 wt% Cu-MOR      | 341                     | 50                      | 291                    | 0.135             | 0.097            | 0.232               |
| 1 wt% CuO/HMOR ⁵   | 454                     | 51                      | 402                    | 0.188             | 0.086            | 0.274               |

¹ Calculated using the BET method. ² Determined using the t-plot method. ³ Determined using BJH method (desorption). ⁴ Sum of meso- and micropore volume. ⁵ Physical mixture of HMOR and CuO nanopowder.

According to the literature [34,35], the reduction of isolated Cu²⁺ species located at cation exchange sites of zeolites [36] occurs by hydrogen via a two-step mechanism; in the first step, isolated Cu²⁺ reacts with hydrogen (1/2 H₂) and gets reduced to Cu⁺ along with proton formation, and in the second step the Cu⁺ reacts further with hydrogen and turns into its metallic state Cu⁰. In contrast, the reduction of bulk copper oxide species takes place in a one-step mechanism to Cu⁰ (TPR profiles of reference commercial CuO, and bulk...
copper oxides are shown in Figure S3) [37,38]. The TPR profiles of Cu-MOR with varying copper content of 0.5–10 wt% are compiled in Figure 1a.

![Figure 1. (a) Temperature-programmed reduction with hydrogen (H₂-TPR) of Cu-MORs. (b) Ammonia temperature-programmed desorption (NH₃-TPD) of Cu-MORs.](image)

All the Cu-MOR catalysts consumed H₂ due to the reduction of Cu²⁺ and experimental H₂:Cu ratios of 0.89–1.0 were found. These values indicate that most of the copper were in the Cu²⁺ state, since a H₂:Cu ratio of 1 is expected if all the copper initially were in the Cu²⁺ state and completely reduced to Cu⁰ (consistent with the XPS results, see Figure S8c). Two low temperature reduction peaks at about 200 and 250 °C were detected for the catalysts with copper loading ≥2.5 wt%, and assigned to the reduction of isolated Cu²⁺ to Cu⁺ ions and CuO to Cu⁰, respectively. The increased peak areas for the catalysts with 5 and 10 wt% Cu suggests that the proportion of CuO increased relative to the isolated Cu²⁺ ions at high metal loading. The catalysts with a lower content of copper (0.5 and 1 wt%) presented less distinct peaks of about 210 and 260 °C, respectively, and a small shoulder at about 325 °C. Analysis of the peaks suggests the copper to be present mainly in the form of isolated Cu²⁺ ions, and the shoulder indicated the presence of small quantities of CuO species. However, at around 400 °C, water desorption started due to dehydroxylation of the MOR lattice, which might have influenced the Cu⁺ to Cu⁰ reduction, though this needs further investigation to be clarified [39–41]. A detailed description of the reduction temperatures of the Cu-MORs from Figure 1a is presented in supplementary information (Table S1).

Interestingly, the reduction peak (Cu⁺ to Cu⁰) shifted towards lower reduction temperatures with increased copper loading, and was finally close to overlap with the peak corresponding to the reduction of CuO to Cu⁰. Furthermore, the progressive shift of the isolated Cu²⁺ to Cu⁺ peak towards lower temperatures, suggested the formation of dimeric copper-species as the copper loading increased. These dimeric copper-species containing bridging oxygen can react with H₂ at comparatively lower temperatures than isolated copper-species [42]. Thus, as expected, the copper dispersion decreased for high copper loadings.

NH₃-TPD is a common tool to determine surface acidity and distribution of weak/strong acid sites. Generally, zeolites with no metal desorbs ammonia at two different temperature ranges: low temperature desorption range (100–270 °C) corresponding to weakly bound ammonia (weak acid strength, type I), and the other moderate to high temperature range (270–600 °C) corresponding to relatively strongly bound ammonia (strong acid sites, type II). The ammonia desorption profiles of HMOR and the Cu-MOR catalysts are depicted in Figure 1b in the temperature range 100–700 °C. The pristine HMOR had, as expected, two desorption peaks at around 180 and 500 °C, respectively. The former peak corresponded to NH₃ adsorbed on weak acid sites (or extra-framework aluminum) [43] and the latter peak
to NH$_3$ adsorbed on strong acid (Brønsted and/or Lewis) sites [44]. The impregnation of HMOR with copper resulted in two extra desorption peaks (merged shoulders), appearing between the two original HMOR desorption peaks, and shifted the original high temperature desorption peaks to even higher temperatures. The new desorption peaks at about 300 °C are attributed to NH$_3$ adsorbed on sites of medium acidity, thus indicating formation of new acidic sites [27]. The extra desorption peaks of ammonia, and thereby increased acidity, can be attributed to the decomposition of copper-ammine complexes likely to be formed under the given conditions [45]. Hence, from the plots in Figure 1b, and Table 2 with the summarized acidity values and copper crystal sizes, the addition of Cu to MOR apparently only influenced catalyst acidity slightly until a copper loading of 2.5 wt%, whereas higher Cu loadings increased the acid sites of type II. However, it should here be noted that acidity measurements of zeolites with redox active metals, such as Cu-MOR, can be affected by undesired reduction of the metal species by the ammonia.

HMOR is structurally composed of 5-member-rings (5MR) of tetrahedra with an additional single tetrahedron secondary building unit (5-1), which in Raman spectra will display as two vibration modes of moderate intensity at 398 and 456 cm$^{-1}$ (along with Si-O-Al-chain asymmetric stretching modes between 950–1250 cm$^{-1}$) [46]. Raman spectroscopy also reveal particle growth as Raman shifts of CuO nanoparticles are size dependent. An increase in CuO particle loading or particle size will accordingly result in sharper and more intense bands shifted slightly to a higher wave number. The characteristic Raman bands of the CuO nanoparticles in the prepared Cu-MOR catalysts are shown in Figure 2 at 314, 514 and 636 cm$^{-1}$, respectively [47]. A small but clear shift toward higher wavenumbers was observed for the 514 and 636 cm$^{-1}$ bands with increasing copper loading, indicating that the CuO particles became larger at higher Cu loading (as expected). This was also confirmed when the particle size of the CuO nanoparticles were estimated by the Scherrer equation [48] (Table 2).

Figure 2. Raman patterns of Cu-MOR catalysts with varying copper loadings.
Table 2. Acid type distribution of MOR and Cu-MOR from NH$_3$-TPD.

| Catalyst   | Type I Acid Sites (100–270 °C) (µmol g$^{-1}$) | Type II Acid Sites (270–600 °C) (µmol g$^{-1}$) | Total Acid Sites (µmol g$^{-1}$) | CuO Particle Size $^1$ (nm) |
|------------|-----------------------------------------------|-----------------------------------------------|---------------------------------|-----------------------------|
| HMOR       | 726                                           | 1045                                          | 1771                            | -                           |
| 0.5 wt% Cu-MOR | 718                                           | 1010                                          | 1728                            | 8                           |
| 1 wt% Cu-MOR  | 699                                           | 986                                           | 1685                            | 14                          |
| 2.5 wt% Cu-MOR | 706                                           | 1005                                          | 1711                            | 17                          |
| 5 wt% Cu-MOR  | 709                                           | 1620                                          | 2329                            | 18                          |
| 10 wt% Cu-MOR | 674                                           | 1624                                          | 2296                            | 22                          |

$^1$ Estimated with the Scherrer equation [48] on the diffraction line at 2θ of 35.5°.

2.2. DME Carbonylation with Cu-MOR Catalysts

The prepared Cu-MOR catalysts with 0.5–10 wt% copper loading were compared with HMOR for DME carbonylation activity towards MA formation at 220 °C (Figure 3). For HMOR, an induction period of about 3 h was observed, where water was removed from the catalyst bed and surface acetyl groups formed by reaction of DME and methanol with bridged hydroxyl groups (i.e., Brønsted acid sites) and silanol groups on the MOR [10]. This induction period not only let the DME saturate the exchange sites with methyl groups, but it also provided time for the 12-MR channels to form aromatic precursors [16] (mostly alkyl benzenes) and light olefins (propylene, and hexene) and as a result suppressed the selectivity towards MA (see Figure S4).

In comparison, the 1 wt% Cu-MOR catalyst provided efficient DME carbonylation resulting in around 93–97% selectivity towards MA (81% yield) after an induction period of about 2 h. This shortened induction time suggests that copper within the MOR channels, 8-MR in particular, reduced coke formation by activating the CO. This is in line with the previous findings that copper, apart from activating CO, also adsorbed DME, resulting in reduced coke formation and increased life-time [14]. For pristine HMOR, the selectivity to MA slowly increased from 76 to 92% after an induction period of 3 h and was maintained at this level of selectivity during the subsequent reaction period (3–9.5 h). However, the
catalyst started losing activity after 5 h, resulting in only 49% MA yield after 9.5 h. Though the 1 wt% Cu-MOR catalyst had a shorter induction period compared to pristine HMOR, a similar but slower deactivation pattern occurred, resulting in 61% conversion of MA with 95% selectivity after 9.5 h time on stream.

The Cu-MOR catalyst with a Cu loading of only 0.5 wt% yielded very similar results as the pristine HMOR, except that the deactivation occurred somewhat slower. In contrast, copper loadings of 2.5, 5 and 10 wt% resulted in significantly lower DME activity, yielding only about 30% of MA with the two former catalysts and 10% MA with the latter catalyst. Interestingly, all of the three catalysts with relatively high copper loadings appeared to deactivate less severely than the other examined catalysts. The lower activity and better stability for catalysts with higher Cu-loadings can be attributed to CuO particle growth in the side pockets (8-MR) of MOR (see Table 2), thereby blocking active sites from being accessible for DME, and competitive adsorption of CO instead of DME. Notably, the selectivity towards MA formation for the catalysts with high copper loadings remained as high as the 1 wt% Cu-MOR catalyst after the induction period, suggesting that the selectivity is not influenced by the coke formation during the induction period.

2.3. Characterization of Spent Cu-MOR Catalysts

TEM images of fresh and spent 1 wt% Cu-MOR catalysts were recorded in order to get an insight into changes in surface morphology and Cu particle agglomeration occurring during the reaction (Figure 4). Well-dispersed copper nanoparticles were recognizable in the fresh catalyst with particle sizes in the range of 6–10 nm, as well as copper grains of about 24 nm in size. Interestingly, the homogeneous distribution of copper nanoparticles on the surface remained intact in the spent catalyst and no particle agglomeration was observed. The absence of particle agglomeration during the reaction was further supported by XRPD, where particle sizes of CuO ($\theta = 51^\circ$) in fresh (14 nm) and spent (16 nm) 1 wt% Cu-MOR catalysts were estimated to be almost identical (Figure S5). From this observation it can be understood that particle migration and aggregation was not contributing to the observed catalyst deactivation.

![Figure 4. TEM images of fresh (top) and spent (bottom) 1 wt% Cu-MOR catalysts.](image-url)
The formation and type of the carbonaceous material (coke) formed during the DME carbonylation reaction in HMOR and 1 wt% Cu-MOR were examined by TPO combined with a CO/CO$_2$ analyzer (Figure 5). Two types of cokes could form; soft coke formed from non-aromatic precursors and light carbon materials associated with MA formation (such as, e.g., surface-bound methyl and acetyl species [20]), and hard coke originating from aromatic precursors, which probably contributed to hindered diffusion of the reactants, thereby leading to catalyst deactivation [27,49,50]. For the pristine HMOR the TPO peaks at around 353 and 590 °C were likely due to combustion of the soft and hard coke, respectively. Interestingly, the coking behavior in the 1 wt% Cu-MOR catalyst was quite different from HMOR, resulting in coke decomposition temperatures of 378 and 508 °C, suggesting that the presence of copper-species might have catalyzed coke oxidation. Moreover, the amount of CO$_2$ evolved compared to CO during coke combustion with Cu-MOR was also much higher than for HMOR, suggesting that the Cu-species catalyzed the oxidation of CO to CO$_2$ under the TPO conditions.

![Figure 5. TPO of spent HMOR and 1 wt% Cu-MOR catalysts.](image)

The nature of the copper-species in the 1 wt% Cu-MOR catalyst was examined before and after the reaction by XPS (Figure S6) and EPR spectroscopy (Figure S7). The characteristic binding energies of Cu at 933.5 and 953.2 eV in XPS resulted from the spin-orbit doublet of the Cu 2p core level transitions. Deconvolution of the Cu transition $2p_{3/2}$ signal resulted in two main contributions located around 933.5 and 935 eV, respectively, which tentatively was assigned to CuO [51] (or to Cu$^{2+}$ introduced by cation exchange [52]) and to Cu$^{2+}$-species with a different coordination or environment [53]. The characteristic satellite features of the Cu 2p transitions can further distinguish oxidation states in the catalysts. In the fresh Cu-MOR catalyst, a satellite doublet peak between 940 and 945 eV confirmed the presence of Cu$^{2+}$ species whereas a weak satellite between 945 and 950 eV suggested the presence of Cu$^{+}$-species in the spent catalyst after the reaction [54]. The intensity of the signal at 935 eV, corresponding to Cu$^{2+}$ with different coordination, was reduced markedly in the spent catalyst in comparison to the fresh catalyst, while the intensity of the peak at 933.5 eV, assigned to CuO, remained intact. This suggest that the CuO nanoparticles remained unchanged throughout the reaction, but Cu$^{2+}$ with a different environment transformed to Cu$^{+}$ or Cu$^{0}$ in the spent catalyst during CO activation and/or preferential
adsorption of DME over methanol or water [55]. A shift of the satellite peaks toward higher binding energies due to Cu$^{2+}$ reduction was also observed with a higher copper loading, even in the fresh catalysts (Figure S8). Higher loadings of copper and formation of larger CuO particles could lead to the reduction process transforming the oxidized Cu$^{2+}$ species in the catalysts [56], which is consistent with the TPR results (Figure 1a). In the XPS spectra, a carbon 1s peak at 284.8 eV further clearly indicated the presence of C-C species on the catalyst surface (Figure S9) [54] (small contribution in the fresh catalyst possibly originated from carbon contamination in the sample preparation).

The fresh 1 wt% Cu-MOR catalyst yielded an EPR spectrum (Figure S7) typical of hydrated copper zeolite materials dominated by a broad peak assignable to tetragonal Cu$^{2+}$ with rotational freedom, such as in a hydrated film on the surface of a zeolite in equilibrium with the atmosphere [57]. A small amount of immobilized tetragonal Cu$^{2+}$ was also visible in the fresh catalyst. The spent Cu-MOR catalyst had a strong, sharp signal corresponding to radical signals ($g \approx 2.00$) from carbon residues as well as a small amount of EPR signal from isolated Cu$^{2+}$ ions. Both showed a more anisotropic signal with roughly the same features as the immobilized Cu$^{2+}$ observed in the fresh catalyst. The observed $g_{//}(2.38)$ and hyperfine splitting ($A_{//}, 520$ MHz) values for the visible Cu$^{2+}$ species corresponded to normal tetragonal 5- or 6-coordinated Cu$^{2+}$ species in the fresh and spent catalyst [58]. After catalyst regeneration, the signal from the carbon residues had disappeared completely and the EPR spectrum was identical to that of the fresh catalyst.

2.4. Characterization of Recrystallized MOR Catalysts

Recrystallized HMOR (RHM) with introduced mesopores were prepared by desilication of HMOR followed by recrystallization for 18 and 36 h, respectively, in order to make DME carbonylation catalysts with increased lifetime and reduced/eliminated diffusion limitations. XRPD of the prepared RHMs (RHM-18 and RHM-36, respectively) revealed no apparent differences in the intensity and crystalline phase compared to the pristine HMOR (Figure S10), confirming that the MOR framework was intact and no other composite materials were formed under the recrystallization conditions. However, the prominent shoulder at the peak at $2\theta = 28.3^\circ$ of the pristine HMOR was less prominent in both of the RHM catalysts, which can be attributed to the formation of new Si-O-Si or Si-O-Al bonds in the framework after destruction [59]. The nitrogen physisorption isotherms of the HMOR and RHM catalysts were attributed to type IV isotherms with microporosity, and the introduction of mesopores was confirmed by the presence of a hysteresis loop between the adsorption and desorption branches at a relative pressure of about 0.4542 (Figure S11).

The textural properties of the pristine HMOR and the recrystallized RHM catalysts are summarized in Table 3. The significant decrease in micropore volume for both of the modified catalysts compared to pristine HMOR suggest that the mesopores were introduced into the MOR framework at the expense of the micropores, resulting in an increase in mesopore volume by a factor of four and two for RHM-18 and RHM-36 catalysts, respectively. These results indicate that partial desilication of HMOR crystals occurred during the alkali treatment, followed by re-assembly of the siliceous fragments in the mesoporous layers on the external surface of the crystal. The extent of zeolite destruction and mesoporous phase overgrowth have previously been shown to be governed by the alkali content in the reaction mixture for the applied stepwise MOR recrystallization procedure [60]. Hence, depending on the alkali content, two types of micro/mesoporous materials with different mesoporous phase overgrowth can be obtained: coated mesoporous zeolite and ordered mesoporous materials containing small zeolite fragments in the walls. Longer recrystallization time for the RHM-36 resulted in a higher crystallinity (larger micropore volume) of the material compared to RHM-18, which may be due to preferential formation of such well-defined zeolite fragments, possibly also by dissolution/re-assembling of the desilicated mesoporous material, which is less stable under the hydrothermal conditions.
Table 3. Textural properties of HMOR and RHM catalysts.

| Catalyst | Specific Surface Area 1 (m² g⁻¹) | External Surface Area 2 (m² g⁻¹) | Micropore Surface Area (m² g⁻¹) | Micropore Volume 2 (cm³ g⁻¹) | Mesopore Volume 3 (cm³ g⁻¹) | Total Pore Volume 4 (cm³ g⁻¹) |
|----------|----------------------------------|---------------------------------|---------------------------------|-----------------------------|-----------------------------|-------------------------------|
| HMOR     | 447                              | 51                              | 396                             | 0.185                       | 0.088                       | 0.274                         |
| RHM-18   | 488                              | 206                             | 282                             | 0.102                       | 0.340                       | 0.442                         |
| RHM-36   | 456                              | 98                              | 358                             | 0.155                       | 0.167                       | 0.322                         |

1 Calculated using the BET method. 2 Determined using the t-plot method. 3 Determined using BJH method (desorption). 4 Sum of meso- and micropore volume.

The amount of acid sites, as well as acid type distribution, was also studied for the modified RHM catalysts by NH₃-TPD (Figure S12 and Table S2). The desilication followed by recrystallization led to an almost unchanged amount and strength of both weak and strong acid sites in comparison to the untreated HMOR as was also previously found using rather mild treatment conditions [60]. The very minor alterations measured (3–5%) was possibly related to the partial destruction of local silicon and aluminum framework during the desilication process [61]. Insignificant changes in the acid types confirm that controlled leaching of framework silicon occurred with surfactants present in the alkaline media during the recrystallization.

2.5. DME Carbonylation with Recrystallized MOR Catalysts

The recrystallized HMOR catalyst and the copper-modified catalysts were tested in DME carbonylation under identical reaction conditions as the pristine MOR catalyst (vide supra) and the results are compared in Figure 6. The catalyst modification introduced by recrystallization did not have any apparent influence on catalyst performance during the initial induction periods, and the MA yield as well as the selectivity remained almost the same as for the unmodified catalysts. However, after the induction period, the RHM-18 catalyst maintained its maximum activity (78% yield MA, 93% selectivity) at a constant level for an additional 5 h and even after 15 h of reaction, 64% MA was formed (95.5% selectivity) corresponding to 82% of the maximum activity (Figure 6a). In contrast, HMOR and RHM-36 maintained only about 50% and 60% of their maximum activity after 15 h of reaction, whereas the selectivity remained still high at 95.5%. The slower deactivation of the RHM catalysts suggests that the introduced mesopores decreased the diffusion limitation of reactants and products to active sites inside the channels.

Enticed by the improved activity of the RHM catalysts, copper (1 wt%)-impregnated RHM-18 and RHM-36 (i.e., Cu-RHM-18 and Cu-RHM-36) were prepared and tested for DME carbonylation under the same reaction conditions as the Cu-MOR catalysts. The introduction of copper clearly improved the activity of the catalysts and reduced the induction periods as shown in Figure 6b. Accordingly, deactivation started for untreated 1 wt% Cu-MOR already after 2.5 h of reaction, while it was extended by a factor of two for 1 wt% Cu-RHM-18 yielding about 90% MA with 97% selectivity. Cu-RHM-36, on the other hand, followed Cu-RHM-18 in terms of deactivation and selectivity, but with lower yields (79%) of MA after 5 h. Notably, the selectivity to MA was also higher during the induction periods with the Cu-RHM catalysts. The key reaction step of DME carbonylation is the insertion of CO into methoxy groups to form surface acetyl species, and this key step was most likely promoted and thus facilitated DME conversion, by the increased acidity of these materials. Higher selectivity during induction has also previously been found with Cu-MOR, and correlated with the formation of an increase in the amount of Lewis acid sites and the formation of new sites with medium and strong acidity after ion exchange [27].
Figure 6. (a) MA yield and selectivity in DME carbonylation using RHM catalysts. (b) MA yield and selectivity in DME carbonylation using 1 wt% Cu-RHM catalysts. Open circle: RHM-18, filled triangle: RHM-36, open triangle: HMOR. Reaction conditions: 500 mg catalyst, 220 °C, 100 mL min⁻¹ gas flow of DME/CO/N₂ = 1.3/92.7/5.0%, 7 bar, GHSV = 6711 h⁻¹. Data reported with an estimated error corresponding to ±2%.

The reusability of the 1 wt% Cu-RHM-18 catalyst was after the first 10 h run examined in four consecutive catalytic reaction runs for 2 h. The catalyst was in reaction run 1–3, regenerated in situ in an air flow (60 mL min⁻¹, 550 °C for 3 h, heating ramp 5 °C min⁻¹), while the catalyst in run 4 was regenerated in static air ex situ under the same conditions (Figure 7). After the initial 10 h run (MA yield of 78%), the activity of the catalyst was reduced gradually from run 1 through 3 providing MA yields of 72% (run 1), 68% (run 2) and 62% (run 3), respectively, while the catalyst selectivity remained high and unchanged. This result suggests that the re-activation process in the reactor did not sufficiently remove all types of deposited coke under the applied conditions, possibly due to internal mass transfer limitations. In contrast, in run 4 after ex situ catalyst regeneration, the catalyst recovered essentially its original performance and provided activity and selectivity comparable to the fresh catalyst (run 1), thus clearly demonstrating that effective catalyst regeneration was possible. Therefore, the in situ reactivation process could probably be optimized to provide a similar regeneration efficacy by adjusting parameters such as air flow or regeneration time.
3. Materials and Methods

3.1. Chemicals

Zeolite MOR (Si/Al = 10) was obtained from Zeolyst International (Delfzijl, The Netherlands) as the ammonium form. The acidic form, HMOR, was obtained by calcination at 550 °C for 6 h. Copper(II) nitrate hydrate (>98%), copper(II) oxide nanopowder (particle size < 50 nm, >98%), cetyl trimethylammonium bromide (CTAB, >98%) and all other reagents were purchased from Sigma-Aldrich (Søborg, Denmark) and used as received. CO gas (99.97%) and DME/CO/N₂ (5/75/20 mol%) certified gas mixture were purchased from AGA A/S (Ballerup, Denmark). Other gases and gas mixtures used for catalyst characterization were instrument quality from Air Liquide (Taastrup, Denmark) or AGA A/S.

3.2. Catalyst Preparation

A series of copper-supported catalysts were prepared with HMOR and copper(II) nitrate solution by incipient wetness impregnation (IWI), resulting in modified Cu-MOR catalysts with up to 10 wt% metal loading. The modified catalysts were dried at 80 °C for 1 h, calcined at 550 °C for 3 h in air (heating ramp of 5 °C min⁻¹) and preserved in a desiccator prior to catalytic testing as well as characterization.

Mesopores were introduced into the MOR framework structure by a stepwise recrystallization method modified from the literature [62] and 2 g of NH₄-MOR was added gradually over 3 h under continuous stirring to 60 mL of 1 M NaOH solution at 80 °C to desilicate MOR. Afterwards, 5 g of CTAB was added and the solution was transferred to an autoclave (100 mL) for hydrothermal treatment at 180 °C under autogenous pressure for 18 or 36 h, respectively. The samples were then recovered by filtration and washed with distilled water until a neutral pH was achieved. The obtained Na-MOR materials were ion-exchanged twice in an aqueous 2.5 M NH₄Cl solution at 80 °C for 3 h, followed by calcination at 550 °C in the air for 3 h and named RHM-18 and RHM-36 depending on the recrystallization times. The copper-modified RHMs (Cu-RHM-18 and Cu-RHM-36) were prepared by the impregnation procedure as described in the previous section.
3.3. Catalyst Characterization

The specific surface area of the samples was calculated by performing a Brunauer-Emmett-Teller (BET) analysis on nitrogen physisorption data measured at liquid nitrogen temperature on a Micromeritics (Norcross, GA, USA) ASAP 2020. The samples were outgassed in a vacuum at 200 °C for 12 h prior to the measurement. Micropore volumes of the samples were estimated from the same measurements using the t-plot method.

XRPD spectra were measured on a Huber (Rimsting, Germany) G670 diffractometer with a Guinier imaging plate camera operated in transmission mode with Cu-Kα1 (λ = 1.54 Å) irradiation from a focusing quartz monochromator. The samples were fixed between two pieces of Scotch tape and rotated during data collection. The diffraction patterns of the samples were recorded at room temperature in the 2θ range 3–100° in steps of 0.005°.

TEM studies were performed on a Tecnai T20 G2 and Titan instrument (FEI Company, Hillsboro, OR USA) operated at 200 and 120 kV, respectively. The Titan was fitted with a field-emission electron source and a spherical aberration corrector on the condenser lens system. The samples were re-dispersed in ethanol by ultrasonication and deposited on plain or holey carbon-coated Cu grids (Agar Scientific, Stansted, UK).

XPS measurements were performed on a ThermoScientific (Waltham, MA, USA) K-Alpha X-ray Photoelectron Spectrometer using Al-Kα1 (1486 eV) as exciting X-ray source. The pressure of the analysis chamber was maintained at 2 × 10⁻10 mbar during measurement. The XPS measurements were performed in the electron-binding energy ranges corresponding to copper 2p and oxygen 1s core excitations.

NH₃-TPD experiments were conducted on a Micromeritics (Norcross, GA, USA) Autochem-II to evaluate the total surface acidity of the catalysts. In a typical TPD experiment, 80 mg of dried sample was placed between quartz wool beds in a quartz tube and preheated in an He flow (75 mL min⁻¹) at 100 °C for 1 h followed by treatment with anhydrous NH₃ gas (Air Liquide, 5% NH₃ in He). After NH₃ adsorption, the sample was flushed with He (50 mL min⁻¹) for 100 min at 100 °C to remove physisorbed NH₃. Finally, the TPD operation was carried out by heating the sample from 100 to 700 °C (10 °C min⁻¹) under He flow (50 mL min⁻¹) and the NH₃ values were calculated from calibration experiments.

H₂-TPR was also conducted on a Micromeritics (Norcross, GA, USA) Autochem-II to study the metal reducibility in Cu-MOR samples. The samples were pretreated in 10% O₂/He mixture gas flow (20 mL min⁻¹) at 500 °C for 1 h, and then cooled down to 30 °C while flushing under an He flow (50 mL min⁻¹) for 1 h. Then the samples were heated to 600 °C (10 °C min⁻¹) in a reducing mixture consisting of 4% H₂ in Ar gas flow (60 mL min⁻¹). The water formed during reduction with H₂ was trapped using a dry ice cold trap. The hydrogen concentration in the effluent stream was continuously monitored by a thermal conductivity detector (TCD) and the H₂ consumption calculated from calibration experiments.

TPO measurements, to determine carbon deposits on the catalysts, were performed by placing 50 mg spent catalyst in an alumina holder (7 cm long, 1 cm wide) in a quartz tube (65 cm long, 24 mm i.d.) positioned in a horizontal, tubular furnace. The sample was subjected to 10% O₂ in N₂ gas flow (40 mL min⁻¹) at room temperature until all air was purged from the reactor (i.e., CO₂ signal zero), where, afterwards, the tube was heated to 750 °C (11 °C min⁻¹). During heating, the concentrations of CO and CO₂ in the effluent were continuously monitored using an AO2020 IR gas analyzer (ABB, Skovlunde, Denmark) calibrated using a certified CO/CO₂/N₂ gas mixture (AGA A/S).

Raman spectra of MOR and Cu-MOR catalysts were recorded by a Dilor XY 800 Raman spectrometer (Horiba, Oberursel, Germany) in the range 800–50 cm⁻¹ at room temperature using 244 nm (UV) and 488 nm (visible, blue) lasers, respectively. The 514.5 nm line of an argon laser was used as the excitation source with the capacity of supplying 250 mW power.
EPR spectra of fresh and spent Cu-HMOR catalysts (10–20 mg) were recorded ex situ with a Bruker EMX-EPR spectrometer (Mannheim, Germany) working in the X-band (Bruker ER 041 XCG Microwave Bridge) at microwave frequencies of around 9.75 GHz. The measurements were done at room temperature on samples transferred directly into a desiccator after calcination (fresh samples) and after the catalytic test (spent catalyst). Data treatment was performed with WIN-EPR software (v. 1.26) provided by Bruker.

3.4. Catalytic DME Carbonylation

The DME carbonylation reaction was performed in a continuous flow setup with a fixed-bed stainless steel vertical reactor (9 mm i.d., 12.6 mm o.d.) and an internal porous grid (pore diameter 2 µm); 500 mg catalyst (250–500 µm) were loaded into the reactor and pre-heated to 500 °C (5 °C min⁻¹) under air flow (60 mL min⁻¹) and maintained at the temperature for 30 min. After the reactor was cooled to the reaction temperature of 220 °C (unless otherwise mentioned), a 1.3/93.7/5.0 mol% DME/CO/N₂ gas mixture was introduced (100 mL min⁻¹; obtained with 75 mL min⁻¹ CO and 25 mL min⁻¹ 5/75/20 mol% DME/CO/N₂) and the reactor was pressurized to 7 bar (GHSV = 6711 h⁻¹). The reaction pressure was controlled by a regulation loop consisting of a pneumatic back-pressure regulator valve (Microvalve 3510; Samson AG, Frankfurt am Main, Germany), an electronic controller (Trovis 6493; Samson AG) and a pressure transducer (Wika S-11; Wika, Birkered, Denmark). The gas phase composition from the reactor was analyzed periodically by an integrated Autosystem XL gas chromatograph (Perkin Elmer, Skovlunde, Denmark; Nukol capillary column, 15 m × 0.53 mm i.d., Supelco; Sigma-Aldrich) equipped with TCD and FID detectors. DME conversion and MA yield and selectivity were calculated from peak areas using N₂ as the internal standard with an estimated error corresponding to ±2% based on preliminary tests with HMOR evaluating the absence of external and internal mass transfer limitations (Figures S12 and S13).

4. Conclusions

A series of Cu-MOR catalysts were prepared and tested for synthesis of MA by DME carbonylation in a continuous flow. The catalytic performance depended significantly on the metal loading with 1 wt% Cu being optimal. The generation of mesoporosity in MOR by a recrystallization method (yielding RHM catalysts) enhanced the catalyst lifetime significantly without compromising the selectivity and productivity of MA. The results with the RHM catalysts, prepared with different treatment times during the recrystallization process, indicated that an intermediate treatment time was optimal with respect to catalyst lifetime and activity, while the selectivity to MA was always high. This was due to a higher level of mesoporosity formed at the intermediate treatment time.

The Cu-RHM catalysts had a superior catalytic activity compared to the other examined catalysts, and yielded similar selectivity as the Cu-MOR catalysts. In this respect, TPO measurements on the Cu-RHM catalysts suggested that copper played an important role in suppressing the formation of hard coke, thereby overcoming diffusion limitations. Importantly, the Cu-RHM catalysts also exhibited very low deactivation rates, resulting in an MA yield loss of only 5–10% from steady-state performance during 10 h time-on-stream, whereas the analogous Cu-MOR and HMOR catalysts deactivated under the same operating conditions by 25–50%. Low deactivation rates of <10% have only recently been reported for CHA-type zeolites (SSZ-13), albeit at a much lower reaction temperature and pressure (165 °C, 1 bar) where MA production is lower and coke formation less pronounced [10].

Finally, the reusability of Cu-RHM-18 was examined in three consecutive catalytic runs with intermediate in situ catalyst regeneration in air; a gradual decrease in catalyst activity was found over the three runs; however, the catalyst regained its original catalytic performance when regenerated ex situ in air under identical conditions.
Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/catal11060696/s1, Figure S1: XRPD patterns of 0.5–10 wt% Cu-MOR catalysts, Figure S2: N2 adsorption-desorption isotherms of HMOR and Cu-HMOR catalysts, Figure S3: TPR of commercial CuO, bulk CuO and Cu2O, Figure S4: Possible coke precursors formed that result in catalyst deactivation by blocking the active sites and/or pores, Figure S5: XRPD patterns of fresh and spent 1 wt% Cu-MOR catalysts, Figure S6: XPS results of spent and fresh 1 wt% Cu-MOR catalysts, Figure S7: EPR spectra of fresh, spent, and regenerated 1 wt% Cu-MOR catalysts, Figure S8: XPS of 1, 5 and 10 wt% Cu-MOR catalysts, Figure S9: Carbon 1s XPS spectra of fresh and spent 1 wt% Cu-MOR catalysts, Figure S10: XRPD patterns of HMOR, RHM-18 and RHM-36 catalysts, Figure S11: N2 adsorption-desorption isotherms of HMOR and RHM catalysts, Figure S12. NH3-TPD of HMOR and recrystallized RHM catalysts. Figure S13: Conversion of DME as a function of reaction time with two different amounts of HMOR catalyst but constant space-time for the evaluation of external mass transfer limitations during DME carbonylation, Figure S14: Conversion of DME as a function of reaction time with two different particle sizes of HMOR catalyst but constant space-time for the evaluation of internal mass transfer limitations during DME carbonylation, Table S1: Reduction temperatures related to TPR profiles of the Cu-MOR catalysts, Table S2: Comparison of acid type distribution in HMOR and RHM catalysts.

Author Contributions: Conceptualization, R.P. and A.R.; methodology, R.P.; formal analysis, R.P. and S.M.; investigation, R.P.; resources, S.M.; writing—original draft preparation, R.P.; writing—review and editing, A.R., S.M. and A.D.J.; supervision, A.R. and A.D.J. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the UNIK research initiative Catalysis for Sustainable Energy funded by the Danish Ministry of Science, Technology and Innovation.

Acknowledgments: The authors express their gratitude to Jakob Munkholt Christensen (DTU Chemical and Biochemical Engineering) for assistance with TPO measurements, and Bodil Flis Holten (DTU Chemistry) for physisorption measurements.

Conflicts of Interest: The authors declare no conflict of interest.

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