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# Theoretical Analysis of Oxidative Carbonylation of Methanol: Saegusa's Scheme of Dimethylcarbonate Synthesis over Binuclear Cationic Oxo-Clusters in CuNaX Zeolite

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**S** Supporting Information

**ABSTRACT:** Possible mechanism of oxidative carbonylation of methanol via >Cu(OCH<sub>3</sub>)<sub>2</sub>Cu< binuclear cationic oxoclusters in the CuNaX zeolite with Cu<sup>2+</sup> cations is analyzed theoretically within the scope of periodic boundary conditions with VASP. Such scheme was first derived by Saegusa et al. (*J. Org. Chem.***1970**, *35*, 2976) and was never tested by theoretical modeling to our best knowledge. For the CO attack we have computed the activation energy value that is close to experimental values obtained in Cu-zeolites. We suppose that this scheme can correctly describe the oxidative carbonylation at medium and high Cu loading when the copper oxo-clusters can be formed.

### 1. INTRODUCTION

The problem of environmentally benign route of dimethylcarbonate (DMC) production compared to phosgene application or liquid-phase synthesis using corrosive solutions of CuCl remains urgent.<sup>1–5</sup> The catalytic process of oxidative carbonylation at the Cu form zeolites is one of the possible "environmentally friendly" alternatives. Most authors accept that there are two steps in CH<sub>3</sub>OH carbonylation,<sup>1–7</sup> i.e., subsequent attacks of the first and second CH<sub>3</sub>OH molecules, while the nature of intermediates is still under discussion. Two principal mechanisms have been proposed for the carbonylation. The first one is via the formation of DMC via Cu<sup>+</sup>(CH<sub>3</sub>OCO) carbomethoxides and Cu<sup>+</sup>(OCH<sub>3</sub>) methoxides<sup>1,3,8–12</sup>

$$Cu^{+}(OCH_3)Z + CO \rightarrow Cu^{+}(CH_3OCO)Z$$
 (1a)

$$Cu^{+}(CH_{3}OCO)Z + Cu^{+}(OCH_{3})Z$$
  

$$\rightarrow 2Cu^{+}Z + (CH_{3}O)_{2}CO \qquad (1b)$$

where Z denotes a zeolite framework. The second route assumes the formation of monomethylcarbonates (MMC) and methoxides:  $^{4,7,13-16}$ 

$$Cu^{+}(CH_{3}OH)Z + \frac{1}{2}O_{2} \rightarrow (OH)Cu^{+}(OCH_{3})Z$$
 (2a)

$$(OH)Cu^{+}(OCH_{3})Z + CO \rightarrow Cu^{+}(CH_{3}OCOOH)Z$$
(2b)



$$Cu^{+}(CH_{3}OCOOH)Z + CH_{3}OH$$
  

$$\rightarrow Cu^{+}Z + (CH_{3}O)_{2}CO + H_{2}O \qquad (2c)$$

The difference between various mechanisms is also related to monocationic site<sup>4,7,11–16</sup> or binuclear cationic sites<sup>2,3,9,10,13,17</sup> involved in the reaction mechanism. Anderson et al. elaborated kinetic multistep schemes including side products (dimethoxymethane or DMM, formaldehyde, and methylformate) for CuX<sup>3,10</sup> and CuZSM-5<sup>4</sup> in agreement with the Eley–Rideal mechanism for CO introduction into methoxide. The final reaction of the scheme (like 1b or R4 in ref 3) between carbomethoxy and methoxy reagents was considered at two Cu sites.<sup>3</sup> DMC syntheses were realized in different Cu form zeolites (ZSM-5,<sup>4,10</sup> X,<sup>3,10</sup> Y,<sup>1,14,15</sup> MOR<sup>18</sup> types). In ref 7, authors referenced the experimental value 14.80 kcal/mol for CuY, while the lower apparent activation energy near 11.70 kcal/mol for DMC production within a close interval of 380–430 K has been measured on the ZSM-5.<sup>4</sup>

Together with two mechanisms for oxidative carbonylation of methanol via methoxy species<sup>7,8,16</sup> and carbomethoxy species,<sup>1,3,9,11,12,17</sup> two other channels were proposed via carbonates<sup>6,19</sup> and >Cu(OCH<sub>3</sub>)<sub>2</sub>Cu< species (the last is named below as Saegusa's scheme).<sup>2,13</sup> The first three of them were analyzed theoretically including the route through carbonates.<sup>19</sup> The methoxy intermediate route at one Cu<sup>+</sup>

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center was first theoretically studied in ref 7 (without theoretical estimation of the activation energy) and then reconsidered in ref 10. A puzzling problem of monocenter (one Cu cation) mechanism is a way to complete the CO oxidation catalytic cycle. Zheng and Bell postulated an oxidation of adsorbed methanol by  $O_2(2a)$ ,<sup>7</sup> but no mechanism of this stage was proposed while its development is a very difficult task. It was demonstrated via O2 dissociation (possibly from singlet state as no multiplicity of the system was given in ref 16) which led to the formation of unusual >Cu=O species in the channel of Cu $\beta$  form<sup>16</sup> with rather high barrier of 42.4 kcal/mol. More precisely, it is larger than the activation energy of CO introduction (14.80 kcal/mol<sup>7</sup>) which limits DMC formation<sup>7</sup> so that this catalytic cycle cannot be justified. Additionally, the charge state of Cu cation in the  $>Cu=O^{16}$  species requires further studies. The direct O<sub>2</sub> involvement in the methoxy intermediate scheme over Cu form zeolites7,10 conflicts with known nearly zero-order O<sub>2</sub> (Figures 10c, 11c, 12c in ref 18) in the DMC formation reaction over all zeolites in a drastic difference to the liquid phase where first order was clearly shown (Figure 13c in ref 9).

Recently the route via carbomethoxide intermediates<sup>11,12</sup> has been theoretically tested at the PBE/DNP level<sup>20,21</sup> with DMOL<sup>3</sup> using the  $30T^{11}$  or 31T,<sup>12</sup> T = Si or Al, clusters cut from CuY. The lowest barrier of CO insertion and formation of carbomethoxide has been evaluated as 13.27 or 15.91 kcal/mol in the presence or without Cs<sup>+</sup> at the nearest SII site (model with optimal Si/Al ratio of 5.3)<sup>12</sup> which is very close to the experimental value 14.80 kcal/mol.<sup>7</sup> We considered in more details these works in our recent paper where CH<sub>3</sub>OH carbonylation over copper carbonate was analyzed<sup>19</sup> following the hypothesis proposed in ref 6.

Together with the evidence of the Cu<sup>1+</sup> activity in the reaction of oxidative carbonylation,<sup>3,7,10</sup> a more general approach which considers a transformation between Cu<sup>1+</sup> and Cu<sup>2+</sup> forms in Cu zeolites was proposed by Raab et al.<sup>2</sup> and Richter et al.<sup>6</sup> Relevant transformation between Cu<sup>1+</sup> and Cu<sup>2+</sup> was considered in the course of redox NO decomposition,<sup>22,23</sup> N<sub>2</sub>O reduction.<sup>24</sup> The parallel presence of Cu<sup>2+</sup> was shown and discussed involving XANES studies by Bell et al.,<sup>14</sup> via pyridine adsorption by Engeldinger et al.<sup>25</sup> An ignorance of the Cu<sup>1+</sup>/Cu<sup>2+</sup> transformation cannot construct full redox cycle for the oxidative carbonylation reaction in which the participation of copper cations as intermediates can explain nearly zero order of O<sub>2</sub> for all three Cu form zeolites (MOR, FAU, ZSM-5) whose activity was confirmed in the DMC formation reaction.<sup>18</sup>

In the case of binuclear mechanism, i.e., via >Cu- $(OCH_3)_2Cu < \text{fragments}_1^{13}$  one can address the formation of the derivatives of the >Cu(OH)<sub>2</sub>Cu< species previously established in the CuMOR<sup>26</sup> and CuZSM-5<sup>27</sup> zeolites. The >Cu(OH)<sub>2</sub>Cu< moieties can be the products of the reactions with a participation of stable CuOCu and CuO<sub>2</sub>Cu clusters. The latter were observed in various zeolite systems  $^{\tilde{\mathbf{2}}\mathbf{8}-\mathbf{31}}$  and are shortly discussed below. Earlier theoretical approaches were mainly oriented toward binuclear CuOCu clusters in zeolites<sup>32,33</sup> and biological objects,<sup>33,34</sup> while recent combined theoretical and experimental investigation addressed trinuclear Cu<sub>3</sub>O<sub>3</sub> species.<sup>35</sup> Both singlet<sup>32,34,36,37</sup> and triplet<sup>32,38</sup> ground states were calculated for >CuO<sub>x</sub>Cu< complexes. Goodman et al.<sup>32</sup> showed possible dependence of favor >CuO<sub>x</sub>Cu< multiplicity on the geometries at the LSDA level with BP86 corrections using Slater-type basis sets of double- $\zeta$  quality plus

polarization over all atoms and of double- $\zeta$  (s-, p-orbitals) and triple- $\zeta$  (d-orbitals) for Cu.

Rich information obtained from IR and mass spectra within the scope of steady state isotopic transient kinetic analysis<sup>39</sup> led the authors to the conclusion that the Mars-van Krevelen mechanism of CO oxidation by the surface lattice oxygen takes place. This may indicate that metal-oxide species CuO<sub>x</sub> can serve as the source for such O atom required for DMC synthesis as was clearly formulated by the authors.<sup>39</sup> The presence of strong oxidant in CuY in the absence of O2 was demonstrated by Zhang and Bell (high rate of CO<sub>2</sub> production after deletion of physisorbed  $O_2$  at 4 ks in Figure 5 of ref 40). One should note that the authors of refs 25 and 39 studied the CuY zeolites within a wide range of Cu loading where the formation of metal-oxide bi- or even polynuclear species with the simplest binuclear  $CuO_xCu$  cases, X = 1 or 2, is possible. The lowest boundary for Cu loadings, when polynuclear species can be formed, can be approximately evaluated as above 3.58% regarding the differences between Figures 6 and 7 in ref 25. The oxidation activity of CuOCu<sup>28–31</sup> and CuO<sub>2</sub>Cu<sup>41</sup> species with respect to CH<sub>4</sub>,  $^{28–31,42}$  N<sub>2</sub>O, CO,  $^{32}$  NO,  $^{43}$  cyclohexane,  $^{44}$  and tolyene<sup>41</sup> oxidation in zeolites<sup>28–31,42</sup> or mesoporous silica<sup>41</sup> at mild conditions was investigated both theoretically<sup>27,28,31,32,45</sup> and experimentally.<sup>28–31,41,42</sup> Essential fraction of CuOCu species in total copper content was demonstrated in CuZSM-5 using mass spectrometric analysis of the amount of oxygen thermally removed.<sup>46</sup> The authors of ref 42 developed the catalytic cycle including the CuO<sub>2</sub>Cu in the  $\mu$ -( $\eta^2$ : $\eta^2$ ) peroxo dicopper (plain or nonplain) form in CuZSM-5 (scheme I in ref 42). Later on, the authors assigned the  $CH_4$  oxidation to the active  $Cu^{2+}-O\bullet^{-}-Cu^{+}$  radical with O atom in "oxyl" form appearing after the transformation of  $\mu$ -( $\eta^2$ : $\eta^2$ ) peroxo dicopper fragment in agreement with ref 47. Such active group with "oxyl" O atom was however never observed according to the authors of ref 45 in an enzymatic or model complex where wide theoretical studies were undertaken over enzymes with CuOCu or CuO<sub>2</sub>Cu fragments and summarized in the reviews.<sup>45,</sup> Some peculiarities of DFT computations of these CuO<sub>x</sub>Cu moieties, X = 1, 2, were recently discussed regarding the differences between results obtained at the DFT and MP2 levels.<sup>49</sup> By combining the enzymatic oxidation with the optimization of the ratio between homogeneous/heterogeneous phases for soft oxidation of tolyene, tridentate Cu(II) complex was recently deposited in pores of mesoporous silica.<sup>41</sup>

Addressing relevant experience in oxidative carbonylation, the methoxy form of  $bis(\mu$ -oxo)dicopper cluster was assumed in a pioneering work of Saegusa et al. in liquid-phase CuCl/ CuCl<sub>2</sub> catalysis:<sup>13</sup>

$$\{Cu^{+2}(OCH_3)_2Cu^{+2}\}Z + CO$$
  

$$\rightarrow \{Cu^{+2}(CH_3OCOOCH_3)Cu^{+2}\}Z$$
(3)

$$\{Cu^{+2}(CH_3OCOOCH_3)Cu^{+2}\}Z$$
  

$$\rightarrow 2Cu^{+}Z + CH_2OCOOCH_2$$
(3a)

The step-by-step transformation between  $Cu^{2+}-O-Cu^+$  species, hydrogenated/methoxy forms of bis( $\mu$ -oxo) dicopper cluster, and  $\mu$ -( $\eta^2:\eta^2$ ) peroxo dicopper cluster was cycled for oxidative CH<sub>3</sub>OH carbonylation mainly in homogeneous media (the 3Å zeolite was also considered as drying bed with the highest DMC yield over all the experiments in the ref 2) (scheme 2 in ref 2). The existence of  $[Cu(OH)_2Cu]^{+2}$  in

solutions of copper salts is well-known<sup>50</sup> and was confirmed via ESR studies in CuMOR (as  $[(H_2O)_2Cu(OH)_2Cu(H_2O)_2]^{+2}$ )<sup>26</sup> and CuZSM-5 zeolites.<sup>27</sup> One should note that the rhombic >Cu(OX)<sub>2</sub>Cu< fragments form the chains in natural Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub> malachite mineral.<sup>51</sup> Two types of intralayer  $Cu(OH)(CO_3)Cu$  and interlayer  $Cu(OH)_2Cu$  fragments can be partitioned. The intralayer  $Cu(OH)(CO_3)Cu$  dimers with one O atom of carbonate anion instead of OH group exhibit XRD experimental Cu-Cu and O-O distances equal to 3.063 and 2.540 Å, respectively.<sup>51</sup> The interlayer  $Cu(OH)_2Cu$ fragments in malachite correspond to longer Cu-Cu and O…O distances of 3.240 and 2.835 Å.51 Similarly, the  $Cu(OH)(CO_3)Cu$  dimers are present in the rosasite family of Mg, Zn, Co, Ni-substituted analogues of malachite.<sup>52</sup> So, it would be interesting to check this oxidative carbonylation scheme applying the >Cu(OCH<sub>3</sub>)<sub>2</sub>Cu< species in a Cu-zeolite media. Methoxy-dicopper Cu(OCH<sub>3</sub>)Cu fragment was obtained in solid state<sup>53</sup> and is one of benchmark substances used for checking how well DFT functionals are suitable for modeling of dicopper complexes and MOFs containing dicopper fragments (Cu-MOF-11, MOF-505, HKUST-1 etc.).<sup>54,55</sup> The aim of this work is to study the mechanism of oxidative carbonylation reaction 3 in the CuNaX zeolite using periodic boundary conditions (PBC). In the next sections we shall present the computational details and the modeling of reactions with PBC using various DFT methods. The first computational section demonstrates the reaction between the >Cu(OH)<sub>2</sub>Cu< complex and CH<sub>3</sub>OH (4a, 4b) to produce  $>Cu(OCH_3)_2Cu <$  species with a close value of barrier compared to the one of the main reaction (3) between the bis-dimethoxy-dicopper complex and CO. The second computational section 3.2 is devoted to the main reaction (3).

### 2. COMPUTATIONAL DETAILS

Plane wave computations with the periodic boundary conditions using the PBE<sup>56</sup> and PBEsol<sup>57</sup> functionals within the projector augmented wave (PAW) method<sup>58,59</sup> were performed with VASP.<sup>60,61</sup> The scripts provided by the Transition State Tools for VASP were used to build initial images for the climbing image nudged elastic band (ciNEB) calculations.<sup>62,63</sup> Since X type zeolites allow the carbonylation,<sup>3,10</sup> the CuNaX structure with the formula of the unit cell  $Cu_{10}Na_4Al_{24}Si_{72}O_{96}$  with  $Cu^{2+}$  at the sites II and  $Na^+$  at the sites I has been considered with periodic boundary conditions. One of 10 Cu cations was positioned at SIII site as determined by ESR analysis.<sup>64</sup> This Cu170 cation is located relatively far from CuIII(169) and CuII(168) cations of the >Cu- $(OCH_3)_2Cu <$  moiety, i.e., separated by ~4.9-5.2 and ~8.2-9.0 Å, respectively, at different reaction steps, and cannot exert a strong influence on the reaction. NaI<sup>+</sup> cations in CuNaX are located in D6R prisms and do not participate in the reaction. The energy cutoff was set to 500 eV. The Brillouin zone ksampling was restricted to the  $\Gamma$ -point for the geometry optimization and transition state (TS) search via ciNEB calculations. All ciNEB calculations were performed assuming the singlet states of the models, which is in agreement with ESR experiment in zeolites.<sup>27</sup> For all cluster zeolite models (8R, extended 8RL, 6R+4R, 10T cut from CuMOR, CuY, CuZSM-5 zeolites, respectively) at the MP2 levels the singlet ground states were confirmed,  $^{49}$  while it might be different relative to the level of DFT modeling (Table S4). Dispersive energy corrections were considered at the PBE-D2,65 zero-damping D3 (PBE-D3) and D3 with Becke-Jonson damping (PBE-

D3(BJ)),<sup>66,67</sup> and Tkachenko and Scheffler (PBE-TS)<sup>68</sup> levels using standard parameters adopted with VASP. The atomic charge density distribution was analyzed using Bader analysis.<sup>69</sup> Figures of geometry configuration of models were made with MOLDRAW2.0.<sup>70</sup> Some illustrative computations were performed using GAUSSIAN09.<sup>71</sup>

## 3. RESULTS

Before the reactions are described, one should note a satisfactory agreement between calculated geometry of CuII<sup>+2</sup> center in our CuNaX model and EXAFS and XANES geometry measured in  $Cu^{1+}Y$  and assigned to  $CuII^+$  cation.<sup>14,15</sup> The authors of previous modeling studies at isolated cluster levels<sup>7,11,12</sup> remarked a difference of three-coordinated CuII<sup>+</sup> in the cluster including 6R windows of initial reagents in their computations as compared to experimental data.<sup>14,15</sup> Despite different charge Cu2+ in our case, the Cu-Al and Cu-O distances of 2.86-2.90 and 1.96-2.04 Å agree with the measured 2.87 and 1.99 Å, respectively. (The Cu1+Y form optimized with PBE by us is characterized by three-coordinated CuII<sup>+1</sup> in 6R windows, even if two-coordinated CuII<sup>+</sup> was optimized in 6R windows of Cu1+CHA72). These lengths are observed for shifted Cu2+ site relative to an exact CuII one at any 6R center. This is one of the possible reasons why the Cu coordination number by O atoms was decreased to 2 in CuY.<sup>14,15</sup> This shift was obtained with all PBE, PBEsol, and PBE-D2 family leading to very similar Cu-Al or Cu-O distances with each of them. So, the presence of partially oxidized  $Cu^{1+} \rightarrow Cu^{2+}$  cations in  $Cu^{1+}Y^{14,15}$  can explain the lower Cu coordination number observed in refs 14 and 15. The presence of Cu<sup>2+</sup> does not contradict the XANES data (Figure 12 from ref 14) and temperature-programmed reduction (TPR) data (Figure 6 from ref 14). The low-temperature (LT) peaks at 533 and 783 K in the course of TPR  $H_2^{14}$ resemble the ones at 495 K (SII), 600 K (SII'), and 770 K (Supporting Information) assigned to  $Cu^{2+} \rightarrow Cu^{1+}$  reduction in CuNaY with Cu<sup>2+</sup> cations.<sup>73</sup> (The peaks are selected from ref 73 for the Cu(76)NaY model with the closest Cu/Al ratio of 0.895.) The exact positions of the LT peaks vary with second exchanged Me cation in the CuMeY zeolite, but they are conserved in its hexagonal analogue CuMeEMT (555 K (SII), 630 K (SII'), and 830 K (Supporting Information), if no Me cation, or 620 K (SII), 690 K (SII'), and 836 K (Supporting Information), if Me = Ca) of cubic CuFAU type.<sup>7</sup>

**3.1. Formation of >Cu(OCH<sub>3</sub>)<sub>2</sub>Cu<.** If the presence of the hydrogenated Cu(OH)<sub>2</sub>Cu form of bis( $\mu$ -oxo)dicopper cluster within zeolites was confirmed experimentally,<sup>26,27</sup> this has not been proven for its methoxy derivative. The easy exchange of one OH group was first illustrated in its hydrogenated Cu(OH)<sub>2</sub>Cu form within the CuNaX framework:

$$\{Cu^{+2}(OH)_{2}Cu^{+2}\}Z + CH_{3}OH$$
  

$$\rightarrow \{Cu^{+2}(OCH_{3})(OH)Cu^{+2}\}Z + H_{2}O$$
(4a)  

$$\{Cu^{+2}(OCH_{3})(OH)Cu^{+2}\}Z + CH_{3}OH$$

$$\rightarrow \{Cu^{+2}(OCH_3)_2Cu^{+2}\}Z + H_2O$$
(4b)

The respective profile of the reaction to replace the first OH group (4a) is shown in Figure 1. The respective geometries of reagent, product, two TSs, and one intermediate are described in Table S1 of the Supporting Information. The activation barriers  $E^{\#}$  of two TSs are 13.6 and 8.4 kcal/mol, while the



**Figure 1.** Reaction coordinate (in Å) for CH<sub>3</sub>OH attack over  $Cu(OH)_2Cu$  (4a) in CuNaX at the PBE/PAW level with PBC. The geometries of the reagents, transition states, and products (see Table S1) are assigned by arrows. The energy is in kcal/mol in all figures. The atomic colors are given in blue, red, yellow, magenta, olive, and gray for Cu, O, Si, Al, C, and H, respectively.

heats of reactions  $\Delta U$  are around -1.6 and 5.7 kcal/mol. The first barrier is related to the rupture of one Cu–OH bond which is accompanied by a stable intermediate due to water formation (the first intermediate product). The smaller  $E^{\#}$  at the second step of 8.4 kcal/mol is required to overcome hydrogen bond between proton of water and O atom of methoxy group and then to reorient the water molecule. Similar  $E^{\#}$ ,  $\omega$ , and  $\Delta U$  parameters are obtained with all DFT functionals and various van der Waals corrections to the conventional DFT energy (Table 1, Figure 2). Relative to the

Table 1. Heat ( $\Delta U$ , kcal/mol), Activation Barrier ( $E^{\#}$ , kcal/mol), and Frequency of Transition State ( $-i\omega$ , cm<sup>-1</sup>) of the Reaction Cu(OH)<sub>2</sub>Cu+CH<sub>3</sub>OH  $\rightarrow$  Cu(OH)(OCH<sub>3</sub>)Cu + H<sub>2</sub>O (4a) and Cu(OH)(OCH<sub>3</sub>)Cu+CH<sub>3</sub>OH $\rightarrow$  Cu

 $(OCH_3)_2Cu + H_2O$  (4b) Obtained with PBE and PBEsol Functionals Using PBE-D2, PBE-TS, and PBE-D3(BJ) vdW Corrections with PBC

reaction	method	$\Delta U$	$E^{\#}$	$-i\omega$
4a	PBE	4.15	13.61	254.6
	PBEsol	8.28	19.58	281.3
	PBE-D3(BJ)	6.76	16.17	262.4
	PBE-D2	8.14	15.54	246.8
	PBE-TS	6.02	14.83	271.0
4b	PBE	-11.16	13.54	223.8
	PBE-D2	-8.09	15.08	123.0

 $\Delta U$  values the inclusion of dispersive corrections (PBE-D2,<sup>65</sup> PBE-D3(BJ),<sup>66,67</sup> PBE-TS<sup>68</sup>) enforce the endothermic character of reaction 4a producing the series of the heats in the following increasing order: PBE < PBE-TS < PBE-3(BJ) < PBE-D2 < PBEsol. The activation barriers obey the similar sequence of PBE < PBE-TS < PBE-D2 < PBE-3(BJ) < PBEsol



Figure 2. Reaction coordinate (in Å) for  $CH_3OH$  attack over  $Cu(OH)_2Cu$  (4a) in CuNaX obtained with different DFT functionals (PBE, PBEsol) and using different vdW corrections (D2, D3-BJ, Tkatchenko–Scheffler) with PBC.

(Table 1) with inverse positions of the PBE-D2 and PBE-3(BJ) cases.

Considering the geometry changes, as a result of total replacement of two OH groups by OCH<sub>3</sub> ones, the Cu…Cu and O…O distances increase up to 3.071 and 2.315 Å instead of 2.867 and 2.359 Å (the PBE geometry in Table S1). These values are longer and shorter, respectively, than 3.063 and 2.540 Å in the malachite mineral (see part 1) which contains similar  $Cu(OH)(CO_3)Cu$  groups.<sup>51</sup> Regarding the close covalent radii of four-coordinated Cu<sup>2+</sup> (0.71 Å), Mg<sup>2+</sup> (0.71 Å), and Zn<sup>2+</sup> (0.74 Å),<sup>74</sup> it is reasonable to compare with the XRD values for Cu(OH)(CO<sub>3</sub>)Mg species in mcguinnessite and Cu(OH)-(CO<sub>3</sub>)Zn species in rosasite minerals.<sup>75</sup> The Cu···Me/O···O distances are 3.177/2.714 (Me = Mg) and 3.206/2.602 Å (Me = Zn), respectively. There are also the  $Cu(CO_3)_2Cu$  moieties in mcguinnessite (|Cu···Cu| = 3.1623 Å) and rosasite (|Cu···Cu| = 3.1622 Å), but they are more strongly distorted so that O…O distances are 3.286 and 3.342 Å, respectively.

A coherent picture of Bader atomic charges is obtained with all DFT functionals used except for PBE-D2 at all reaction steps. The largest  $\Delta Q = Q(Cu166) - Q(Cu167)$  (numbers of atoms are given in Figure S1 in the Supporting Information) charge difference at the Cu atoms of the Cu(OH)(OCH<sub>3</sub>)Cu product is observed (from 0.194 to 0.177 e) with all DFT methods applied. The  $\Delta Q$  variation along the reaction 4a profile is repeated with all methods as well. The largest absolute  $\Delta Q$  for the first TS step (Table 2) as compared to the others (i.e., 0.042 *e* for REA, -0.005 *e* for INT, and -0.034 *e* for PRO with PBE-D2) shows that Cu167 has the poorer coordination at the TS step than Cu166 near the 6R window (the SII site). But Cu167 remains better coordinated than Cu168 at the SIII site.

Since we received comparable results for heats of reactions, activation barriers, and TS frequencies values on the one hand and for the Bader type charges (Table 2) on the other hand, with all five DFT methods, this indicates a unique conclusion about this reaction mechanism. Hence, for analogous exchange of the second OH group in  $Cu(OH)_2Cu$  via (4a) we performed the calculations with only two DFT levels, i.e., PBE and PBE-D2 methods (Figure 3, Table S2, and Figure S2 in the Supporting Information) and revealed a slightly lower value of the activation energy relative to the one at the first step (4a)

Table 2. Bader Atomic Charges Q and Charge Difference  $\Delta Q = Q(166) - Q(167)$  (all in *e*), for the Reagent (REA), Transition State (TS), Intermediate (INT), and Product (PRO) of the Reaction of CH<sub>3</sub>OH Attack (4a) over Cu167(OH)<sub>2</sub>Cu166 in CuNaX Obtained with PBE and PBEsol Functionals Using PBE-D2, PBE-TS, and PBE-D3(BJ) Types of vdW Corrections with PBC<sup>a</sup>

		Cu160	Cu163	Cu166	Cu167	Cu168	$\Delta Q$
PBE	REA	1.055	1.085	1.139	1.095	0.944	0.044
	TS1	1.074	1.085	1.179	0.998	0.949	0.181
	INT	1.050	1.092	1.098	1.101	0.961	-0.003
	TS2	1.019	1.083	1.039	1.089	0.959	-0.050
	PRO	1.041	1.096	1.069	1.105	0.970	-0.036
PBEsol	REA	1.045	1.082	1.134	1.092	0.940	0.042
	TS1	1.070	1.082	1.166	0.984	0.948	0.182
	INT	1.042	1.087	1.090	1.090	0.959	0.000
	TS2	1.027	1.090	1.047	1.108	0.975	-0.061
	PRO	1.037	1.091	1.058	1.095	0.968	-0.037
PBE-D2	REA	1.053	1.083	1.142	1.100	0.944	0.042
	TS1	1.069	1.085	1.194	1.000	0.949	0.194
	INT	1.046	1.092	1.101	1.106	0.960	-0.005
	TS2	1.034	1.094	1.057	1.124	0.973	-0.067
	PRO	1.039	1.095	1.071	1.105	0.969	-0.034
PBE-TS	REA	1.052	1.088	1.143	1.098	0.939	0.045
	TS1	1.074	1.089	1.178	0.997	0.945	0.181
	INT	1.047	1.092	1.095	1.105	0.959	-0.010
	TS2	1.035	1.095	1.052	1.120	0.974	-0.068
	PRO	1.042	1.094	1.069	1.105	0.965	-0.036
PBE-D3(BJ)	REA	1.054	1.085	1.142	1.100	0.943	0.042
	TS1	1.070	1.085	1.176	0.999	0.948	0.177
	INT	1.045	1.092	1.104	1.107	0.961	-0.003
	TS2	1.034	1.095	1.058	1.122	0.975	-0.064
	PRO	1.039	1.096	1.07	1.105	0.971	-0.035

<sup>a</sup>The numbers of atoms listed in the table are given in Figure S1.



**Figure 3.** Reaction coordinate (in Å) for  $CH_3OH$  attack over  $Cu(OH)(OCH_3)Cu$  (4b) in CuNaX at the PBE/PAW level with PBC. The geometries of the reagent, transition states, and product are assigned by arrows.

(Table 1). This step (4a) can be a continuation of the reaction scheme for DMC production via CuOCu

$$\{Cu^{+2}OCu^{+2}\}Z + CH_{3}OH \rightarrow \{Cu^{+2}(OCH_{3})(OH)Cu^{+2}\}Z + H_{2}O$$
(4c)

whose green color is supposed to appear upon thermal treatment and dehydration at 500 °C.<sup>27</sup> The reaction (4c) leads to the same Cu(OCH<sub>3</sub>)(OH)Cu product as reaction (4a) but with two smaller activation barriers (~0.14 and 6.46 kcal/mol) and total heat of the reaction around of 10.14 kcal/mol (Figure 7 below). The following step of the DMC synthesis scheme via CuOCu with second CH<sub>3</sub>OH passes as (4b) producing Cu(OCH<sub>3</sub>)<sub>2</sub>Cu.

3.2. CO Attack on the >Cu(OCH<sub>3</sub>)<sub>2</sub>Cu< Species in **CuNaX and DMC Formation.** Using the >Cu(OCH<sub>3</sub>)<sub>2</sub>Cu< species in CuNaX, we have performed the modeling of the CO attack regarding the oxidative carbonylation. The mechanism of reaction was proposed in 1970,<sup>13</sup> but it was not theoretically tested yet. We obtained the value of activation energy  $E^{\#}$  of 12.68 for PBE (13.61 for PBEsol and 16.37 for PBE-D2, Table 4, below) and the value of heat of the reaction  $\Delta U$  of -70.51for PBE (-72.58 for PBEsol and -59.39 for PBE-D2, Table 4). These  $E^{\#}$  values are in a reasonable agreement with the experimental value on CuY (14.80 kcal/mol<sup>7</sup>). In the transition state both OCH<sub>3</sub> species are moved to one cation, where the reaction with CO takes place (Figure 4). During the reaction OCH<sub>3</sub> species and CO move synchronously toward each other (movie in the Supporting Information). Simultaneously the distance between Cu cations increases by more than 1.2 Å, and the second cation becomes coordinated to the zeolite framework (Table S3 of the Supporting Information). Although the process is similar to the reaction on one site in the

				PBE		PBEsol		PBE-D2			
value	site	Cu atom	REA	TS	PRO	REA	TS	PRO	REA	TS	PRO
Q	II	162	1.071	1.035	1.001	1.069	1.021	1.003	1.070	1.007	1.002
		165	1.087	1.085	1.079	1.085	1.088	1.076	1.089	1.093	1.081
		168	1.116	0.966	0.924	1.100	0.922	0.891	1.117	0.925	0.904
	III	169	0.985	1.097	0.974	0.965	1.120	0.958	0.980	1.156	0.979
		170	0.951	0.951	0.923	0.952	0.938	0.938	0.953	0.945	0.942
$\Delta Q$	_	_	0.131	-0.131	-0.05	0.135	-0.198	-0.067	0.137	-0.231	-0.075
V	II	162	37.64	38.38	40.91	36.94	38.51	39.48	37.48	39.25	40.40
		165	28.19	26.71	25.43	28.02	24.85	24.79	28.27	22.59	24.90
		168	19.14	20.86	27.84	18.58	24.32	28.45	19.04	26.98	28.58
	III	169	13.55	10.21	14.84	13.05	9.84	14.28	13.73	11.11	14.41
		170	58.78	57.04	57.61	55.70	53.05	54.00	59.22	57.01	57.08
<sup>a</sup> Atomic 1	nositions	of Cu cations	of the Cul	68(OCH) C	1160 clustor	ara shawn ir	Figure 4 Th	a numbaring	is given in	Jimuro S3 and	diffore from

"Atomic positions of Cu cations of the Cu168(OCH<sub>3</sub>)<sub>2</sub>Cu169 cluster are shown in Figure 4. The numbering is given in Figure S3 and differs from the one for reaction 4 (Table 2)

Table 4. Activation Barrier ( $E^{\#}$ , kcal/mol), Heat ( $\Delta U$ , kcal/mol), and Frequency of Transition State ( $-i\omega$ , cm<sup>-1</sup>) of the Reaction {Cu<sup>+2</sup>(OCH<sub>3</sub>)<sub>2</sub>Cu<sup>+2</sup>}Z + CO  $\rightarrow$  2Cu<sup>+</sup>Z + CH<sub>3</sub>OCOOCH<sub>3</sub> (3) Obtained with Different DFT Functionals and Using vdW Corrections

method	$E^{\#}$	$\Delta U$	$-i\omega$
PBE	12.68	-70.56	85.5
PBEsol	13.61	-72.64	99.0
PBE-D2	16.37	-59.49	169.1
PBE-D3(BJ)	11.76	-62.72	70.0
PBE-D3	11.76	-63.55	67.6



**Figure 4.** Reaction coordinate (in Å) for CO attack over  $Cu(OCH_3)_2Cu$  in CuNaX at the PBE/PAW level with PBC. The geometries of the reagents, transition states, and products are assigned by arrows. The color agreement of atoms is given in Figure 1.

transition state, the collapse of the binuclear cluster (breaking of three of the four Cu-O bonds) leads to the barrier value of 12.68 kcal/mol (PBE), which is close the experimental value of 14.80 kcal/mol in CuY.<sup>7</sup> Partially this barrier is lowered due to the formation of Cu-C(O) bond. A comparison of barrier values of reaction (3) calculated using various DFT functionals and dispersive energy corrections is shown in Figure 5 and



**Figure 5.** Reaction coordinate (in Å) for CO attack over  $Cu(OCH_3)_2Cu$  (3) in CuNaX obtained with different DFT functionals (PBE, PBEsol) and using vdW corrections (PBE-D2, PBE-D3(BJ), PBE-D3) with periodic boundary conditions.

Table 4. Both the activation barriers and TS frequencies  $(-i\omega)$  obey the unique order in the PBE-D3 ~ PBE-D3(BJ) < PBE < PBEsol < PBE-D2 series (Table 4). It is interesting that dispersive energy corrections also moderate the heat of the reaction (3) making it a less exothermic one as for reaction 4b or a more endothermic one as for reaction 4a above (Table 1).

The analysis of atomic charges and volumes in the course of DMC formation was given in terms of the Bader partition scheme as realized with VASP (Table 3, Figure 6). It showed qualitative agreement between their variations, but the volume looks to be in a better agreement with physical intuition. For



**Figure 6.** Bader atomic volumes V (Å<sup>3</sup>) of Cu atoms at the SIII (dashed line, circles) and SII (dot-dot-dashed line, triangles) sites versus Bader charges Q (e) at three steps (REA, TS, PRO) of CO reaction 3 with Cu(OCH<sub>3</sub>)<sub>2</sub>Cu in CuNaX at the PBE-D2/PAW level. Cu cations participating (open symbols) or not (closed symbols) in the reaction of the Cu(OCH<sub>3</sub>)<sub>2</sub>Cu cluster are shown in Figure 4.

comparison with the Cu cations that have not participated in the reaction, the largest atomic volume (Cu170 at the SIII site, the numbering of atoms is given in Figure S3 in the Supporting Information) and the smallest (Cu165 at the SII site) volume are also shown. Cu170 cation helps to serve as a landmark for comparison of the atomic parameters of both CuII and CuIII cations. The main difference between Cu170 (SIII) and Cu165 (SII) is the Cu-O distances, i.e., 2.048-2.151 Å and 1.997-2.042 Å, respectively, at the initial (REA in Table 1) configuration. The tighter Cu165 (SII) coordination corresponds to its larger charge and the smaller volume than other CuII and Cu170(III) atoms. The two dotted lines in Figure 6 limit the domain of calculated atomic volumes for all CuII type atoms (between Cu162 and Cu165). Only CuIII type and Cu168 charges are outside this domain, being included into the reaction cluster, but after the transformation of the active center Cu168 cation approaches the parameters of the typical CuII cations. The Cu169 coordination along the reaction formally corresponds to the SIII location, but it participates in the reaction cluster at all the steps so that its volume varies very little. Due to the permanent tight participation in the active zone of the reaction, the Cu169 holds a minimal volume at all the steps being smaller than any one of the CuII or CuIII atoms. The relative variation of atomic Cu168 charges from REA to PRO geometries correlates with its volumes at different stages as well as "charge-volume" changes for all other CuII or CuIII atoms with the two Cu169 (atom on the cluster) and Cu165 (the lowest cationic charge throughout CuII sites) exceptions. Moreover, similar slopes for different CuII (162, 168) and CuIII (170) atoms can be noted in Figure 6. This volume behavior illustrates the reasonability of the estimation of electronic density partition via atomic volumes as adopted by Tkachenko and Scheffler to calculate the dispersive interaction energy.<sup>68</sup> (One should note that the dispersive energy was calculated in our earlier works<sup>77,78</sup> considering the atomic polarizability and radii as the functions of effective atomic charges (fitted in accordance with IR data of H<sub>2</sub> adsorbed in the zeolite) of all zeolite atoms that are similar to respective proportionality constants in the first scheme of dispersive DFT-

TS corrections for molecules developed by Tkachenko and Scheffler.<sup>68</sup>)



Figure 7. Reaction coordinate (in Å) for  $CH_3OH$  attack over CuOCu (4c) in CuNaX obtained with PBE functional using periodic boundary conditions. The color agreement of atoms is given in Figure 1.

In order to cycle this DMC production, one can evaluate the possible energy losses at the steps of the following scheme, where sequence numbers of reactions and added reagents are given under and above arrows, respectively. All the numbers of reactions in (5) from eq (3) to eq (4a) correspond to the

$$\begin{array}{c} CH_{3}OH & CH_{3}OH \\ \{Cu(OH)_{2}Cu\}Z \xrightarrow{} \{Cu(OCH_{3})(OH)Cu\}Z \xrightarrow{} (4b) \\ H_{2}O & CH_{3}OH \\ CH_{3}OH & (4c) \\ (CuOCu\}Z \xleftarrow{} O_{2} \\ 2CuZ \xleftarrow{} (3a) \\ \{Cu(CH_{3}OC(O)OCH_{3})Cu\}Z \end{array}$$
(5)

reaction schemes in the text above. The step of  ${}^{3}O_{2}$  trapping in CuNaX (CuNaX = (2Cu)Z, Z = Cu<sub>8</sub>Na<sub>4</sub>Al<sub>24</sub>Si<sub>72</sub>O<sub>96</sub>) is slightly endothermic (+5.7 kcal/mol)

$$(2Cu)Z + \frac{1}{2}^{3}O_{2} \rightarrow \{CuOCu\}Z$$
(6)

where the energies of (2Cu)Z, O<sub>2</sub>, and {CuOCu}Z are -1126.44, -9.86, and -1131.14 eV, respectively, at the PBE/ PAW level. This minor endothermic effect cannot be a problem in the media above 100 °C. The DMC desorption step (3a) was calculated by us for the 8R cluster at the B3LYP/6–31G level using GAUSSIAN09.<sup>71</sup> Desorption of the DMC coordinated via carbonyl-O atom to Cu of the Cu–O– Cu(H<sub>2</sub>O) species is accompanied by the moderate energy loss of 9.08 kcal/mol; cluster models are shown in the Supporting Information (Figure S4).

## 4. CONCLUSIONS

Various experimental conditions with high Cu loading allow the formation of metal-oxide bi- or even polynuclear  $Cu_XO_Y$  species. Such binuclear species and their derivatives as participants of oxidative carbonylation of methanol were proposed by Saegusa et al. in 1970. Despite the fact that this scheme was proposed for liquid-phase reactions, it turned out that it is suitable for solid state chemistry in the CuNaX zeolite because it explains the zero order of  $O_2$  which acts through the formation of oxo-clusters. As we demonstrated herein above,  $>Cu(OCH_3)_2Cu<$  species can be obtained with a moderate

barrier from initial >Cu(OH)<sub>2</sub>Cu< moieties whose presence in the zeolites was shown. This barrier has a value close to the one for the CO attack over >Cu(OCH<sub>3</sub>)<sub>2</sub>Cu< in CuNaX (12.68 kcal/mol at the PBE/PAW level). This activation energy is close to the experimental barrier of 14.80 kcal/mol in CuY and 11.70 kcal/mol in CuZSM-5 and thus confirms the reaction scheme with the Cu(OCH<sub>3</sub>)<sub>2</sub>Cu at least at moderate and high Cu content in the CuNaX zeolite when such binuclear oxoclusters can be formed. Full catalytic cycle which can pass via either >Cu(OH)<sub>2</sub>Cu< moieties or >CuOCu< ones is evaluated.

At least two factors should be considered while applying this mechanism for other Cu-containing systems. The first one is the sufficiently high concentration of the Cu-oxospecies which can nucleate forming the structures with three or more Cu atoms as discussed recently.<sup>35</sup> This is more probable when the Cu content in the system is higher than the threshold value. Respective evaluations of the threshold concentration of Cu could be obtained based on the experimental data.<sup>25</sup> The second factor is the sufficient concentration of the binuclear clusters. The similar activity of the trinuclear Cu-oxospecies looks very likely but was not yet demonstrated. The role of the zeolite type can be determined by the stabilization of binuclear Cu-oxospecies closely to a pair of Al atoms inside large channels or cages of a possible zeolite.

## ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b10341.

Data about geometry parameters of the reactions involved in the discussion (PDF)

Movie of reaction  $\{Cu^{2+}(OH)_2Cu^{2+}\}Z + CH_3OH \rightarrow \{Cu^{2+}(OCH_3)(OH)Cu^{2+}\}Z + H_2O (AVI)$ Movie of reaction  $\{Cu^{2+}(OCH_3)(OH)Cu^{2+}\}Z + H_2O (AVI)$ 

 $CH_3OH \rightarrow \{Cu^{2+}(OCH_3)_2Cu^{2+}\}Z + H_2O (AVI)$ 

Movie of CO reaction with  $\{Cu(OCH_3)_2Cu\}Z$  in CuNaX (AVI)

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#### Notes

The authors declare no competing financial interest.

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