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## Cu(dppf) complexes can be synthesized from Cu-exchanged solids and enable a quantification of the Cu-accessibility by $^{31}\text{P}$ MAS NMR spectroscopy†

Elif Kaya, Daniel Dittmann, Maximilian Schmidt and Michael Dyballa \*

Herein, we apply three different copper-exchanged materials (Na-[Al]SBA-15, silica, Na-MCM-22) as hosts for a direct synthesis of Cu<sup>I</sup>(1,1'-bis(diphenylphosphino)ferrocene = dppf) complexes in cationic ion exchange position. Using  $^{31}\text{P}$  MAS NMR spectroscopy, we show that identical complexes as after ion exchange are generated if the solids are applied as reactants directly. The homogeneity of copper exchanges is evaluated by EDX spectroscopy. Both Cu<sup>I</sup> and Cu<sup>II</sup> result in the formation of complexes, thereby oxidizing dppf. Cu-particles were not reactive. Optimized conditions for a maximized complex formation are identified applying quantitative  $^{31}\text{P}$  MAS NMR spectroscopy and ICP-OES. Only accessible copper in cationic position of the solids forms the complexes. This enables a quantification of the amount of copper in mesopores vs. the total copper amount. Thus, besides a new synthesis of the complex a suitable method for quantitative elucidation of the location of copper cations is demonstrated herein.

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## Introduction

Most industrially relevant large-scale conversions are conducted catalytically. Usually, catalyst and reactant and/or products are thereby present in different phases. The support in such heterogeneous catalysis systems is usually a solid, as this can cost-efficiently be separated from the reaction mixture.<sup>1</sup> Typical solid catalysts are porous in order to enlarge the surface area for an efficient contact between reaction medium and catalyst. Exemplary supports are zeolites, metal-organic frameworks, and mesoporous materials.<sup>2–5</sup> The diameter of the pores determines the dimension of the species that can be hosted, which leads to shape-selectivity effects during catalysis.<sup>6</sup> The support must furthermore stabilize the catalytically active sites in the solid. Copper is a frequently investigated active site, and a variety of ways is applied to support active copper in form of a heterogeneous catalyst.

One form of stabilization is ion exchange into the cation position of bridging Si(OX)Al groups (with X = monovalent cation) that are found in silicoaluminates.<sup>2,7</sup> For catalyst synthesis, the Cu<sup>II</sup> ions are typically ion exchanged into porous silicoaluminates prior to the conversion of the hydrocarbons. This metal cations catalyse, for example, the selective oxidation

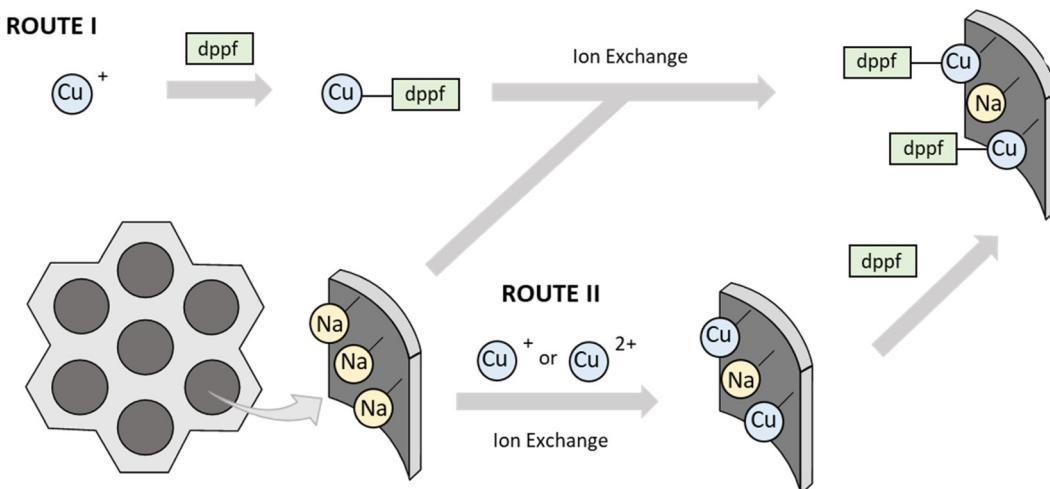
of methane and ethane by solid catalysts.<sup>8–14</sup> In contrast to heterogeneous catalysis, where ion exchange is applied frequently, this is a seldom investigated technique for metalorganic complex immobilization. Copper complexes can be (1) adsorbed onto the surface, (2) bound to the surface using it as ligand (referred to as surface organometallic chemistry, SOMC), (3) bound to the surface using a linker (molecular heterogeneous catalysts) and finally (4) charged complexes can be immobilized by ion exchange.<sup>15–18</sup> In the case of surface organometallic chemistry (SOMC), the complex formation takes place inside the pores with the surface as a ligand.<sup>15,16,19</sup> A potential application of SOMC is also the formation of defined nanoparticles<sup>20</sup> or the better understanding of processes occurring on often ill-defined heterogeneous catalysts.<sup>21,22</sup> Counter-intuitively also for covalently bound molecular heterogeneous catalysts a strong interaction with the surface can be present.<sup>15,16</sup> Such strong surface interactions impact on the catalytic performance of the materials. Complexes formed by methods of SOMC and likewise molecular heterogeneous catalysts form part of the surface or are covalently bound to the surface, respectively, and used for catalytic applications. As synthesis of complexes on a solid support means also removing these complexes in a second step, thus, only ion exchange and adsorption remain as industrially feasible pathways. Herein we synthesize complexes in ion exchange position of a solid support to enable their later release.

In catalytic reactions, interactions between copper and surface play an important role. For example, copper-based cat-

Institute of Technical Chemistry, University of Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany. E-mail: [michael.dyballa@itc.uni-stuttgart.de](mailto:michael.dyballa@itc.uni-stuttgart.de)

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**Scheme 1** Reaction scheme for visualizing the synthesis of  $\text{Cu}^{\text{I}}(\text{dppf})$  complexes in counter ion position synthesized by ion exchange (route I) or by reaction with  $\text{Cu}^{\text{I/II}}$  counter ions (route II).

alysts immobilized on  $\text{Al}_2\text{O}_3$  were shown to outperform their homogeneous counterparts in terms of selectivity in atom-transfer radical cyclizations.<sup>23</sup> Also location-dependent selectivity changes during catalysis by Rh-complexes in 1,2-additions were found, indicating that the location of the active site within the solid is important for the application as catalyst.<sup>24</sup> Unfortunately, if immobilized in porous materials, such complexes remain often in the outer parts of the catalysts.<sup>24,25</sup> The reason is the large diameter of the complexes and the strong interactions with the surface. Conclusively, it was also shown that ion exchange can lead to a very strong binding between  $\text{Cu}^{\text{I}}(\text{dppf})$  ( $\text{dppf} = 1,1'\text{-bis}(\text{diphenylphosphino})\text{ferrocene}$ ) complexes and surfaces.<sup>26</sup> This motif was previously identified to be interesting for electrochemical or anticancer applications.<sup>27,28</sup> In this favourable cases, metalorganic complexes bear a phosphorus nucleus ( $I = \frac{1}{2}$ ) which can be investigated quantitatively using  $^{31}\text{P}$  MAS NMR spectroscopy.<sup>29–34</sup> Finally it can be summarized that techniques to finely distribute such complexes in pores are of interest for the community. We herein thus also focus on how synthesized cationic complexes as counter ions in ion exchange position can be applied to characterize the support.

The typical way to place a cationic complex in counter ion position of an inorganic support is as follows: first the metalorganic complex, in this case consisting of  $\text{Cu}^{\text{I}}$  and dppf, is synthesized. Then the cationic complex is ion-exchanged into the solid. This procedure is visualized in route I in Scheme 1.<sup>26</sup> In this work, it shall thus be investigated whether a direct  $\text{Cu}^{\text{I}}(\text{dppf})$  complex formation in an ion exchanger is possible. This new, alternative route involves a direct synthesis of the copper-exchanged solid and then the dppf is reacted directly with the cations. A schematic presentation of this procedure is shown in route II in Scheme 1. To maximize the surface and the amount of ion exchange sites, the copper-exchanged aluminated  $[\text{Al}]\text{SBA-15}$  is used as support. This amorphous silicoaluminate has a large surface area and is

capable of a quantitative ion exchange inside its mesopores of usually 6 nm and above, which is large enough to host metalorganic complexes inside the pores.<sup>35</sup> Typical heterogeneous catalysts contain copper in its highest oxidation state ( $\text{Cu}^{\text{II}}$ ). It should be noted that this cation might form a variety of oxidizing copper-oxo species, for example  $\text{Cu}^{\text{II}}(\text{OH})$ , depending on the surface of the support and the conditions.<sup>36–40</sup> Thus it shall be tested if the complex formation occurs also with a precursor containing this cation. In route II the complex forms inside a porous solid. It is important to note that a complex formation is only possible if (1) the dppf has access to the copper and if (2) there is enough space available to form a complex.<sup>32</sup> A similar picture is observed if noble metals react with phosphines in inorganic complexes as triphenylphosphines and higher analogues. Also in this case a complex forms directly inside a mesopore that is large enough to host the resulting complex.<sup>41,42</sup> The sensitivity of synthesis route II for space and accessibility determined by the solid can be used as tool for characterization. In other words, the direct complex synthesis enables information about the location of the formerly present ions inside the solid. This makes route II interesting for quantitative elucidating the spatial distribution of ion exchanged copper.

## Results and discussion

### Physicochemical characterization of supports

In this work three different supports for copper are applied. The standard characterization of these materials is found in Table 1. For checking the presence of regular mesoporosity, small-angle X-ray powder diffraction patterns (XRD) were recorded (see Fig. S1 in the ESI†). Likewise, the crystalline zeolite Cu-MCM-22 was investigated by wide-angle XRD (see Fig. S2 in the ESI†). Both patterns agree with those reported in literature for SBA-15 and MCM-22.<sup>35,43,44</sup> Thus, we conclude



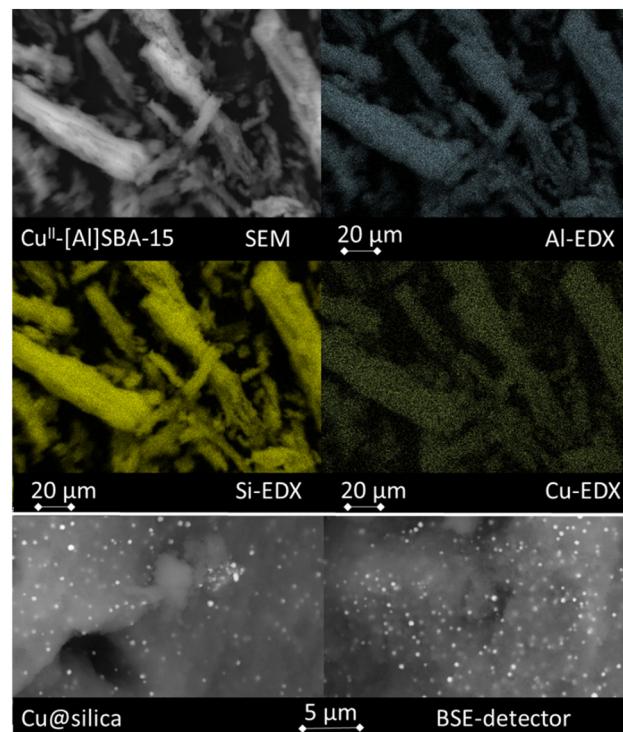
**Table 1** Physicochemical characterization data of the materials under study

Material	Si/Al <sup>a</sup>	Cu <sup>a</sup> [mmol g <sup>-1</sup> ]	BET surface <sup>b</sup> [m <sup>2</sup> g <sup>-1</sup> ]	V <sub>pore</sub> <sup>b</sup> [ml g <sup>-1</sup> ]	V <sub>micro</sub> <sup>b</sup> [ml g <sup>-1</sup> ]	V <sub>meso</sub> <sup>b</sup> [ml g <sup>-1</sup> ]	Si(OH) density <sup>c</sup> [mmol g <sup>-1</sup> ]	BAS content H-form <sup>d</sup> [mmol g <sup>-1</sup> ]
Cu-[Al]SBA-15	14	0.27	850	1.34	—	1.34	1.19	—
Cu@silica (A200)	>1700	1.26	185	0.24	—	0.24	0.39	—
Cu-MCM-22	19	1.02	630	0.79	0.18	0.61	0.18	0.17

<sup>a</sup> Determined by ICP-OES, error  $\pm 1$ . <sup>b</sup> From N<sub>2</sub> physisorption. <sup>c</sup> From <sup>1</sup>H MAS NMR after subtracting BAS density. <sup>d</sup> From <sup>1</sup>H MAS NMR after NH<sub>3</sub> adsorption.

that our materials have an intact meso- or micropore structure. The Cu-[Al]SBA-15 synthesized with a Si/Al ratio of 14 shows in comparison to literature a higher BET surface area.<sup>35</sup> This is a result of the large surface area of the siliceous parent SBA-15 (1160 m<sup>2</sup> g<sup>-1</sup>) before alumination. In accordance with literature,<sup>35</sup> no micropores were detected after alumination while a large mesopore volume V<sub>meso</sub> of 1.34 ml g<sup>-1</sup> was maintained. Thus, the support can not only host cations but also larger complexes within its mesopores. The silica A200 is a commercial, fumed silica support with negligible aluminum impurities, a BET surface area of 185 m<sup>2</sup> g<sup>-1</sup>, and secondary mesopores as described previously.<sup>45</sup> The state of aluminum in Cu-[Al]SBA-15 and Cu-MCM-22 was investigated by <sup>27</sup>Al MAS NMR spectroscopy (see Fig. S3 in the ESI†). The spectrum of Na-[Al]SBA-15 contains a single peak at a chemical shift of  $\delta_{27\text{Al}} = 53$  ppm. This peak is assigned to a tetrahedral aluminum within the framework and proves a maximum in well-exchangeable cationic sites.<sup>35</sup> In silica A200, we find no aluminum, neither by ICP-OES nor by <sup>27</sup>Al MAS NMR. The <sup>27</sup>Al MAS NMR spectrum of MCM-22 shows two peaks. A peak at  $\delta_{27\text{Al}} = 56$  ppm can again be assigned to aluminum in the framework. The peak at  $\delta_{27\text{Al}} = 0$  ppm indicates presence of extra-framework aluminum, which agrees well with previous findings on the aluminum state in this zeolite structure.<sup>44</sup>

The copper content of the materials was investigated by ICP-OES (see Table 1). Cu-[Al]SBA-15 has thus 0.27 mmol g<sup>-1</sup> copper cations. In addition to the directly evaluation of copper, we also cross-checked by ICP-OES that the Na-content of the material decreased after ion exchange, from 1.07 to 0.34 mmol g<sup>-1</sup> Na<sup>+</sup>. The larger decrease in mmol g<sup>-1</sup> is reasonable, as the 2-fold charged copper cations will exchange cations stoichiometrically. Furthermore, an incomplete ion exchange indicates that some Na-cations could not be exchanged. For a better understanding, despite Na-cations are still present, the resulting material is labeled Cu-[Al]SBA-15. The copper content of impregnated silica A200 (labeled Cu@silica) was 1.26 mmol g<sup>-1</sup> while the copper content of the ion-exchanged zeolite Cu-MCM-22 was 1.02 mmol g<sup>-1</sup>. SEM images of the support after ion exchange with copper are provided in Fig. 1. The elongated structures of SBA-15 particles are typical for this mesoporous material.<sup>35</sup> To prove a homogeneous alumination of the SBA-15 material and a homogeneous exchange with copper, EDX mappings were performed. The Si-EDX mapping resembles the structures of the SEM as this element constitutes the backbone of the material.



**Fig. 1** SEM and EDX screenings on copper-exchanged [Al]SBA-15 (top). Characteristic Cu-particles formed on Cu@silica are revealed by the BSE-detector.

The Al-EDX mapping shows identical structures, in lower intensity due to the lower abundance of aluminum. Absence of bright spots indicates absence of aluminum deposits and conclusively, a homogeneous alumination distribution was achieved by alumination, as expected from tests in previous work.<sup>35</sup> Also the Cu-EDX mapping resembles the structures from the SEM pictures. Again, an absence of bright spots indicates a homogeneous distribution of ion exchanged copper and absence of copper particles. As further proof of a homogeneous copper distribution, the backscattered electron detector (BSE-detector) was applied. No bright spots appeared and thus no copper particles formed. We conclude that the copper cations are homogeneously stabilized at ion exchange sites associated with aluminum and that no copper deposits were formed on Cu-[Al]SBA-15. Comparable figures of EDX on Cu@silica and Cu-MCM-22 are found in Fig. S4 and S5 in the



ESI.† Thereby, for Cu-MCM-22 a similar picture as for Cu-[Al] SBA-15 is observed as also here all copper is introduced by ion exchange. In contrast, bright spots occur on Cu@silica when using the BSE-detector. Thus, Cu-particles form on the silica surface as result of the impregnation and the absence of stabilizing ion exchange sites. These Cu-particles give characteristic bright spots in the BSE-detector and indicate a bad stabilization of cationic copper.<sup>46</sup>

The density of Si(OH) groups on the material surfaces was quantified applying <sup>1</sup>H MAS NMR spectroscopy. A density of 1.19 mmol g<sup>-1</sup> was found for Na-[Al]SBA-15 and agrees well with the 1.14 mmol g<sup>-1</sup> reported previously.<sup>45</sup> Thus, this surface can be considered polar, compared to the other two material surfaces. A lower Si(OH) density of 0.24 mmol g<sup>-1</sup> was found for silica A200, in agreement with a literature value of 0.39 mmol g<sup>-1</sup>.<sup>45</sup> The Si(OH) density of the zeolite H-MCM-22 is, with 0.18 mmol g<sup>-1</sup>, comparable. The higher Si(OH) density on [Al]SBA-15 results from the amorphous surface structure. In contrast, on the crystalline structure of MCM-22 or on the heat-treated fumed silica surface more Si(OH) groups formed siloxane bridges upon water release. MCM-22 and [Al]SBA-15 are aluminum-dotted, which results in Brønsted acid site (BAS) formation on the material H-form (after ion exchange).<sup>7</sup> Quantitative <sup>1</sup>H MAS NMR spectroscopy was thus applied to evaluate the acidity of the respective H-forms (see Fig. S6 in the ESI†). All materials show peaks of Si(OH) groups at a chemical shift of  $\delta_{1\text{H}} = 1.8$  ppm, while broad peaks at  $\sim 2.5$  ppm are assigned to interacting Si(OH) groups. The latter peak broadens for Na-[Al]SBA-15 after NH<sub>3</sub>-loading as a result of the heat treatment applied during NH<sub>3</sub>-desorption.<sup>35</sup> The H-MCM-22 shows peaks at 3.9 ppm and above, caused by Brønsted acidic bridging Si(OH)Al groups in free or disturbed state.<sup>47-49</sup> These groups react with NH<sub>3</sub> to form NH<sub>4</sub><sup>+</sup> which gives a quantifiable peak at 6.4 ppm.<sup>32,50</sup> The peak intensity indicates the accessibility of 0.17 mmol g<sup>-1</sup> BAS. This is low compared to the  $\sim 0.8$  mmol g<sup>-1</sup> BAS expected from the Si/Al ratio. However, this is reasonable due to the formation of EFAL, as it was indicated by <sup>27</sup>Al MAS NMR spectra (*vide supra*). This is in-line with previous findings for similar H-MCM-22.<sup>44</sup> Note that MCM-22 was copper ion exchanged from its Na-form and that all copper-bearing materials applied in this study for complex formation experiments were free of detectable BAS.

### Reaction of Cu-[Al]SBA-15 with dppf

The formed Cu<sup>I</sup>(dppf) complexes are in the following investigated using <sup>31</sup>P MAS NMR spectroscopy (see Fig. 2). The neat dppf results in a slim signal at a chemical shift of  $\delta_{31\text{P}} = -15$  ppm. From literature it is known that adsorption of phosphines at silicoalumina surfaces usually leads to downfield shifts of the peaks.<sup>24,41</sup> In seldom cases also for dppf, an additional peak at  $-9$  ppm, caused by dppf in surface interaction, is found herein. In Fig. 1, below the spectrum of neat dppf, the benchmark in form of an ion exchanged complex Cu-[Al]SBA-15, synthesized according to route I in Scheme 1, is shown. The spectrum contains a multitude of lines, since each resonance is split into  $2I + 1 = 4$  individual lines due to <sup>1</sup>J

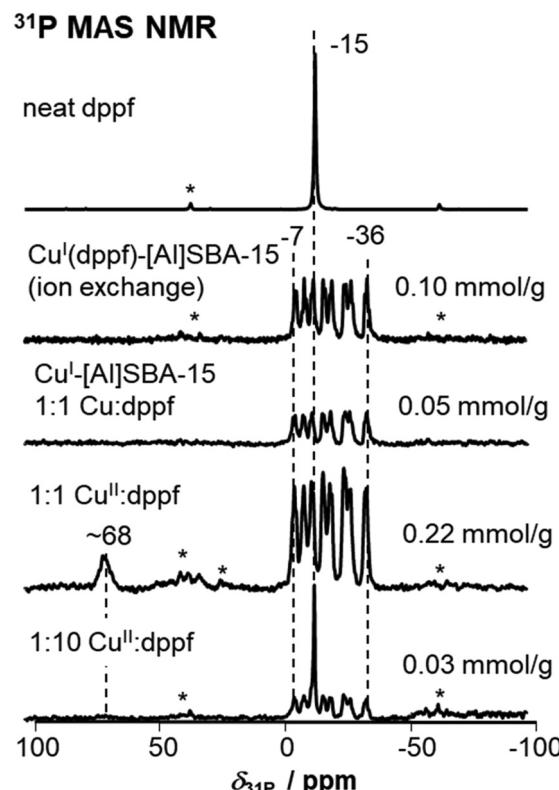


Fig. 2 <sup>31</sup>P MAS NMR spectra of (from top to bottom) neat dppf, Cu<sup>I</sup>(dppf) ion exchanged into Na-[Al]SBA-15, dppf reacted with Cu<sup>I</sup>-[Al]SBA-15, and dppf reacted with Cu<sup>II</sup>-[Al]SBA-15. The stoichiometry 1:1 and 1:10 indicates the molar ratios between copper and dppf, while the loading amounts in mmol g<sup>-1</sup> indicate the amount of Cu<sup>I</sup>(dppf) derived from quantitative <sup>31</sup>P MAS NMR spectroscopy.

coupling of the <sup>31</sup>P nuclei of the dppf ligand with the <sup>63</sup>Cu/<sup>65</sup>Cu ( $I = 3/2$ ) cations. We see that there are two different spins associated with the central copper and, due to a higher natural abundance of <sup>63</sup>Cu, the lines belonging to <sup>65</sup>Cu are less intense. Due to a  $\gamma(^{65}\text{Cu})/\gamma(^{63}\text{Cu}) = 1.07$  larger <sup>1</sup>J coupling, the lines belonging to <sup>65</sup>Cu complexes are furthermore found outside of the lines belonging to <sup>63</sup>Cu complexes.<sup>51</sup> As previously shown, both <sup>31</sup>P nuclei present in the dppf become inequivalent upon ion exchange.<sup>26</sup> Thus, a characteristic splitting into 8 overlapping lines is observed (4 lines for each <sup>31</sup>P nucleus in dppf). The outer lines of the coupling pattern are found at chemical shifts of about  $\delta_{31\text{P}} = -7$  and  $-37$  ppm, respectively. This supports the conclusion, that the herein investigated complexes are cations in ion exchange position and agrees with literature findings, <sup>1</sup>H-<sup>31</sup>P FSLG HETCOR spectra provided herein (*vide infra*), and the spectra of similar ion exchanged materials provided previously.<sup>26</sup> Next, the reaction of Cu<sup>I</sup>-[Al]SBA-15 with dppf was investigated. For the reaction, a 1:1 stoichiometry between Cu<sup>I</sup> and dppf was applied. An identical spectrum as for the benchmark is received and it will later become important to remark that no additional peaks are found at higher or lower field, respectively. This clarifies, that exclusively Cu<sup>I</sup>(dppf) complexes, but no by-pro-



ducts were formed upon reaction of  $\text{Cu}^{\text{I}}$  in cationic ion exchange position with dppf. The complexes can be quantified with an external standard applying  $^{31}\text{P}$  MAS NMR spectroscopy. This results in amounts of 0.10 to 0.05 mmol g<sup>-1</sup> complexes within the mesoporous [Al]SBA-15 support after ion exchange of reaction with  $\text{Cu}^{\text{I}}$ , respectively (see also quantitative indications in Fig. 2).

In a next step, the reaction of dppf with  $\text{Cu}^{\text{II}}$  is addressed. This formation of  $\text{Cu}^{\text{I}}(\text{dppf})$  requires a reduction of the  $\text{Cu}^{\text{II}}$  cations present. The species responsible for oxygen-transfer could be a  $\text{Cu}(\text{OH})^+$  unit that forms upon ion exchange in aqueous media to balance the charge of  $\text{Cu}^{\text{II}}$  on an ion exchange site with single negative charge. Furthermore, similar sites were identified by XAS in copper-exchanged zeolite catalysts.<sup>39,52</sup> Additional peaks at higher chemical shift at  $\delta_{31\text{P}}$  of  $\sim 68$  ppm appear. Typically, peaks at such low-field chemical shift of  $\delta_{31\text{P}} \approx 68$  ppm originate from the oxidation of phosphines to the corresponding phosphine oxide, which is supported by previous work on a variety of phosphines.<sup>24,53-56</sup> Unfortunately, it was herein not possible to isolate this oxidation product and to further characterize it. As this happens only in case of  $\text{Cu}^{\text{II}}$  presence, oxidation due to oxygen impurities during sample handling can be excluded. Also a previous calcination at 823 K after copper ion exchange of  $\text{Cu}-[\text{Al}]$  SBA-15 leads to identical  $^{31}\text{P}$  MAS NMR spectra. This excludes that any surface impurity caused this peak. It is thus associated with dppf oxidation to the corresponding oxide. The  $^{31}\text{P}$  MAS NMR spectrum of the resulting  $\text{Cu}^{\text{I}}(\text{dppf})$  is identical to the spectra recorded after ion exchange or reaction with  $\text{Cu}^{\text{I}}$  (*vide supra*). In accordance with the reactivity of other phosphines we conclude that herein the dppf reduces the  $\text{Cu}^{\text{II}}$  to  $\text{Cu}^{\text{I}}$ . The latter subsequently forms a complex identical to those received after ion exchange of  $\text{Cu}^{\text{I}}(\text{dppf})$  into the material or after reaction with  $\text{Cu}^{\text{I}}-[\text{Al}]$  SBA-15. Quantification shows that a reaction in a 1:1 stoichiometry between  $\text{Cu}^{\text{II}}$  and dppf leads to an amount of 0.22 mmol g<sup>-1</sup>  $\text{Cu}^{\text{I}}(\text{dppf})$  complex formed. This is a reasonable quantity with respect to the 0.27 mmol g<sup>-1</sup> copper initially present on the  $\text{Cu}-[\text{Al}]$  SBA-15 material. Note that not all copper has reacted to form complexes. Furthermore, the reaction with dppf was also tested in absence of solvent to check if solvent is necessary. This was done according to the solid state loading approach previously applied for loading a variety of other phosphines and phosphine oxides on solids.<sup>35,42,57-59</sup> Briefly, the  $\text{Cu}-[\text{Al}]$  SBA-15 solid was mixed with neat, solid dppf and the mixture was heated over 2 h with a heating rate of 1 K min<sup>-1</sup> at 333 K under  $\text{N}_2$ . However, on  $\text{Cu}-[\text{Al}]$  SBA-15 no  $\text{Cu}^{\text{I}}(\text{dppf})$  complex formed and only the slim  $^{31}\text{P}$  MAS NMR peak associated with the neat dppf was found. We conclude that the formation of  $\text{Cu}^{\text{I}}(\text{dppf})$  complexes from cationic copper requires a solvent. It is not relevant if the solvent is acetonitrile or ethanol, however, a larger quantity of the complex forms if ethanol is applied.

$^1\text{H}$ - $^{31}\text{P}$  FSLG HETCOR was performed to further clarify the identity of complexes synthesized by the two routes indicated in Scheme 1. For the 2D spectra in Fig. 3 it is immediately noted that similar correlations exist for both synthesis routes I

### $^1\text{H}$ - $^{31}\text{P}$ FSLG HETCOR

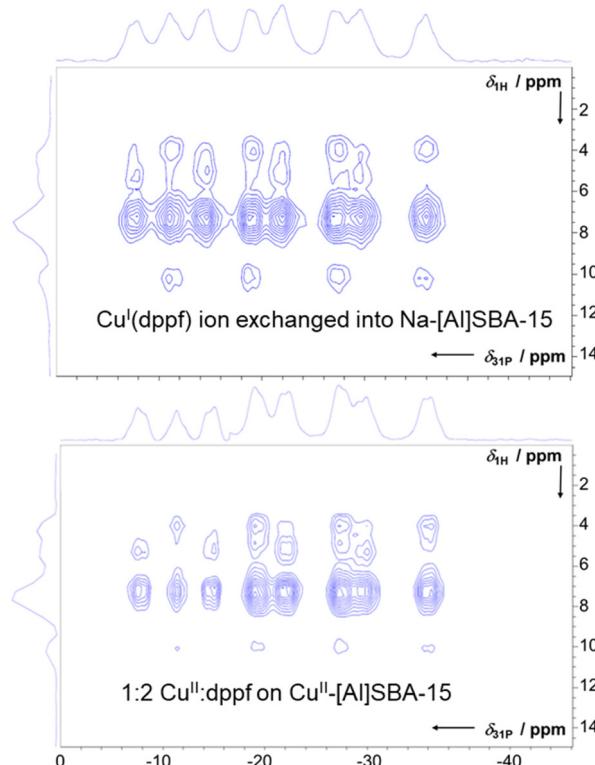


Fig. 3  $^1\text{H}$ - $^{31}\text{P}$  FSLG HETCOR spectra on (top)  $\text{Na}-[\text{Al}]$  SBA-15 after ion exchange of  $\text{Cu}^{\text{I}}(\text{dppf})$  complexes and (bottom) after reaction of dppf with  $\text{Cu}^{\text{II}}-[\text{Al}]$  SBA-15 with indicated loading stoichiometry 1:2  $\text{Cu}$  : dppf.

and II. Correlation peaks at  $\delta_{1\text{H}} \approx 4, 5$  and 7 ppm are associated with the protons of the cyclopentadienyl and phenyl rings, respectively. The splitting of the cyclopentadienyl ring protons into two individual signals with 4 lines each is caused by magnetic inequivalence of the  $^{31}\text{P}$  nuclei of dppf upon ion exchange (*vide supra* and elsewhere<sup>26</sup>). As result,  $^1\text{J}({}^{63/65}\text{Cu}, {}^{31}\text{P})$  scalar couplings of 1200 and 1340 Hz are found, in agreement with previous findings.<sup>26</sup> A proton at  $\delta_{1\text{H}} \approx 10$  ppm is found in both 2D spectra and indicates an interaction between complexes and  $\text{Si}(\text{OH})$  on the surface. Thus, it was verified that identical structures have formed within mesoporous [Al] SBA-15 also after reaction of the copper-exchanged  $\text{Cu}-[\text{Al}]$  SBA-15 with dppf. This is the first proof that both route I and route II indicated in Scheme 1 are applicable to generate cationic  $\text{Cu}^{\text{I}}(\text{dppf})$  complexes.

### Quantitative study of the complex formation

Quantitative  $^{31}\text{P}$  MAS NMR spectroscopy applied on (neat) metalorganic complexes is hampered by usually long  $T_1$ -times.<sup>29-31,33,34,51,60</sup> However, if the phosphine is tightly bound to the surface the  $T_1$ -relaxation of the  $^{31}\text{P}$  nuclei is significantly decreased.<sup>33,42</sup> In order to approximate the  $T_1$ -time we performed a delay time variation (see Fig. S7 and S8 in the ES<sup>†</sup>). For the neat  $\text{Cu}^{\text{I}}(\text{dppf})$  complex, an increasing  $^{31}\text{P}$  signal intensity is found for increasing delay time between scans from 5 to



240 s. In other words, even 240 s delay yields no quantitative spectrum of the pure complex under our measurement conditions (see Fig. S7 in the ESI†). Also for neat dppf, the peak intensity at  $\delta_{31\text{P}} = -15$  ppm is not constant after 240 s delay time. However, the relaxation behavior changes dramatically if the complex is ion exchanged into the support. In our case, a delay between scans of 10 s or longer is sufficient, to yield spectra of similar intensity (see Fig. S8 in the ESI†). The shorter  $T_1$ -time is rationalized by the strong interaction between complex and surface (see cross-peak with  $\text{Si}(\text{OH}) \delta_{1\text{H}} \approx 10$  ppm in Fig. 3) and the close proximity to  $^{27}\text{Al}$  in the ion exchange position. Conclusively, delays above 10 s were quantitative. However, to include a safety threshold, herein 60 s delay were applied for quantitative evaluation of the  $^{31}\text{P}$  spectra. We furthermore verified that for each individual sample that indeed quantitative spectra were gained. Therefore, a second measurement with a delay time of 40 s was performed. Only if peak intensities after applying 40 and 60 s delay were identical, a quantification was performed. It is fair to note that this was the case for all herein investigated complexes. To reveal potential pitfalls, it is worth showing  $^1\text{H}$  MAS NMR spectra of materials (see Fig. S9 in the ESI†). Peaks of ethanol appear at  $\delta_{1\text{H}} = 3.6$  and 1.2 ppm and indicate its adsorption on the surface. The peak intensity, and thus the quantity of adsorbed ethanol, varies from sample to sample. However, for a quantification the dry material mass needs to be determined. This makes a treatment in vacuum, to remove adsorbed ethanol prior a mass determination, necessary. The successful ethanol removal can, in reverse, be checked by  $^1\text{H}$  MAS NMR.

In Fig. 2 it was found that the stoichiometry between copper and dppf ligand impacts the amount of finally formed complexes. Because, counter-intuitively, fewer  $\text{Cu}^{\text{I}}(\text{dppf})$  complexes ( $0.03 \text{ mmol g}^{-1}$ ) were formed after reaction in 1 : 10 Cu : dppf stoichiometry than in 1 : 1 stoichiometry ( $0.22 \text{ mmol g}^{-1}$ ). Furthermore, a strong and slim peak at  $\delta_{31\text{P}} = -15$  ppm is present after probing in 1 : 10 Cu : dppf stoichiometry. This peak belongs to neat dppf, which indicates that previously formed  $\text{Cu}^{\text{I}}(\text{dppf})$  complex decomposed over time. To further investigate this decomposition,  $^{31}\text{P}$  MAS NMR measurements on the sample (1 : 10 stoichiometry) were performed over a period of several days (see Fig. 4). Thereby, a decreasing intensity of the peaks associated with the  $\text{Cu}^{\text{I}}(\text{dppf})$  complex and in parallel an increasing intensity of the peak of neat dppf at  $\delta_{31\text{P}} = -15$  ppm is observed. This supports a decomposition of the initially formed  $\text{Cu}^{\text{I}}(\text{dppf})$  complexes within the time span of 43 h. Such a decomposition is only observed, if dppf is used in large excess. Conversely, in case of a 1 : 1 stoichiometry, samples are often stable over days without loss in signal intensity and thus complex decomposition. Of course, this requires storage in a closed, air-free container. The stability of the complex in this case proves that the dppf is stable against oxidation over time and supports that it is only oxidized in presence of  $\text{Cu}^{\text{II}}$  cations (*vide supra*).

Next, optimized formation conditions for a maximized  $\text{Cu}^{\text{I}}(\text{dppf})$  complex formation were identified. First the stoichiometry between dppf and  $\text{Cu}^{\text{II}}$  ions during reaction was

### $^{31}\text{P}$ MAS NMR

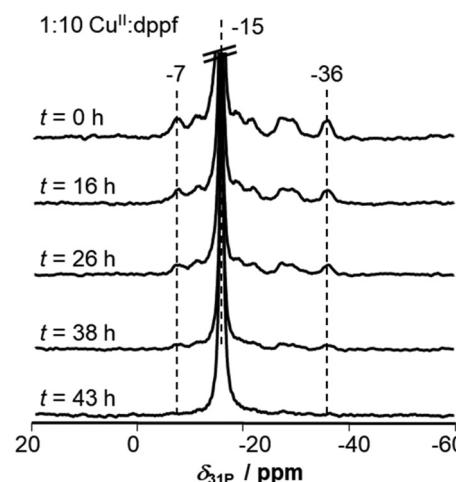
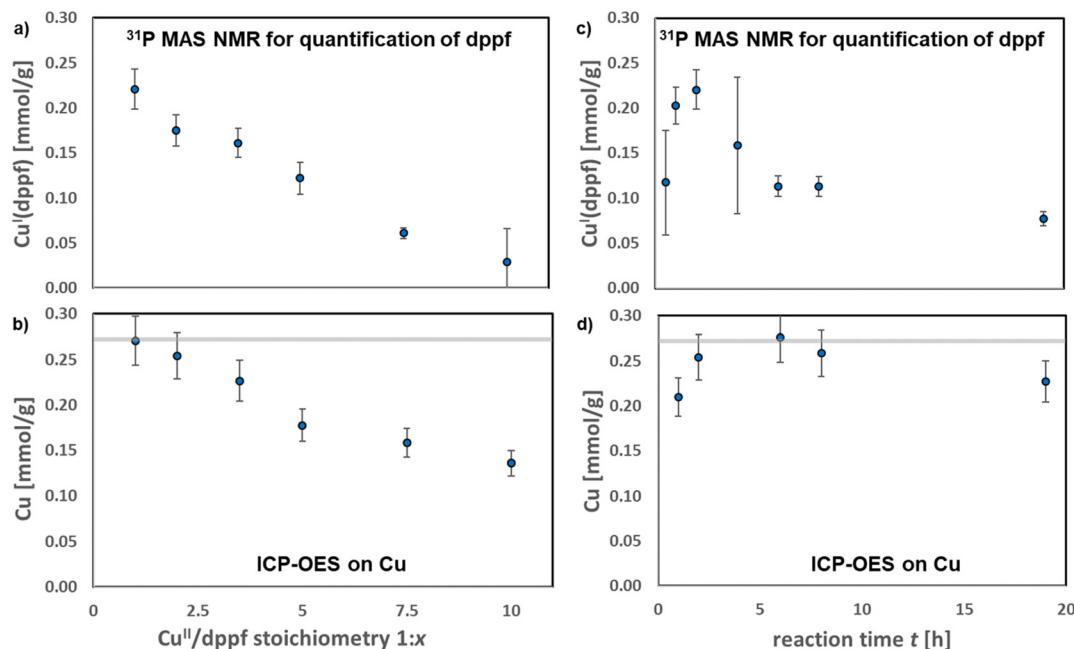


Fig. 4  $^{31}\text{P}$  MAS NMR after different storage time  $t$  on a  $\text{Cu}^{\text{II}}\text{--[Al]SBA-15}$  sample after reaction with dppf in 1 : 10 stoichiometry. The intensity of the peak at  $-15$  ppm increases over time.

addressed (see Fig. 5a). A 1 : 1 stoichiometry between  $\text{Cu}^{\text{II}}$  and dppf results in the largest complex amount formed. Conversely, more dppf applied during reaction leads to a strong decrease of the number of complexes finally observed. Apart from complex decomposition, proven in Fig. 4, leaching of copper cations could potentially be a reason for a decreased complex amount. The copper-content of the samples after loading was thus cross-checked by ICP-OES (see Fig. 5(b)). After 2 h reaction time in a 1 : 1 stoichiometry the initial copper content is maintained ( $0.27 \text{ mmol g}^{-1}$ ). As, according to  $^{31}\text{P}$  MAS NMR spectroscopy,  $0.22 \text{ mmol g}^{-1}$  complex was formed, it is calculated that 81% of the initially available copper reacted to  $\text{Cu}^{\text{I}}(\text{dppf})$  complexes. This shows that the present copper cations reacted nearly quantitatively to the complex. The 19% discrepancy is rationalized by inaccessible copper cations, not reachable by dppf for a reaction. Potentially, also the space available around these cations inside the SBA-15 pores is insufficient for a  $\text{Cu}^{\text{I}}(\text{dppf})$  complex formation. If larger dppf quantities are used for the reaction, a strong decrease of the copper-content of the samples is found by the ICP-OES measurements. This decrease is supported by  $^{31}\text{P}$  MAS NMR spectroscopy. Thus, leaching of the copper in higher  $\text{Cu}^{\text{II}} : \text{dppf}$  stoichiometry is the reason for a lower quantity of cationic  $\text{Cu}^{\text{I}}(\text{dppf})$  complexes observed.

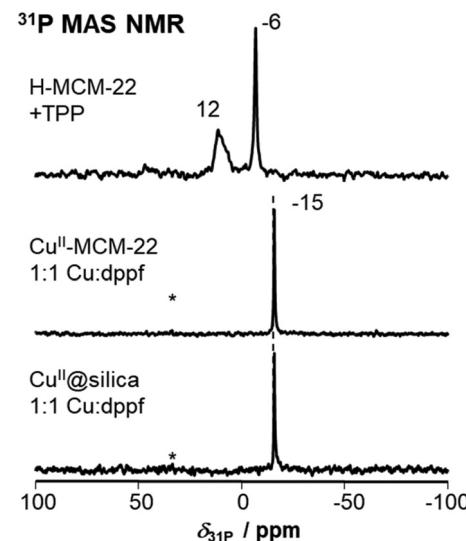
Also the reaction time influences the quantified amount of  $\text{Cu}^{\text{I}}(\text{dppf})$  complexes (see Fig. 5(c) and (d)). For a maximized amount of complexes an intermediate reaction time of 1 to 2 h is beneficial. After longer reaction times, the quantity of complexes decreases remarkably. The reason for the lower quantity of  $\text{Cu}^{\text{I}}(\text{dppf})$  formed is not leaching, as clarified by the ICP-OES measurements and a maintained Cu-content. As discussed previously for larger dppf quantities (see Fig. 4), the initially formed complexes decompose. Summarizing, in order to maximize the amount of  $\text{Cu}^{\text{I}}(\text{dppf})$  complexes, a  $\text{Cu}^{\text{II}}/\text{dppf}$



**Fig. 5** Quantitative screening of  $\text{Cu}^{\text{I}}(\text{dppf})$  complex formation conditions. In the first column a varied  $\text{Cu}^{\text{II}}/\text{dppf}$  stoichiometry after 2 h reaction time was investigated by (a)  $^{31}\text{P}$  MAS NMR and (b) by ICP-OES on the Cu-content. On the right hand side, a reaction time screening in a 1:1  $\text{Cu}^{\text{II}}/\text{dppf}$  stoichiometry was investigated by (c)  $^{31}\text{P}$  MAS NMR and (d) by ICP-OES on the Cu-content. For the evaluation of  $^{31}\text{P}$  MAS NMR spectra a minimum error of  $\pm 10\%$  was assumed, even if smaller errors were obtained. Likewise, for ICP-OES measurements an error of  $\pm 10\%$  is indicated. The initial Cu-content of the samples prior reaction is indicated by a grey bar.

stoichiometry of 1:1 and a reaction time of 2 h is suggested. These are the conditions that should be applied if the copper cation accessibility is investigated using dppf.

Now the accessibility of copper cations in various supports is compared using dppf. The until here applied solid,  $\text{Cu}-[\text{Al}]$  SBA-15, contains large mesopores of 6.7 nm diameter. However zeolites, frequently used heterogeneous catalysts, have micropores with a diameter far below 1 nm.<sup>2,43</sup> As the reaction with dppf probes the available copper cations almost quantitatively, this reaction is suited to track accessible copper cations on zeolite surfaces. In particular Cu-MCM-22 (MW structure) is applied herein, as this material was recently shown to be active in the oxidation of methane to methanol.<sup>13</sup> The amount of external ion exchange sites was investigated using triphenylphosphine, which was applied on the H-form of the material according to literature.<sup>44</sup> In the spectrum in Fig. 6, top, a broad peak at 12 ppm indicates the formation of protonated TPP ( $<0.01 \text{ mmol g}^{-1}$ ). Thus, only negligible amounts of ion exchange sites are located on the external surface. The copper cations introduced by ion exchange will thus be located nearly exclusively inside the micropores or pore mouths. There, they should not be accessible for the large dppf ligand. Indeed, the  $^{31}\text{P}$  MAS NMR spectrum (see Fig. 6, middle) after reaction with dppf shows only the peak of neat dppf at  $\delta_{^{31}\text{P}} = -15 \text{ ppm}$ . No peaks of cationic  $\text{Cu}^{\text{I}}(\text{dppf})$  complexes appear and thus no such complexes formed. It is concluded that both methods, loading with dppf and TPP probe molecules, lead to similar results. Namely, the copper



**Fig. 6**  $^{31}\text{P}$  MAS NMR spectra after TPP loading on H-MCM-22 (top) and after reaction of  $\text{Cu}^{\text{II}}\text{-MCM-22}$  (middle) and  $\text{Cu}^{\text{II}}\text{@silica}$  (bottom) with dppf.

cations are located exclusively in MCM-22 micropores. Finally, the question arises if dppf is also reacting with Cu-particles, commonly observed side products of a copper exchange into zeolites.<sup>46</sup> Thus,  $\text{Cu}@\text{silica}$  synthesized by impregnation was also investigated in the reaction with dppf (see Fig. 6, bottom).



This material contains exclusively Cu-particles, as verified by the BSE detector in Fig. 1. After reaction with dppf, the  $^{31}\text{P}$  MAS NMR spectrum contains only the slim peak of neat dppf and no peaks associated with formed complexes. Thus, the quantitative evaluation of formed  $\text{Cu}^{\text{I}}(\text{dppf})$  complexes is a valuable tool to quantify the accessibility of copper cations. The reaction does not occur if the copper is not accessible and the formation of  $\text{Cu}^{\text{I}}(\text{dppf})$  complexes is not observed if the copper is not in cationic position.

## Conclusion

Herein a new pathway to synthesize  $\text{Cu}^{\text{I}}(\text{dppf})$  complexes (dppf = 1,1'-bis(diphenylphosphino)ferrocene) as cations within mesoporous  $[\text{Al}]\text{SBA-15}$  is introduced. Therefore, ion exchanged copper cations were directly reacted with dppf. These complexes can later be released from the solid by ion exchange to enable their industrial production.  $^{31}\text{P}$  MAS NMR proves the identity of  $\text{Cu}^{\text{I}}(\text{dppf})$  complexes after conventional ion exchange and after reaction with the solid. This is supported by  $^1\text{H}$ - $^{31}\text{P}$  FSLG HETCOR measurements.  $\text{Cu}^{\text{II}}$  cations are *in situ* reduced to  $\text{Cu}^{\text{I}}$  upon oxidation of dppf to the respective phosphine oxide. Maximized amounts of  $\text{Cu}^{\text{I}}(\text{dppf})$  are received if a  $\text{Cu}^{\text{II}}/\text{dppf}$  stoichiometry of 1 : 1 and a reaction time of 2 h is applied during synthesis. On our  $\text{Cu}-[\text{Al}]$  SBA-15 material 81% of the initially present copper cations formed the complex. Copper leaching can occur if dppf is applied in too high stoichiometry. Also a decomposition of  $\text{Cu}^{\text{I}}(\text{dppf})$  complexes to dppf over multiple hours is observed if unfavorable reaction conditions are applied. Cu-particles or copper located inside zeolite micropores does not contribute to the  $\text{Cu}^{\text{I}}(\text{dppf})$  complex formation. Thus, the quantitative evaluation of peaks caused by *in situ* formed  $\text{Cu}^{\text{I}}(\text{dppf})$  complexes is a potential tool to evaluate the amount of accessible cationic copper. The method introduced herein is thus not only of potential use for synthesizing complexes, but also for determining the accessibility of supported copper cations.

## Experimental

### Material preparation

The synthesis of  $[\text{Al}]\text{SBA-15}$  by synthesis of SBA-15 and subsequent alumination was performed according to literature.<sup>4,35</sup> Briefly, Pluronic® P123 (16.0 g, 2.76 mmol) was dissolved in a solution of demineralized water (520 mL) and 37 wt% hydrochloric acid (80 mL) at room temperature. After addition of tetraethyl orthosilicate (36.6 mL, 165 mmol) the solution was stirred at 318 K for 7.5 h and aged at 353 K for 15.5 h under static conditions. For the synthesis of  $\text{Na}-[\text{Al}]\text{SBA-15}$ , sodium aluminate (0.12 g) was added to calcined SBA-15 (1.0 g) in water (200 mL) and the reaction mixture was stirred at room temperature for 16 h.  $\text{Na}-[\text{Al}]\text{SBA-15}$  was obtained after calcination at 823 K for 5 h.

For the copper ion exchange, 0.45 mmol metal salt (copper (i) chloride for  $\text{Cu}^{\text{I}}-[\text{Al}]\text{SBA-15}$  or copper(ii) acetate for  $\text{Cu}^{\text{II}}-[\text{Al}]\text{SBA-15}$ ) was diluted in 100 mL water, then 1 g  $\text{Na}-[\text{Al}]\text{SBA-15}$  was added and stirred at room temperature for 24 h. After ion exchange,  $\text{Cu}-[\text{Al}]\text{SBA-15}$  was thoroughly washed. MCM-22 was synthesized according to literature<sup>61</sup> and subsequently calcined at 813 K for 48 h. It was 2-fold ion exchanged with 1 M aqueous  $\text{NaNO}_3$  solution and washed nitrate-free before copper ion exchange was performed, as described above. Fumed silica A200 was purchased from Evonik Industries AG, Germany.  $\text{Cu}@\text{silica}$  was obtained by wet impregnation (0.045 mmol metal salt, 10 mL demin. Water, 1 g A200) and calcined at 823 K for 5 h. The reaction with 1,1'-bis(diphenylphosphino)ferrocene (dppf) was performed by stirring a reaction mixture of  $\text{Cu}-[\text{Al}]\text{SBA-15}$  (0.075 g) and dppf (0.3–3.0 mmol) at room temperature in ethanol or acetonitrile (50 mL) for  $x$  h ( $x = 0.5$  to 24 h, if not otherwise stated 2 h). After measurement, the weight of the solid was determined after desorbing solvent molecules (ethanol) for 6 h at 333 K in vacuum. A complete removal of the solvent checked by  $^1\text{H}$  MAS NMR spectroscopy. The reaction of dppf with  $\text{Cu}@\text{silica}$  and  $\text{Cu}-\text{MCM-22}$  was performed analogously. Also a solid state approach for reaction between dppf and copper was applied, by mixing the respective Cu-bearing solid with neat dppf in a 1 : 2 stoichiometry ( $\text{Cu} : \text{dppf}$ ) and heating it 2 h at 333 K (heating rate of 1 K min<sup>-1</sup>) under  $\text{N}_2$ .

### Characterization

Chemical analysis was conducted using inductively coupled plasma optical emission spectrometry (ICP-OES) on an IRIS Advantage instrument. The structure of the samples was investigated by X-ray diffraction (XRD). Therefore, a Bruker D8 diffractometer equipped with an X-ray tube for  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) was used. The XRD patterns were recorded in a  $2\theta$  range of 0.7–5° for mesoporous and 5–55° for microporous samples. Nitrogen physisorption was performed at 77 K using a Quantachrome Autosorb 3B. Prior to measurements, the samples were activated at 623 K for 16 h. The surface of materials was evaluated using the Brunauer–Emmett–Teller (BET) equation. The micropore volume was determined according to the  $V$ - $t$  method (deBoer) and the mesopore volume was determined as difference to the total pore volume of  $p/p_0 = 0.99$ . SEM images using SE and BSE-detectors were recorded on a Tescan Vega3 equipped with an energy dispersive X-ray spectroscopy (EDX) detector using APEX software for evaluation.

$^1\text{H}$ ,  $^{27}\text{Al}$ , and  $^{31}\text{P}$  MAS NMR spectroscopy was performed on a Bruker Avance III 400 WB spectrometer with a magnetic field of 9.4 T. The resonance frequencies were 400.1 MHz ( $^1\text{H}$ ), 104.2 MHz ( $^{27}\text{Al}$ ), and 161.9 MHz ( $^{31}\text{P}$ ).  $^1\text{H}$  and  $^{31}\text{P}$  measurements were performed after  $\pi/2$  excitation, whereas for qualitative  $^{27}\text{Al}$   $\pi/8$  excitation was used. The samples for the  $^{27}\text{Al}$  MAS NMR measurements were in a fully hydrated state. 4 mm rotor spinning rates of 8 kHz were applied, if not stated otherwise. Typical recycle delays were 5 s (qualitative  $^1\text{H}$ ), 20 s (quantitative  $^1\text{H}$ ), 5 s ( $^{31}\text{P}$  CP), and 0.5 s ( $^{27}\text{Al}$ ).  $^{31}\text{P}$  MAS NMR



direct excitation measurements were recorded using high-power proton decoupling (HPDEC) with recycle delays of 40 and 60 s, if not stated otherwise. For quantification of  $^{31}\text{P}$  MAS NMR spectra, hydrated VPI-5 was used as an external standard, as described elsewhere.<sup>62</sup>  $^{1}\text{H}$ - $^{31}\text{P}$  FSLG HETCOR spectra were collected at 11 kHz spinning rate with a repetition time of 5 s. The indirect ( $^{1}\text{H}$ ) dimension was referenced using the phenyl protons as internal standard.

For a determination of the BAS density, an ammonia loading with 60 mbar ammonia gas (Westfalen, Germany) was performed through a vacuum line. To desorb excess ammonia, a subsequent evacuation at 453 K for 2 h was performed. Activation of the samples before quantitative  $^{1}\text{H}$  measurements was done at elevated temperature in vacuum, with a heating rate 1 K min $^{-1}$  applying 723 K for 12 h. For quantification of  $^{1}\text{H}$  MAS NMR spectra a dehydrated zeolite H,Na-Y (35% ammonium exchanged) was used as an external standard. The amount of external ion exchange sites was performed after activating the  $\text{NH}_4$ -form of the respective zeolites and evaluating the triphenylphosphine (TPP) loaded material by quantitative  $^{31}\text{P}$  MAS NMR spectroscopy as described elsewhere.<sup>44</sup> Briefly, under  $\text{N}_2$  the material was combined with pre-calculated amounts of TPP, then 0.8–1 mL of dried dichloromethane (DCM) was added, before the mixture was stirred 1 h and the vessel was finally opened under  $\text{N}_2$  until complete evaporation of the solvent. NMR spectra were evaluated using TopSpin and Dmfit.<sup>63</sup>

## Conflicts of interest

There is nothing to declare.

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