Communication

Rapid Ammonia Carriers for SCR Systems Using MOFs [M₂(adc)₂(dabco)] (M = Co, Ni, Cu, Zn)

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Abstract: Ammonia is one of the most common reductants for the automotive selective catalytic reduction (SCR) system owing to its high NO₂ reduction (deNO_x) efficiency. However, ammonia carriers for the SCR system have sluggishly evolved to achieve rapid ammonia dosing. In this study, the MOFs [M₂(adc)₂(dabco)] (M = Co, Ni, Cu, Zn) were synthesized and characterized as ammonia carriers. Among the four obtained MOFs, Ni₂(adc)₂(dabco) possessed the highest surface area, 772 m²/g, highest ammonia uptake capacity, 12.1 mmol/g, and stable cyclic adsorption-desorption performance. All the obtained MOFs demonstrated physisorption of ammonia and rapid kinetics of ammonia adsorption and desorption. Compared with halide ammonia carrier MgCl₂, the obtained MOFs showed four times faster adsorption kinetics to reach 90% of the ammonia uptake capacity. For the ammonia desorption, the Ni₂(adc)₂(dabco) provided 6 mmol/g ammonia dosing when temperature reached 125 °C in the first 10 min, which was six times of the ammonia dosing from Mg(NH₃)₆Cl₂. The results offer a solution to shorten the buffering time for ammonia dosing in the SCR system.

Keywords: SCR; ammonia; MOFs; kinetics; deNO_x

1. Introduction

Nitrogen oxides (NO_x) are regarded as one of the most harmful air pollutants, resulting in a series of environmental problems such as acid rain, smog, and global warming, and severe health impact to human beings [1,2]. Millions of premature deaths are related to NO_x pollution worldwide [3,4]. Therefore, NO_x reduction (deNO_x) has drawn extensive attention. For example, the NO_x emission standards have become increasingly stringent as vehicle exhaust is one of the main sources of NO_x emission [5]. The selective catalytic reduction (SCR) system, one of the most common approaches to eliminate NO_x from vehicle exhaust onboard, typically uses ammonia (NH₃) as the reductant to react with NO_x and produce harmless H₂O and N₂ [6,7]. To meet the elevated requirements of the emission standards, the NO_x conversion efficiency of the SCR system was enhanced in many aspects, including the reductant system, the catalyst, the dosing control system, etc., among which the reductant system is essential, yet sluggishly evolved [1,8–10].

Ammonia is the most common reductant due to its high NO_x conversion efficiency and fewer side reactions compared with hydro-carbon reductants [11,12]. However, the toxic and corrosive nature of ammonia imposes challenges in achieving safe and stable ammonia storage onboard for SCR systems [13]. Instead, urea solution (Adblue®, or diesel exhaust fluid (DEF)), an indirect ammonia carrier, has been widely used in SCR systems for over 30 years [7,14,15]. With the heat from the exhaust, urea hydrolyzes and releases ammonia and carbon dioxide (CO₂). However, as the temperature of the exhaust goes lower, the inadequacy of urea hydrolysis could result in insufficient ammonia dosing and catalyst damage by urea residuals [16]. Moreover, at a low temperature (below −11 °C), there is

the risk to freeze the urea solution and impede the urea-injection to the SCR system [17]. Therefore, the solid SCR system, using alkaline earth metal halides (AEMH, such as SrCl_2 , MgCl_2) as ammonia carriers, emerges as a new trend for automotive NO_x abatement [18–20]. The ammonia is stored in AEMH in the form of metal ammine complexes [21,22]. By heating the AEMH- NH_3 complex, direct ammonia dosing can be achieved, which has high NO_x conversion efficiency and no residual risk [23,24]. One big challenge for AEMH as ammonia carriers in the SCR system is the ammonia dosing kinetics. The AEMH- NH_3 complex is required to reach the decomposition temperature to release ammonia. In practical cases, with cold engine start and urban driving, there could be NO_x escaping before the sufficient ammonia dosing. In the industry, an extra start-up unit is added to shorten the ammonia buffer time, which would still take 5 to 10 min in low-temperature regions [24–26]. Therefore, an ammonia carrier with rapid ammonia dosing is needed to elevate the NO_x abatement performance for the solid SCR system.

Metal-organic frameworks (MOFs) are a new emerging class of porous materials consisting of metal ions and organic linkers. MOFs demonstrate remarkable characteristics such as ultrahigh surface area, tunable pore size, and functionalities, which imply their wide applications in gas storage, gas separation, and catalysis [27]. Unlike the chemisorption mechanism in AEMH, MOFs give direct gaseous ammonia dosing with a physisorption mechanism, which has rapid adsorption-desorption kinetics [28]. Moreover, the structural change during ammonia adsorption and desorption is negligible in MOFs, compared with approximately four times molar volume swing in AEMH [29,30]. Therefore, MOFs as ammonia carriers have a higher structural stability than the AEMH system. Previous studies on MOFs as ammonia adsorbents mostly focused on the ammonia capacity, instead of ammonia adsorption-desorption kinetics [31–37]. The highest reported ammonia uptake capacity by MOF yielded at 19.79 mmol/g by $\text{Cu}_2\text{Cl}_2\text{BBTA}$. However, the crystallinity and porosity was found degraded for $\text{Cu}_2\text{Cl}_2\text{BBTA}$ after the first ammonia adsorption cycle [38]. Other reported MOFs with reversible ammonia sorption performance demonstrated ammonia uptake capacity—5 to 15 mmol/g [33,35,36,39–41]. The mechanism of ammonia adsorption in MOFs has been elucidated in two aspects. One is the binding with the organic links, such as the -OH groups [37], Lewis acid sites [42]. Another possible binding of ammonia is with the metal ions [43,44]. Combining these binding mechanisms with the physical high surface area and tunable chemical composition, it is promising to achieve high performance ammonia carriers with MOFs. In this work, MOFs $[\text{M}_2(\text{adc})_2(\text{dabco})]$ ($\text{M} = \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$; $\text{adc} = \text{anthracene-9,10-dicarboxylate}$, $\text{dabco} = 1,4\text{-diazabicyclo}[2.2.2]\text{-octane}$) were synthesized and investigated for their ammonia adsorption-desorption performance. $\text{Ni}_2(\text{adc})_2(\text{dabco})$ possessed the highest ammonia uptake capacity and excellent cyclic performance compared with Co, Cu, and Zn analogues. A comparison of adsorption kinetics with chemi-sorbent MgCl_2 has been made with physisorbent MOFs to evaluate the potential to shorten the ammonia dosing buffer time for the SCR system.

2. Results and Discussion

2.1. Structure Characterization of the MOFs

Figure 1a–d show the microstructure of the obtained MOFs, $[\text{M}_2(\text{adc})_2(\text{dabco})]$ ($\text{M} = \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$). These four MOFs demonstrated different morphology, including brick-like crystals for $\text{Co}_2(\text{adc})_2(\text{dabco})$ in Figure 1a, cuboid-like crystals for $\text{Ni}_2(\text{adc})_2(\text{dabco})$ in Figure 1b, plate-like crystals for $\text{Cu}_2(\text{adc})_2(\text{dabco})$, and $\text{Zn}_2(\text{adc})_2(\text{dabco})$ in Figure 1c,d. The morphology variation could be attributed to the different ions' interaction with the other reagents, since all the MOFs were synthesized with identical cation-to-dabco ratio, temperature, and reaction time, in this work. Future study on the optimized synthesis condition for each cation to achieve specific MOFs morphology would be of interest. The cation-to-dabco ratio has been reported as a key factor for the MOFs' crystal geometry [45]. The $[\text{M}_2(\text{adc})_2(\text{dabco})]$ ($\text{M} = \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$) nanocrystals were obtained due to competition between two organic linkers for one metal center. This excessive number of organic linkers in reaction deplete the

metal ion concentration and suppress the growth rate of the crystals, leading to nanocrystal formation. According to the powder X-ray diffraction (PXRD) patterns in Figure 1e, all of the MOFs had an identical crystal structure with two strongest peaks at $2\theta = 7.8\text{--}8.3^\circ$ and $2\theta = 8.9\text{--}9.4^\circ$, which matches the simulated XRD pattern of the reported $\text{Zn}_2(\text{adc})_2(\text{dabco})$ from the CCDC database (CCDC: 814078) (Supplementary information S1) [46]. The width of the strongest peak in $\text{Ni}_2(\text{adc})_2(\text{dabco})$ was wider than the other MOFs, which could be attributed to the small crystal size ~ 100 nm, compared to 300–1200 nm (detailed particle size distribution in Supplementary information S2) in other obtained MOFs, as shown in Figure 1a–d.

Figure 1. The scanning electron microscopy (SEM) images for the obtained MOFs. (a) $\text{Co}_2(\text{adc})_2(\text{dabco})$; (b) $\text{Ni}_2(\text{adc})_2(\text{dabco})$; (c) $\text{Cu}_2(\text{adc})_2(\text{dabco})$; (d) $\text{Zn}_2(\text{adc})_2(\text{dabco})$. (e) The powder X-ray diffraction (PXRD) patterns of the MOFs $[\text{M}_2(\text{adc})_2(\text{dabco})]$ ($\text{M} = \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$) and the simulated pattern for the reported $\text{Zn}_2(\text{adc})_2(\text{dabco})$ (CCDC: 814078) [46].

The N_2 adsorption isotherms of the obtained MOFs $[\text{M}_2(\text{adc})_2(\text{dabco})]$ ($\text{M} = \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$) in Figure 2 demonstrate high uptake at low-pressure regime (Type I isotherm), indicating that all the obtained MOFs were microporous materials according to the IUPAC classification [47,48]. $\text{Ni}_2(\text{adc})_2(\text{dabco})$ exhibited highest N_2 uptake capacity as compared to other analogues and subsequently highest Brunauer-Emmett-Teller (BET) surface area of $772 \text{ m}^2/\text{g}$, followed by $670 \text{ m}^2/\text{g}$, $640 \text{ m}^2/\text{g}$, $550 \text{ m}^2/\text{g}$, in Co, Zn, and Cu analogues, respectively as summarized in Table 1. However, with almost identical crystal structure, all four MOFs yielded similar micropore area of $473 (\pm 31) \text{ m}^2/\text{g}$ and similar micropore volume of $0.25 (\pm 0.02) \text{ cm}^3/\text{g}$. $\text{Ni}_2(\text{adc})_2(\text{dabco})$ possessed highest external surface area, which would be attributed to the small crystal size and voids between the nanocrystals. The variation of the crystal shape and size resulted in different external surface area, as shown in Figure 1a–d and Table 1. All obtained MOFs demonstrated superior specific surface area $500\text{--}800 \text{ m}^2/\text{g}$ compared to the MgCl_2 at $3 \text{ m}^2/\text{g}$.

Figure 2. The isotherms of nitrogen adsorption in MOFs [$M_2(adC)_2(dabco)$] ($M = Co, Ni, Cu, Zn$) at $-196\text{ }^{\circ}C$.

Table 1. A summary of textural properties of MOFs [$M_2(adC)_2(dabco)$] ($M = Co, Ni, Cu, Zn$).

	BET Surface Area (m^2/g)	Micropore Area (m^2/g)	External Surface Area (m^2/g)	Micropore Volume (cm^3/g)
$Co_2(adC)_2(dabco)$	670	501	169	0.26
$Ni_2(adC)_2(dabco)$	772	472	299	0.25
$Cu_2(adC)_2(dabco)$	550	475	74	0.25
$Zn_2(adC)_2(dabco)$	640	444	195	0.23
$MgCl_2$	3	1	2	0.00

2.2. Ammonia Uptake Capacity

The ammonia uptake capacity of the obtained MOFs [$M_2(adC)_2(dabco)$] ($M = Co, Ni, Cu, Zn$) was measured with ammonia isotherms from high vacuum to 1 bar at $22\text{ }^{\circ}C$ for 3 cycles. The average ammonia uptake capacity for three cycles of each MOF and their corresponding BET surface area were plotted in Figure 3a. $Ni_2(adC)_2(dabco)$ demonstrated the highest average ammonia uptake capacity for 3 cycles of 12.1 mmol/g, compared with 11.2 mmol/g, 8.3 mmol/g, and 6.5 mmol/g in Co, Zn, and Cu analogues, respectively. The differential enthalpy of ammonia adsorption in $Ni_2(adC)_2(dabco)$ was around 18 kJ/mol (Supplementary information S3). The ammonia uptake capacity of each of the MOFs corresponds to its BET surface area, which revealed that higher surface area could offer higher ammonia adsorption sites for the physisorption. However, ammonia uptake capacity cannot be predicted only based on the surface area, since there could be other interactions involved in ammonia sorption, such as metal binding sites and Lewis acid–base interactions [33,38,40]. The cyclic performance of ammonia adsorption and desorption were excellent with almost no drop of the ammonia uptake capacity in $Ni_2(adC)_2(dabco)$ for three cycles. The $Cu_2(adC)_2(dabco)$, however, decreased 44% ammonia uptake capacity from 8.3 mmol/g in the first cycle to 4.6 mmol/g in the third cycle (Supplementary information S4). According to the ammonia isotherms of the MOFs for the third cycle, $Cu_2(adC)_2(dabco)$ did not present a steep ammonia uptake before 0.1 bar, indicating the collapse of the microporous structure. Other MOFs with Cu^{2+} as cations have been reported with poor cyclic ammonia adsorption performance with structural collapse. For instance, Cu-MOF-74 [44], $Cu_3(BTC)_2$ [49], Cu_2Cl_2BBTA , and Cu_2Cl_2BTDD [38] were reported to lose their crystallinity after ammonia adsorption. One explanation could be the Cu^{2+} is less kinetically inert than the Co^{2+} , Ni^{2+} , and Zn^{2+} [38,50]. During ammonia adsorption, the Cu-carboxylate bonds tend to break to have more ammonia coordinated to Cu^{2+} ,

resulting in the structural collapse in the MOFs [44,49]. According to the thermal analysis for the obtained MOFs before and after the ammonia adsorption-desorption cycles (Supplementary information S5), all the synthesized MOFs presented a stable structure with a degradation temperature at 300 to 400 °C. The $\text{Co}_2(\text{adc})_2(\text{dabco})$, $\text{Ni}_2(\text{adc})_2(\text{dabco})$, and $\text{Zn}_2(\text{adc})_2(\text{dabco})$ demonstrated identical weight retention (~30%) before and after the ammonia adsorption-desorption cycles and similar degradation temperature, implying that these MOFs have a stable structure before and after the ammonia adsorption-desorption cycles. However, for $\text{Cu}_2(\text{adc})_2(\text{dabco})$, the weight retention was much higher (~50%) after three cycles of ammonia adsorption-desorption, compared to the original $\text{Cu}_2(\text{adc})_2(\text{dabco})$ (~30%), which is attributed to the degradation of the $\text{Cu}_2(\text{adc})_2(\text{dabco})$ during the ammonia adsorption-desorption cycles. The PXRD patterns of the $\text{Ni}_2(\text{adc})_2(\text{dabco})$ before and after the ammonia adsorption-desorption cycles remained identical, indicating the $\text{Ni}_2(\text{adc})_2(\text{dabco})$ possessed structural stability as ammonia carriers (Supplementary information S6).

Figure 3. (a) The bar chart of the BET surface area and the average ammonia uptake capacity for three cycles of the MOFs [$\text{M}_2(\text{adc})_2(\text{dabco})$] ($\text{M} = \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$). (b) The isotherms of ammonia adsorption in the MOFs [$\text{M}_2(\text{adc})_2(\text{dabco})$] ($\text{M} = \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$) at 22 °C from high vacuum to 1 bar.

2.3. Kinetics of the Ammonia Adsorption and Desorption

The ammonia adsorption-desorption kinetics of the ammonia carriers were evaluated using a simultaneous thermal analyzer. In this regard, instant ammonia dosing was switched on after 2 min stabilization for ammonia adsorption. The ammonia adsorption/desorption percentage in Figure 4a,b was normalized to the corresponding saturated ammonia uptake capacity of each absorbents (Supplementary information S7). As shown in Figure 4a, all the tested MOFs demonstrated rapid ammonia adsorption with ~90% of ammonia uptake in 2 min, which was four times faster than MgCl_2 (11 min) according to our previous study [51]. After the adsorption step, the saturated MOFs desorbed ammonia with a heat treatment under the ammonia atmosphere. As the temperature reached 125 °C in 10 min, $\text{Co}_2(\text{adc})_2(\text{dabco})$ and $\text{Ni}_2(\text{adc})_2(\text{dabco})$ offered ~6 mmol/g ammonia dosing, which is 6 times than ~1 mmol/g in the saturated MgCl_2 , as shown in Figure 4b and Table 2. This is attributed to different ammonia sorption mechanisms in MOFs and AEMH. For MOFs, due to the physisorption mechanism, ammonia can start dosing instantly with temperature or pressure swing due to lower binding energy. However, for the AEMH, ammonia is stored in the form of ammine complexes, which requires a certain temperature or pressure to initiate the desorption. For example, it requires 139 °C for $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$ to start sufficient ammonia desorption at 1 bar, as shown in Figure 4d. The cyclic kinetics performance of $\text{Ni}_2(\text{adc})_2(\text{dabco})$ for ammonia adsorption and desorption was verified steady for three cycles (Supplementary information S8). This rapid desorption property of MOFs can be beneficial to the solid SCR systems by replacing the AEMH with $\text{Ni}_2(\text{adc})_2(\text{dabco})$ in the start-up unit to provide a rapid ammonia dosing before the AEMH reaches the desorption temperature. Consequently this can be coupled with the AEMH to provide sufficient ammonia dosing with its extraordinary ammonia

capacity [26]. Combining the ammonia uptake capacity, rapid kinetics for ammonia adsorption and desorption, and cyclic performance, $\text{Ni}_2(\text{adc})_2(\text{dabco})$ demonstrated promising potential as an ammonia carrier for the SCR system for rapid ammonia dosing to elevate deNO_x efficiency.

Figure 4. (a) Ammonia adsorption percentage in the MOFs [$\text{M}_2(\text{adc})_2(\text{dabco})$] ($\text{M} = \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$) and MgCl_2 at 25 °C, 1 bar with 100 mL/min ammonia flow after 2-min stabilization. Ammonia desorption in ammonia-saturated MOFs [$\text{M}_2(\text{adc})_2(\text{dabco})$] ($\text{M} = \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$) and MgCl_2 with 10 °C/min heat at 1 bar under 100 mL/min ammonia flow, (b) ammonia desorption percentage in the first 10 min from 25 °C to 125 °C; (c) ammonia desorption capacity in the first 10 min from 25 °C to 125 °C; (d) ammonia desorption capacity from 25 °C to 200 °C.

Table 2. Kinetics of ammonia adsorption and desorption of the obtained MOFs and MgCl_2 .

	Net Adsorption Time to Reach 90% Ammonia Uptake (min)	Ammonia Desorption Percentage within 10 min [1 bar, 125 °C]	Ammonia Desorption within 10 min [1 bar, 125 °C] (mmol/g)
$\text{Co}_2(\text{adc})_2(\text{dabco})$	2	67%	7
$\text{Ni}_2(\text{adc})_2(\text{dabco})$	2	57%	6
$\text{Cu}_2(\text{adc})_2(\text{dabco})$	2	63%	6
$\text{Zn}_2(\text{adc})_2(\text{dabco})$	2	54%	4
MgCl_2	11	1%	1

3. Materials and Methods

3.1. MOFs Synthesis

$M_2(\text{adc})_2(\text{dabco})$ ($M = \text{Cu, Co, Ni, Zn}$) MOFs were synthesized based on literature procedure [45,48]. Copper (II) nitrate hemi(pentahydrate) $[\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}]$ ($\geq 99.99\%$), Cobalt(II) nitrate hexahydrate $[\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ ($\geq 99.99\%$), Nickel(II) acetate tetrahydrate $[\text{Ni}(\text{OCOCH}_3)_2 \cdot 4\text{H}_2\text{O}]$ ($\geq 99.99\%$), zinc nitrate hexahydrate $[\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ ($\geq 99.99\%$), and N,N-dimethylformamide (anhydrous DMF), 1,4-diazabicyclo[2.2.2] octane [DABCO] ($\geq 99\%$), 9,10-anthracenedicarboxylic acid [H_2adc] (95%) were purchased from Sigma Aldrich Chemie GmbH, Germany. All of the above-mentioned chemicals were used as received.

The metal salt (1 mmol) was dissolved in 9 mL DMF using a magnetic stirrer. After complete dissolution, the metal salt solution was added to organic linker solution, prepared from mixing DABCO (0.83 mmol) and H_2adc (1 mmol) in DMF (18 mL). The mixture was stirred for 20 min and heated in 30 mL Teflon lined autoclave at 120 °C for 48 h. The precipitated crystalline material was collected and washed with DMF to remove the excess unreacted precursors. Further, the crystals were immersed in ethanol for three days during which ethanol was replenished three times per day for the solvent exchange.

3.2. Structure Characterization

The microstructure of the obtained MOFs was characterized with scanning electron microscopy (SEM, Magellan 400 XHR-SEM, FEI Company, Eindhoven, Netherlands), with a 15-nm platinum coating to avoid the charging by Leica EMACE 200 coating system. The crystal structure of the MOFs was characterized by a $\text{Cu K}\alpha$ radiation X-ray diffractometer (Empyrean, Malvern Panalytical, Malvern, UK). The BET surface area of the MOFs was obtained by N_2 adsorption at -196°C using a surface area analyzer (Gemini VII 2390, Micromeritics, Norcross, GA, USA). All MOFs were degassed at 200 °C under high vacuum overnight prior to the N_2 adsorption measurements. The thermal stability of each of the obtained MOFs was characterized using a simultaneous thermogravimetric analysis and differential scanning calorimetry (TGA/DSC) thermal analyzer (SDT 650, TA instruments, New Castle, DE, USA). The MOFs were heated from 25 °C to 500 °C with a ramp of 10 °C/min in an argon atmosphere, before and after the 3-cycle ammonia adsorption-desorption tests. The particle size distribution was measured with dynamic light scattering (Zetasizer Nano Z, Malvern Panalytical, Malvern, UK).

3.3. Ammonia Adsorption and Desorption Measurement

The ammonia isotherms were obtained with the IsoSORP[®] sorption analyzer (TA Instruments, New Castle, DE, USA), which includes a magnetic suspension balance, an electrical heater, a thermostatic oil bath, and a chemistry diaphragm vacuum pump. All MOFs were degassed at 200 °C under high vacuum for 3 h, following a buoyancy test with helium at 22 °C to determine the mass and volume of each sample. Then, the ammonia adsorption isotherms were measured with ammonia dosing from vacuum to 1 bar until the deviation of mass was less than 0.1 mg per 10 min. Three cycles were repeated for each MOF. The kinetics of ammonia adsorption-desorption in the MOFs was studied with aforementioned thermal analyzer, SDT 650. The MOFs were first degassed at 200 °C with argon flow (50 mL/min) for 12 h; once the sample cooled down to 25 °C, the protective argon gas was cut off following a 100 mL/min NH_3 flow for the adsorption measurement until saturation for the adsorption kinetics. Ammonia desorption kinetics was characterized under ammonia atmosphere with a heating rate of 10 °C/min from 25 °C to 200 °C then held isothermally.

4. Conclusions

MOFs [$M_2(\text{adc})_2(\text{dabco})$] ($M = \text{Co, Ni, Cu, Zn}$) were synthesized and characterized for ammonia storage with the equilibrium ammonia uptake capacity and the kinetics of ammonia adsorption and

desorption. The obtained MOFs illustrated identical crystal structure, but the geometry and size of the crystal varied from each different metal cations. $\text{Ni}_2(\text{adc})_2(\text{dabco})$ presented the highest surface area at $772 \text{ m}^2/\text{g}$. For the ammonia uptake capacity, $\text{Ni}_2(\text{adc})_2(\text{dabco})$ yielded the highest average capacity at 12.1 mmol/g with a stable cyclic performance for three cycles. While the porous structure of $\text{Cu}_2(\text{adc})_2(\text{dabco})$ collapsed after the ammonia cycles, resulting in a 44% ammonia capacity drop after three cycles. All four obtained MOFs demonstrated excellent kinetics of ammonia adsorption and desorption compared to the MgCl_2 by the physisorption mechanism. Particularly for the ammonia dosing, $\text{Ni}_2(\text{adc})_2(\text{dabco})$ offered six times ammonia in the first 10 min compared to $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$. With the obtained results, $\text{Ni}_2(\text{adc})_2(\text{dabco})$ demonstrated promising ammonia carrier characteristics to elevate the ammonia dosing kinetics and corresponding deNO_x efficiency for the SCR system.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4344/10/12/1444/s1>.

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