



HAL
open science

Facile modifications of HKUST-1 by V, Nb and Mn for low-temperature selective catalytic reduction of nitrogen oxides by NH₃

Katarzyna Świrk, Gérard Delahay, Abdelali Zaki, Karim Adil, Amandine Cadiou

► To cite this version:

Katarzyna Świrk, Gérard Delahay, Abdelali Zaki, Karim Adil, Amandine Cadiou. Facile modifications of HKUST-1 by V, Nb and Mn for low-temperature selective catalytic reduction of nitrogen oxides by NH₃. *Catalysis Today*, 2022, 384-386, pp.25-32. 10.1016/j.cattod.2021.07.017 . hal-03517472

HAL Id: hal-03517472

<https://hal.science/hal-03517472>

Submitted on 7 Jan 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1 **Facile modifications of HKUST-1 by V, Nb and Mn for low-temperature**
2 **selective catalytic reduction of nitrogen oxides by NH₃**

3 Katarzyna Świrk*, Gérard Delahay, Abdelali Zaki, Karim Adil, Amandine Cadiou*

4 ICGM, Univ. Montpellier, CNRS, ENSCM, Montpellier, France

5

6 **Abstract**

7 HKUST-1 catalysts were impregnated with vanadium, niobium and manganese species and
8 tested in NH₃-SCR for NO removal. No reduction of NO by NH₃ was registered for the
9 unmodified HKUST-1 and disappearance of NO was attributed to adsorption. After a pre-
10 treatment at 185°C, the best catalytic performance was found for HKUST-1-Mn with 100%
11 and 80% conversion of NH₃ and NO, respectively at 185°C. For the first time, the H₂O
12 tolerance was examined on the modified HKUST-1 catalyst. The addition of water vapor
13 resulted in decrease of NO and NH₃ conversions, which was immediately recovered when
14 H₂O feeding was stopped. The NO conversion dropped from 76% to 68% after 35 min of H₂O
15 addition.

16

17

18

19

20

21 **Corresponding authors:**

22 e-mails: katarzyna.swirk@umontpellier.fr; amandine.cadiou@umontpellier.fr

23 † Electronic Supplementary Information (ESI)

24 **Keywords:**

25 Metal-organic frameworks, HKUST-1, manganese, NH₃-SCR, NO_x

26 **Highlights:**

27 • Disappearance of NO was attributed to adsorption during NH₃-SCR over unmodified

28 commercial HKUST-1

29 • Modification of HKUST-1 with V, Nb, Mn resulted in the reduction of NO by NH₃

30 • Promotion with manganese led to the most promising results in NH₃-SCR

31 • Partial decomposition of MOF can be prevented by maintaining temperature of 185°C

32 • NH₃-SCR with H₂O over HKUST-1-Mn catalyst led to the NO conversion decrease from

33 76% to 68%

34 1. Introduction

35 Air quality preservation is undoubtedly one of the major environmental issue facing
36 by our modern society. The emissions of nitrogen oxides (NO_x) are targeted to be
37 reduced as they cause serious hazards to earth climate, biological ecosystems, and
38 human health. Selective catalytic reduction of nitrogen oxides by NH₃ (NH₃-SCR) is a
39 well-known process with an efficient approach for removing air-polluting NO_x [1]. At
40 present, for stationary sources, the most common applied catalyst is V₂O₅-
41 WO₃(MoO₃)/TiO₂ deposited on a ceramic monolith (vanadium plays the role of active
42 phase). This material allows high conversion of NO_x, however, its application is
43 limited by relatively narrow temperature window (300-400°C) and toxicity of
44 vanadium oxide [1,2]. This commercial catalyst is installed in the “high-dust” position,
45 i.e., in contact with SO₂, particles of fly ash and alkaline metals which impact its
46 lifetime. The optimal placement of a catalyst would be at the “tail-end”, behind the
47 electrostatic precipitator and the flue-gas desulfurization unit. However, this position
48 will require reheating of the flue gases, so that the commercial catalyst can work
49 efficiently [3]. Therefore, finding a novel eco-friendly material with high NH₃-SCR
50 activity at temperatures lower than 250°C is a big challenge. Up to now, fruitful
51 research has been made on the alternative oxides or zeolites materials containing Mn
52 or Nb species, being active and stable in the NH₃-SCR [4,5].

53 On the other hand, the use of Metal-Organic Frameworks (MOFs), a recent class of
54 crystalline materials can offer an alternative to the inorganic compounds. MOFs are
55 hybrid porous solids, built from organic linkers and inorganic nodes [6,7]. Their
56 enhanced specific surface area, porosity and tunable topologies have already attracted
57 much attention in different applications such as gas separation, adsorption, and
58 catalysis [7–12]. Since copper-containing materials are a great alternative for NO_x

59 removal, Cu being an essential redox center for the NH₃-SCR reaction [13–16], we
60 choose to explore the potential of HKUST-1, a MOF based on copper paddle-wheel
61 and benzene-1,3,5-tricarboxylate (Cu-BTC) with high specific surface area (ca. 1400–
62 2000 m²/g) and containing open metal sites (OMS) for NH₃-SCR of NO_x [7,17]. Some
63 authors assume a decomposition of HKUST-1 material and its usage as a template for
64 CuO catalyst [18]. Surprisingly, only four reports can be found on HKUST-1 for NH₃-
65 SCR in which the structure of MOF has been preserved [19–21]. In these studies, no
66 NH₃ conversion is demonstrated despite the fact that the authors reported remarkable
67 activity at a low-temperature window, i.e. till 280°C. Li et al. [19] assumed usage of
68 Cu-BTC activated in vacuum at different temperatures varied from 180 to 250°C. The
69 series of experiments revealed 230°C as optimal pre-treatment temperature, giving the
70 highest NO conversion of 100% from 220 to 280°C. The stability of the samples was
71 not examined by the authors. The same conclusion was drawn by the authors in their
72 second study, in which 230°C was found satisfactory as pre-treatment temperature
73 assuming nitrogen flow for 3 h [20]. In the report of Jiang et al. [21], the effect of
74 acetic acid (AA) solutions added during the synthesis of Cu₃(BTC)₂ was examined. The
75 authors showed that 25% of AA can significantly improve NO conversion, giving
76 95.5% at 280°C. Yao et al. [9] studied Cu-BTC promoted with Mn by post-synthetic
77 exchange method, assuming dispersion of the support in the ethanol-based solution and
78 usage of autoclave. In the temperature window of 230 to 260°C, the novel
79 Mn@CuBTC catalyst showed NO conversion close to 100%. The superior
80 performance in NH₃-SCR was ascribed to the suitable pore sizes, enhanced redox
81 activity arising from strong oxidizing Mn⁴⁺ ions, as well as a synergistic effect between
82 Mn and Cu ions in the metal-organic framework.

83 Herein, we proposed a facile modification of commercially available HKUST-1 by
84 V, Nb and Mn salts. The catalysts were obtained by incipient wetness impregnation
85 method assuming 2.5 wt.% of metal in the individual sample. The promotion with Nb
86 and V is reported for the first time in this type of MOF materials. The vanadium-
87 promoted HKUST-1 catalyst was synthesized in order to compare the performance
88 with the commercial catalyst containing V_2O_5 as an active phase. The influence of the
89 addition of a promoter (V, Nb, Mn) on the materials properties and the catalytic
90 performance was also discussed in detail.

91 **2. Experimental**

92 **2.1. Synthesis of catalysts**

93 HKUST-1-x (x=V, Nb, Mn) catalysts were prepared by incipient wetness
94 impregnation using ammonium monovanadate (Merck), ammonium niobate (V)
95 oxalate hydrate (Sigma-Aldrich), and manganese (II) nitrate tetrahydrate (Sigma-
96 Aldrich), respectively (as described in detail below). HKUST-1 powder was purchased
97 from Sigma-Aldrich, under the commercial name of Basolite® C300. For the aqueous
98 solutions, ultra-pure water was used. The assumed metal loading in the individual
99 sample was 2.5 wt.%. After the impregnation step, the samples were sonicated for 20
100 min at 30°C, and subsequently dried overnight at 70°C. No washing was applied
101 during the syntheses.

102 HKUST-1-V: 0.0589 mg of ammonium monovanadate was dissolved in ca. 3 ml of
103 ultra-pure water. 1 g of commercial HKUST-1 was impregnated drop wisely with the
104 so-prepared aqueous solution of the salt.

105 HKUST-1-Nb: 0.0836 mg of ammonium niobate (V) oxalate hydrate was dissolved
106 in ca. 3 ml of ultra-pure water. 1 g of commercial HKUST-1 was impregnated drop
107 wisely with the so-prepared aqueous solution of the salt.

108 HKUST-1-Mn: 0.1208 mg of manganese (II) nitrate tetrahydrate was dissolved in
109 ca. 3 ml of ultra-pure water. 1 g of commercial HKUST-1 was impregnated drop
110 wisely with the so-prepared aqueous solution of the salt.

111

112 **2.2. Characterization methods**

113 Powder X-ray diffraction analysis was carried out on a D8 Advance Bruker
114 diffractometer equipped with Cu K α radiation of $\lambda=0.15406$ nm. The diffraction
115 patterns were obtained in an angle range of $2\theta = 4-80^\circ$ with a 0.02° step and an
116 accumulation time of 1 s per step.

117 Textural properties of the studied HKUST-1 catalysts were determined by nitrogen
118 adsorption-desorption at -196°C using a Micromeritics ASAP 2020 – surface area and
119 porosity analyzer. Before the analysis, the samples were pretreated under vacuum at
120 150°C for 6 h. The Brunauer–Emmett–Teller (BET) equation was used to calculate the
121 specific surface area, and the Barrett–Joyner–Halenda (BJH) desorption method was
122 applied to determine the volume of mesopores. The t-plot was used for calculation of
123 microporous volume.

124 The morphology of metal-organic frameworks was studied by a scanning electron
125 microscope Hitachi 4800S with an acceleration voltage of 5 kV. Energy Dispersive
126 Spectroscopy (EDS) chemical analyses (in atomic %) were carried out on a FEI
127 Quanta 200F (15 kV) equipment. The elemental analysis was performed with the aid of
128 AZtec software.

129 Thermogravimetric analysis (TGA) and differential thermal analyses (DTA) were
130 carried out by a PerkinElmer STA 6000 Simultaneous Thermal Analyzer. The sample
131 (approximately 15 mg) was loaded into a crucible, and heated in a flow of air (60 cm^3
132 min^{-1}) from 40°C to 900°C with a heating rate of 5°C min^{-1} .

133 Temperature-programmed desorption of NH_3 (NH_3 -TPD) of as-synthesized
134 catalysts was conducted on a Micromeritics AutoChem 2910 apparatus using a thermal
135 conductivity detector (TCD) to monitor the NH_3 evolution. Firstly, the samples were
136 heated from 40°C to 250°C with a heating rate 5°C min^{-1} . Thereafter, they were cooled
137 down to 140°C , and NH_3 was adsorbed at 140°C for 30 min (a mixture 5 vol.%
138 NH_3/He , flow rate= $30 \text{ cm}^3 \text{ min}^{-1}$). The physisorbed ammonia was removed by flowing
139 He (flow rate= $30 \text{ cm}^3 \text{ min}^{-1}$) for next 30 min. Finally, ammonia desorption was carried
140 out in helium (flow rate= $30 \text{ cm}^3 \text{ min}^{-1}$) by increasing the temperature to 250°C with a
141 heating rate of 2°C min^{-1} . The sample was kept for 60 min at 250°C .

142

143 **2.3. Catalytic tests**

144 Three types of NH_3 -SCR tests were performed: (i) temperature programmed surface
145 reaction (TPSR) from 145°C to 250°C , with the pre-treatment at 250°C , (ii) isothermal
146 tests at 185°C for 480 min, assuming either pre-treatment at 250°C , or 185°C , and (iii)
147 isothermal test at 185°C , involving the presence of H_2O in the reaction feed for 35 min.
148 The tests were performed in a U-shaped glass reactor with 0.075 g of a catalyst. For
149 heating, an electric furnace was used. The experiments were conducted at atmospheric
150 pressure with the total flow rate of 100 ml min^{-1} , corresponding to a weight hourly
151 space velocity (WHSV) of $80,000 \text{ ml g}^{-1}\text{h}^{-1}$. Prior to the NH_3 -SCR tests, the catalyst
152 was pre-treated in He from 40°C to either 250°C or 185°C with a heating rate of 5°C
153 min^{-1} . In the first type of tests, heating rate of 2°C min^{-1} . The reactant gas mixture was

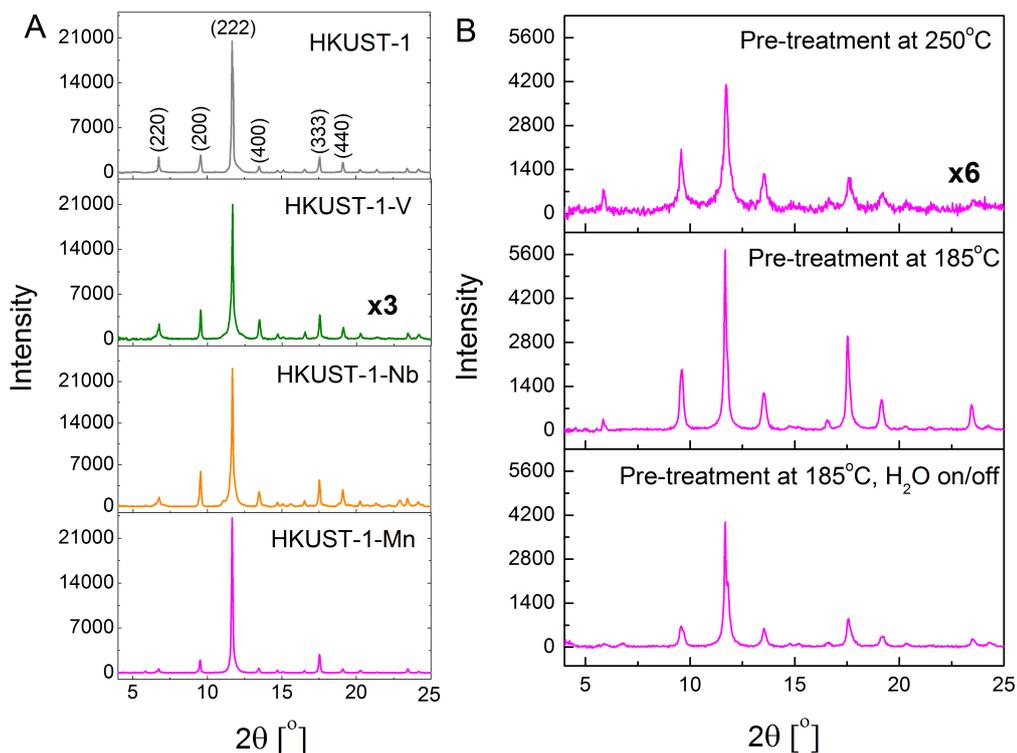
154 adjusted to 1000 ppm NO, 1000 ppm NH₃, 8 vol.% O₂ and balance with helium. In the
155 H₂O-resistance test, water was injected by circulating the helium flow for 35 min via a
156 gas bubbler containing deionized water heated at 30 °C which corresponds to 3.5%
157 H₂O vapor. The gas lines were heated to prevent condensation of water. The outlet gas
158 composition was constantly monitored by vacuum stripping a fraction of the exit gas
159 with a capillary towards the mass spectrometer (Pfeiffer Omnistar) equipped with
160 Channeltron and Faraday detectors following the specific masses of: NO (m/z = 30),
161 NH₃ (m/z = 15), N₂ (m/z = 28), H₂O (m/z = 18), N₂O (m/z = 44), CO₂ (m/z = 44), and C
162 (m/z = 12).

163

164 **3. Results and discussion**

165 The structure of the MOFs was confirmed by PXRD, SEM/EDS and N₂ adsorption/
166 desorption characterization methods. Fig. 1A presents PXRD diffractograms, where
167 typical reflections of the commercial Basolite® C300 (here as HKUST-1) were
168 observed at 2θ=6.7°, 9.5°, 11.7°, 13.5°, 17.4°, 19.3° for (200), (220), (222), (400),
169 (333) and (440) planes [21–23]. For the HKUST-1-(V, Nb, Mn) the registered
170 reflections did not change compared to the parent sample, proving the phase-purity of
171 the as-modified materials. The absence of crystalline metal species suggests their well
172 dispersion, as proven by SEM and EDS (Fig. 2; Fig. S2 and S3, ESI†). The reflections
173 intensities of V-containing catalyst were, however, three times lower than for the other
174 catalysts, pointing the loss of crystallinity in V-sample. This may be attributed to
175 formation of some defect sites in the crystal lattice of HKUST-1 [24].

176 Textural properties of the studied samples are listed in Table 1 (Fig. S1, ESI†). The
 177 values of specific surface area (S_{BET}) for HKUST-1 is in accordance to the data
 178 postulated by the chemical provider (Basolite® C300: 1500–2100 m^2/g). For the
 179 modified samples, S_{BET} and pore volume decreased as a consequence of a partial
 180 blockage of the cavities by V, Nb and Mn species.



181 **Fig. 1** PXRD patterns of parent HKUST-1 and modified with V, Nb and Mn salts (A), and of the spent
 182 HKUST-1-Mn: pre-treated at 250°C and tested at 185°C for 480 min; pre-treated at 185°C and tested at
 183 185°C for 480 min; and pre-treated at 185°C and tested at 185°C assuming H₂O on/off step (B). The PXRD
 184 pattern of HKUST-1-V is multiplied by three in Fig. 1A. The PXRD pattern of HKUST-1-Mn pre-treated
 185 at 250°C is multiplied by six in Fig. 1B.

186
 187 However, the impregnation of HKUST-1 led to the formation of new mesopores. Their
 188 existence can be also confirmed by the adsorption-desorption isotherms. For the
 189 modified samples, type-IV isotherms with type H4 hysteresis loop were observed, [25]

190 whereas no hysteresis was registered for the parent sample (type-I isotherm). The co-
 191 existence of micro- and mesopores in HKUST-1 structure has been already reported
 192 for materials where mixed-ligand was assumed during a synthesis,[24,26,27] or
 193 impregnation with metal salts was used [28]. In the latter studies, the S_{BET} decreased
 194 with the non-intraframework mesoporosity formation, alike to our results.

195

196 **Table 1** Textural properties, relative elemental composition and acid amount of HKUST-1 catalysts.

Catalyst	S_{BET} [m ² /g] ^a	V_{mic} [cm ³ /g] ^b	V_{mes} [cm ³ /g] ^c	C/Cu [mol/mol] ^d	Acidity [μmol/g] ^e
HKUST-1	1709	0.60	0.02	9.8	965
HKUST-1-V	1248	0.43	0.05	8.1	1073
HKUST-1-Nb	1043	0.36	0.06	12.6	1324
HKUST-1-Mn	1315	0.44	0.13	9.2	1408
HKUST-1-Mn ^f	335	0.09	0.35	n.m.	n.m.
HKUST-1-Mn ^g	533	0.16	0.41	n.m.	n.m.
HKUST-1-Mn ^h	465	0.15	0.37	n.m.	n.m.

197 ^a calculated from the Brunauer-Emmett-Teller (BET) equation;

198 ^b determined by means of t-plot;

199 ^c determined from the BJH desorption cumulative volume of pores;

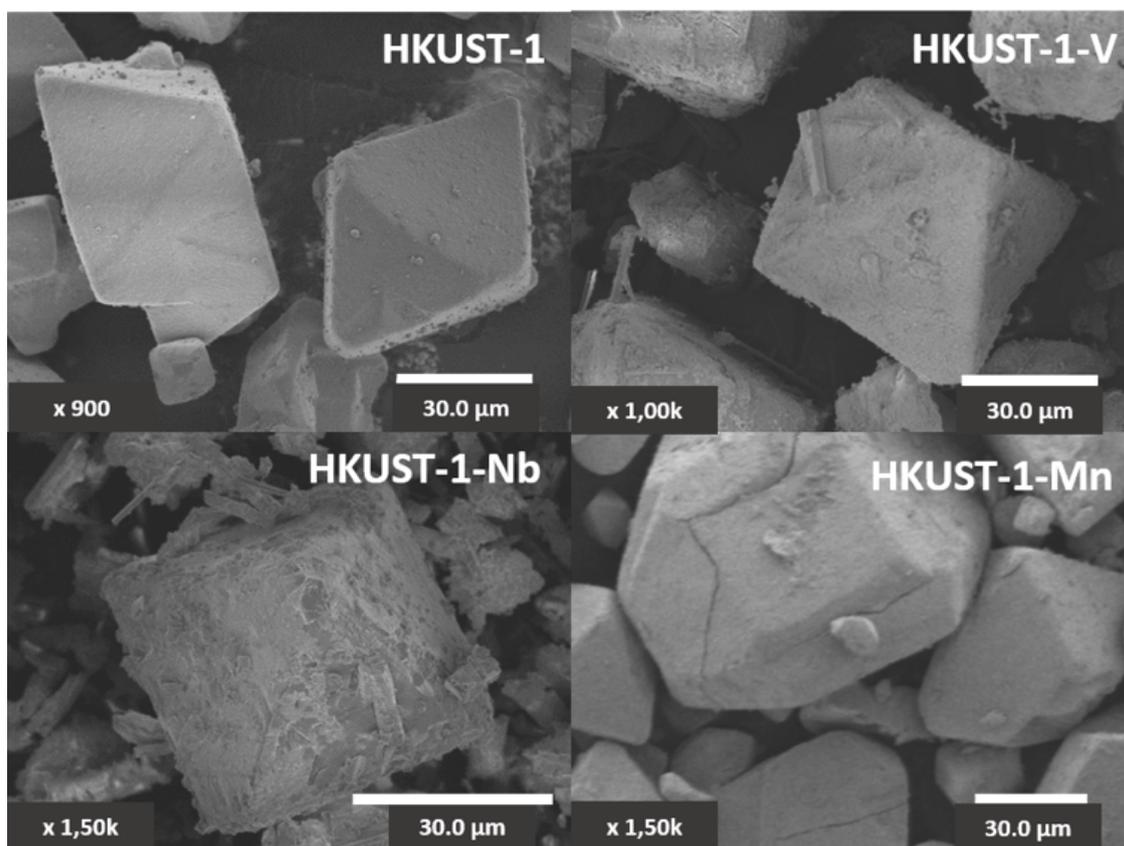
200 ^d average atomic ratio from SEM/EDS;

201 ^e NH₃ desorption determined by the NH₃-TPD;

202 ^{f, g} pre-treated at 250°C and 185°C, NH₃-SCR test at 185°C for 480 min, respectively;

203 ^h pre-treated at 185°C, NH₃-SCR test at 185°C assuming water on/off step; n.m. – not measured.

204 SEM images of HKUST-1 and HKUST-1-(V, Nb, Mn) samples are presented in
205 Fig. 2, exposing mostly octahedron and some cuboctahedral crystal shape in agreement
206 with the literature [21,23,29]. A magnification of V and Nb modified MOFs revealed a
207 presence of rods, possibly arising from ammonium monovanadate and ammonium
208 niobate, respectively, and covering the HKUST-1 crystals, leading to a blockage of the
209 porous surface. The magnification of HKUST-1-Mn revealed aggregates with a
210 laminar structure, perhaps as a part of manganese nitrate used during the synthesis
211 (Fig. S2, ESI†). Moreover, Mn-catalyst showed numerous cracks on the crystals
212 surface (Fig. 2; Fig. S2, ESI†).



213 Fig. 2 SEM images of HKUST-1 catalysts modified with V, Nb and Mn.

214

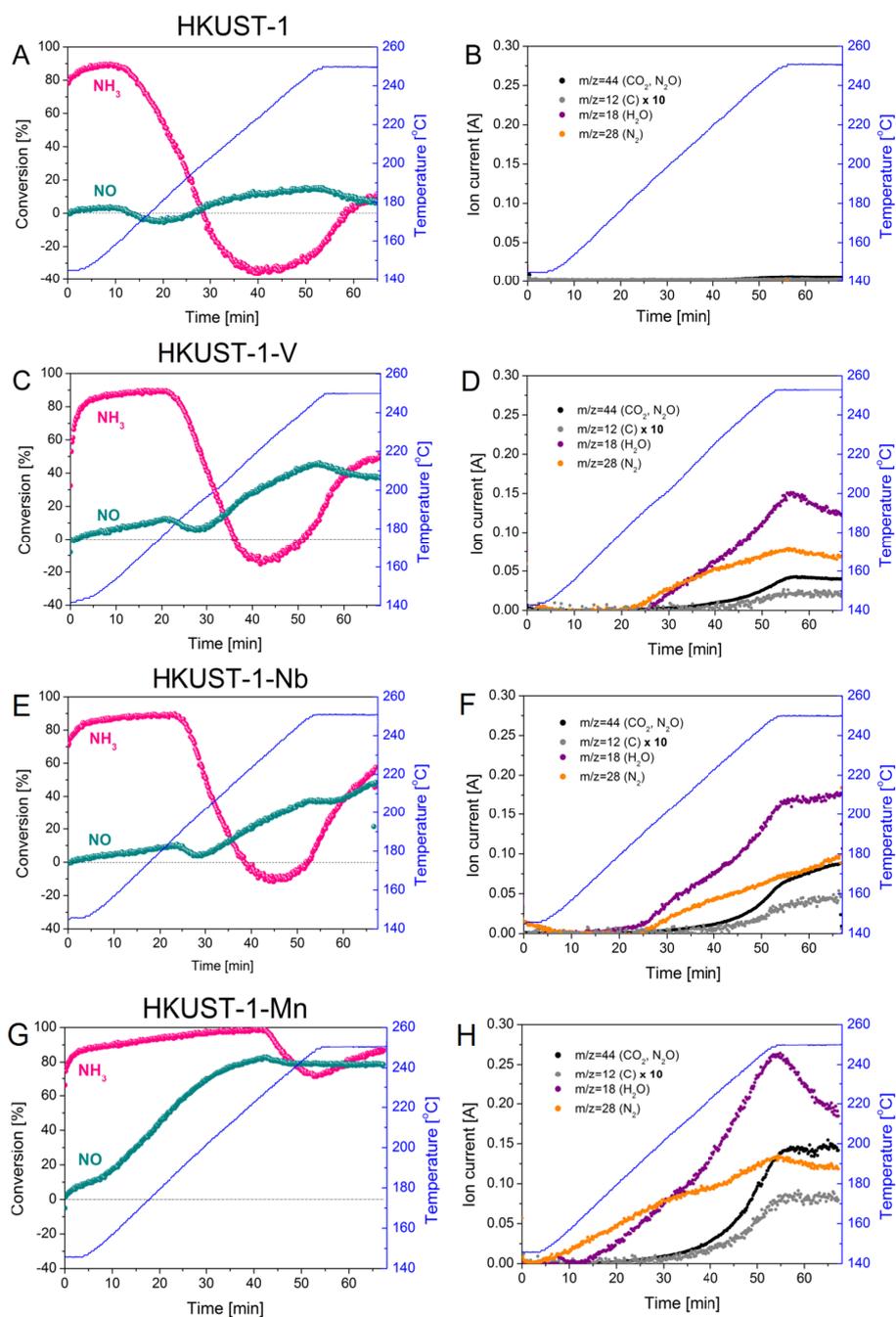
215 The EDS elemental mapping displayed the even distribution of vanadium, niobium, and
216 manganese elements in the modified samples (Fig. S3, ESI†). The average C/Cu ratio was

217 9.8, 8.1, 12.6, 9.2 for the HKUST-1, HKUST-1-V, HKUST-1-Nb, HKUST-1-Mn,
218 respectively (Table 1). The highest carbon content in HKUST-1-Nb can be attributed to
219 $C_4H_4NNbO_9 \cdot xH_2O$ used during the synthesis. The calculated C/Cu ratio for HKUST-1 is
220 similar to one registered by SEM/EDS in the study of Li et al. [30]. The authors reported
221 C/Cu of 8.4. Moreover, this ratio has been confirmed by XPS in the work of Yao et al. [9].
222 The latter authors found C/Cu for HKUST-1 and Mn-modified HKUST-1 in the range of 7.8 -
223 8.3.

224 Thermogravimetric analysis was carried out in order to determine the thermal
225 stability (Fig. S4, ESI†). All samples revealed ca. 15% mass loss up to 150°C, which is
226 assigned to the removal of water and guest molecules [23]. A second weight loss began
227 at 282, 280, 277 and 275°C, respectively for HKUST-1, HKUST-1-V, HKUST-Nb,
228 and HKUST-1-Mn catalysts, following a sudden mass reduction after a slight increase
229 of the temperature (ca. 50°C). The latter resulted from the decomposition of BTC
230 linker. The PXRD analysis of the residues, formed upon the thermal treatment at
231 900°C, exhibits the presence of CuO, $CuNb_2O_6$, and $CuMn_2O_4$ for HKUST-1, HKUST-
232 Nb, and HKUST-1-Mn, respectively (Fig. S5, ESI†). A lack of V-phases in HKUST-1-
233 V sample arises from a sublimation of vanadium species at 900°C (Fig. S6, ESI†) [31].

234 Since HKUST-1 material exhibits Lewis-acidity, temperature programmed
235 desorption of ammonia (NH_3 -TPD) was carried out to examine the catalyst. The
236 materials were pre-treated in helium in the temperature range of 40-250°C to remove
237 water molecules (Fig. S6, ESI†). Table 1 presents the calculated values of NH_3
238 desorption previously adsorbed at 140°C (from the profiles presented in Fig. S7A,
239 ESI†), showing the positive effect of the V, Nb, and Mn-modifications. Total amounts
240 of NH_3 desorbed were: HKUST-1 (965 $\mu\text{mol/g}$) < HKUST-1-V (1073 $\mu\text{mol/g}$) <
241 HKUST-1-Nb (1324 $\mu\text{mol/g}$) < HKUST-1-Mn (1408 $\mu\text{mol/g}$). The obtained TPD- NH_3

242 desorption curve of the parent sample is similar to the one reported by Gao et al.[32]
 243 (Fig. S7B; ESI†). The open-metal sites, located on the interior of the pore wall,
 244 facilitate the NH_3 desorption in HKUST-1 [33]. For the modified samples, the
 245 desorption profiles were more intense, and a distinctive behavior was observed for
 246 HKUST-1-Mn. For the latter, a gradual increase of desorbed NH_3 was registered,

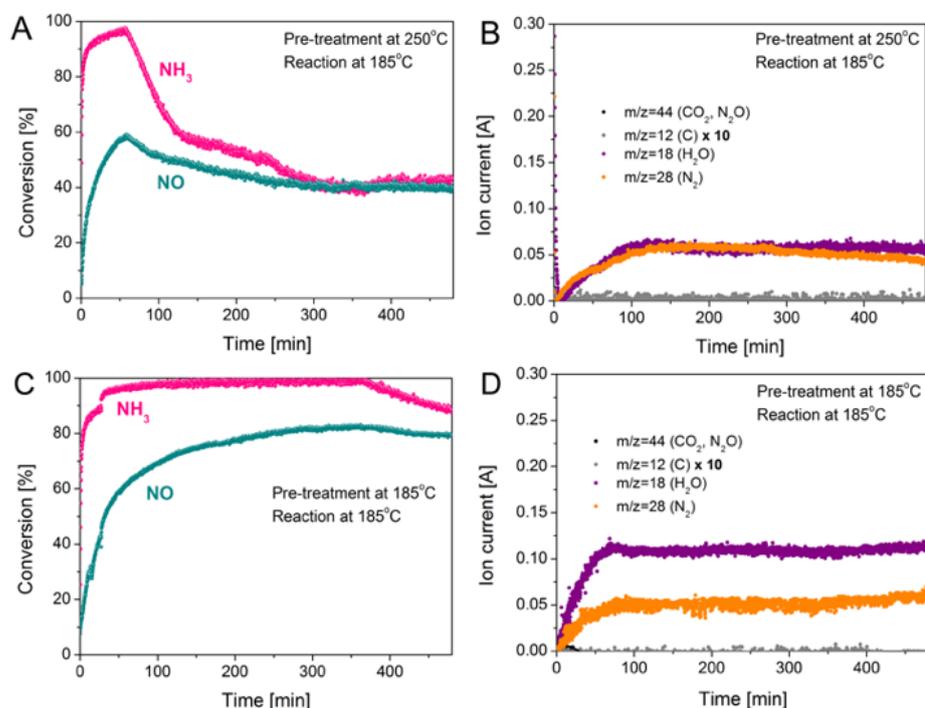


247 whereas for the other samples a peak with a shoulder at ca. 200°C was observed. A
 248 slight increase at ca. 240°C for Nb- and V-catalysts was also recorded.

249 Fig. 3 NH₃-SCR catalytic results (left) and ion current of the products (right) for HKUST-1 (A, B),
250 HKUST-1-V (C, D), HKUST-1-Nb (E, F), and HKUST-1-Mn (G, H). Reaction conditions: [NO] =
251 [NH₃] = 1000 ppm, [O₂] = 8 vol.%, He balance, temperature range = 145-250°C, WHSV = 80,000
252 ml·g⁻¹·h⁻¹.

253
254 Temperature-programmed surface reaction (TPSR) tests are presented in Figs. 3A-
255 H. HKUST-1 was inactive in NH₃-SCR, but reveals significant adsorption of NH₃ in
256 the temperature range of 145-200°C, and its subsequent desorption at 200-250°C
257 (negative conversion values) (Fig. 3A). During this desorption phase, low NO
258 conversion was registered (maximum 10%), suggesting a competitive
259 adsorption/desorption of NH₃ and NO in HKUST-1, as no signals of possible NH₃-
260 SCR products (N₂ and/or H₂O) were recorded (Fig. 3B). The modification with V led
261 to the similar NH₃ adsorption behavior (Fig. 3C). A significant increase of NO
262 conversion was recorded just after NH₃ desorption step (ca. 210°C), further reaching
263 maximum of 45% at 250°C, and slightly decreasing in 15 min time period. Both main
264 products were registered during NH₃-SCR for this sample, i.e., N₂ and H₂O. Also, CO₂
265 production was observed, as supported by the signal arising from carbon (Fig. 3D).
266 Since the trend of the ion current signals for both CO₂ and C is similar, the existence of
267 N₂O can be ruled out. The presence of carbon dioxide implies a certain damaging of
268 the structure, i.e. a possible partial decomposition of catalyst. For HKUST-1-Nb
269 catalyst a very similar performance to V-catalyst was observed (Fig. 3E). The former
270 showed the maximum NO conversion of ca. 38%, which was progressively increasing
271 in time-on-stream at 250°C. Meanwhile, promotion with Mn resulted in a considerably
272 higher catalytic activity at 250°C with 80% and 100% of NO and NH₃ conversions,
273 respectively (Fig. 3G). Conversions for both reactants were rapidly increasing as a
274 function of temperature. In contrast to the other catalysts, no NH₃ desorption

275 phenomenon was registered for Mn-sample. The same like for Nb and V modified
276 MOFs, nitrogen and steam were recorded as products (Fig. 3H). Some CO₂ is detected,



277 starting from 190°C. In order to prevent its production, we decided to carry out our
278 next experiments at the highest possible (and carbon-free) temperature, i.e. 185°C.

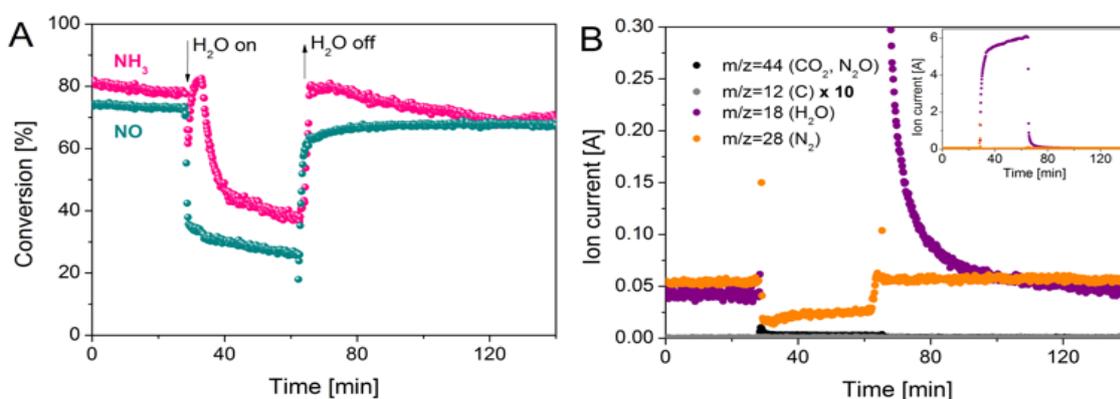
279 Fig. 4 NH₃-SCR over HKUST-1-Mn at 185°C for 480 min assuming different pre-treatment conditions:
280 250°C for 15 min (A, B), 185°C for 15 min (C, D). Reaction conditions: [NO] = [NH₃] = 1000 ppm, [O₂] =
281 8 vol.%, He as balance, WHSV = 80,000 ml·g⁻¹·h⁻¹.

282

283 A stability test was performed for HKUST-1-Mn at 185°C for 480 min, evaluating
284 pre-treatment either at 250°C (Fig. 4A), or 185°C (Fig. 4C). For the former, increasing
285 conversions of NH₃ and NO were registered reaching almost 100% and 60%,
286 respectively in the first 60 min. Furthermore, a remarkable decrease of both was
287 observed, giving a steady value of ca. 45% in the next 230 min. This agrees with NO
288 conversion obtained in TPSR test (cp. Fig. 3G). Moreover, only N₂ and H₂O were
289 recorded as products in this catalytic test (Figs. 4 B, D). The pre-treatment at 185°C,

290 however, led to complete conversion of NH_3 , while NO was reduced in maximum 80%
291 to N_2 and H_2O . This shows that temperature of pre-treatment determines the catalytic
292 activity, as a partial degradation of the MOF structure negatively affects the NH_3 -SCR
293 performance.

294 Since the existence of water vapor in exhaust gases is unavoidable, H_2O -resistance
295 was also examined for HKUST-1-Mn catalyst pre-treated at 185°C . As presented in
296 Fig. 5A, the NO and NH_3 conversions rapidly reduced from 74% to 26% and from 78%
297 to 37%, respectively, when H_2O was introduced as a reactant for 35 min. When H_2O
298 was cut off, the conversions recovered quickly giving 68% for both NO and NH_3 after
299 one hour of H_2O -free reaction. This shows that the inhibiting water effect is reversible
300 for HKUST-1-Mn. The obtained products were N_2 and H_2O , whereas, during the H_2O -
301 feeding, a slight formation of CO_2 was observed, indicating that water presence
302 negatively affected the modified-MOF (Fig. 5B). In the framework of HKUST-1, four
303 carboxylate groups per one copper forms a so-called paddle-wheel unit. A weak bond
304 between Cu^{2+} ions and the residual axial coordination site can be attracted by water
305 molecule [9,33]. During the H_2O -feeding, a competitive adsorption between H_2O and
306 NH_3 seems to be a plausible explanation [34,35].



307

308 Fig. 5 NH_3 -SCR catalytic tests over HKUST-1-Mn at 185°C in the presence of H_2O . Reaction conditions:

309 $[\text{NO}] = [\text{NH}_3] = 1000$ ppm, $[\text{O}_2] = 8$ vol.%, 3.5 vol.% H_2O , He balance, $\text{WHSV} = 80,000$ $\text{ml}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$.

