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*

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

Abstract

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

Corresponding authors:

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

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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%

1. Introduction

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

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

removal, Cu being an essential redox center for the NH_3 -SCR reaction [13–16], we choose to explore the potential of HKUST-1, a MOF based on copper paddle-wheel and benzene-1,3,5-tricarboxylate (Cu-BTC) with high specific surface area (ca. 1400–2000 m^2/g) and containing open metal sites (OMS) for NH_3 -SCR of NO_x [7,17]. Some authors assume a decomposition of HKUST-1 material and its usage as a template for CuO catalyst [18]. Surprisingly, only four reports can be found on HKUST-1 for NH_3 -SCR in which the structure of MOF has been preserved [19–21]. In these studies, no NH_3 conversion is demonstrated despite the fact that the authors reported remarkable activity at a low-temperature window, i.e. till 280°C. Li et al. [19] assumed usage of Cu-BTC activated in vacuum at different temperatures varied from 180 to 250°C. The series of experiments revealed 230°C as optimal pre-treatment temperature, giving the highest NO conversion of 100% from 220 to 280°C. The stability of the samples was not examined by the authors. The same conclusion was drawn by the authors in their second study, in which 230°C was found satisfactory as pre-treatment temperature assuming nitrogen flow for 3 h [20]. In the report of Jiang et al. [21], the effect of acetic acid (AA) solutions added during the synthesis of $\text{Cu}_3(\text{BTC})_2$ was examined. The authors showed that 25% of AA can significantly improve NO conversion, giving 95.5% at 280°C. Yao et al. [9] studied Cu-BTC promoted with Mn by post-synthetic exchange method, assuming dispersion of the support in the ethanol-based solution and usage of autoclave. In the temperature window of 230 to 260°C, the novel Mn@CuBTC catalyst showed NO conversion close to 100%. The superior performance in NH_3 -SCR was ascribed to the suitable pore sizes, enhanced redox activity arising from strong oxidizing Mn^{4+} ions, as well as a synergistic effect between Mn and Cu ions in the metal-organic framework.

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

2. Experimental

2.1. Synthesis of catalysts

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

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

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

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

2.2. Characterization methods

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

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

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

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

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

2.3. Catalytic tests

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

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

3. Results and discussion

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

Textural properties of the studied samples are listed in Table 1 (Fig. S1, ESI†). The values of specific surface area (S_{BET}) for HKUST-1 is in accordance to the data postulated by the chemical provider (Basolite® C300: 1500–2100 m²/g). For the modified samples, S_{BET} and pore volume decreased as a consequence of a partial blockage of the cavities by V, Nb and Mn species.

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

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

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

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.

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

^b determined by means of t-plot;

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

^d average atomic ratio from SEM/EDS;

^e NH₃ desorption determined by the NH₃-TPD;

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Fig. 5 NH_3 -SCR catalytic tests over HKUST-1-Mn at 185°C in the presence of H_2O . Reaction conditions: $[\text{NO}] = [\text{NH}_3] = 1000$ ppm, $[\text{O}_2] = 8$ vol.%, 3.5 vol.% H_2O , He balance, WHSV = $80,000 \text{ ml} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$.