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### COMMUNICATION

# Kinetics of degradation of sulfur mustard and sarin simulants on HKUST-1 metal organic framework<sup>†</sup>

Anuradha Roy, Avanish K. Srivastava, Beer Singh,\* Dilip Shah, Timir Haran Mahato and Anchal Srivastava

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The applicability of HKUST-1 for the degradation of sulfur mustard and sarin simulants was studied with and without coadsorbed water. Degradation was found to be *via* hydrolysis and dependent on the nucleophilic substitution reaction, vapour pressure and molecular diameter of the toxicants.

In the last few years the scientific community has shown an interest in establishing rapid and reliable decontamination processes for nerve agents, sarin (GB) and VX and for the blister agent sulfur mustard (HD). The extensive reviews on decontamination procedures published in 1992<sup>1</sup> and 2007<sup>2</sup> were mostly focused on liquid or soluble decontamination agents (mostly alkaline and oxidizing solutions): minor attention was paid to heterogeneous decontamination systems. Metal organic frameworks (MOFs) comprising metal ions or metal ion clusters and bridging organic ligands are referred to as porous coordination polymers.<sup>3</sup> In the last few years several groups have reported the use of MOFs for guest molecule binding properties and adsorption of various gases such as CCl<sub>4</sub>, DMMP.<sup>4,5</sup> Cu-BTC MOF, HKUST-1 was one of the earlier MOFs which showed interesting applications such as gas storage<sup>6,7</sup> nitric oxide adsorption<sup>8</sup> and removal of tetrahydrothiophene odorant from natural gas.<sup>9</sup>

Encouraged by the adsorption and guest molecule binding properties of MOFs, in this communication, we report the applicability of HKUST-1 for the degradation of simulants of sulfur mustard and sarin such as 2-chloroethylphenyl sulfide (CEPS), 2-chloroethyl ethyl sulfide (CEES) and diethyl chloro phosphate (DECIP), diethyl cyano phosphonate (DECNP) respectively.

Herein we have synthesized HKUST-1 by a solvothermal method and thereafter, characterized it using a surface area analyzer, a scanning electron microscope, a powder X-ray diffractometer, a Fourier transform infrared spectrophotometer and a thermogravimetric analyzer. Thereafter HKUST-1 was studied for the degradation kinetics of sulfur mustard and sarin simulants.

 $N_2BET$  adsorption isotherm was type-I and the surface area (ESI, Fig. S1<sup>†</sup>) was found to be 1645 m<sup>2</sup> g<sup>-1</sup>. The total pore volume and  $N_2$ -DR micropore volume was measured to be 0.833

and 0.804 cc g<sup>-1</sup>. The average pore size and pore maxima were found to be 20.27 Å and 5.7 Å respectively. The SEM image (ESI, Fig. S2a†) of the synthesized HKUST-1 indicated the formation of octahedral crystals while the phase purity was checked by powder XRD and the spectra (ESI, Fig. S3†) obtained was in accordance with the one reported in the literature for this specific network.<sup>6</sup>

TGA data (ESI, Fig. S4<sup>†</sup>) showed the first weight loss at 100 °C corresponding to the removal of physically adsorbed water and a sharp decrease of weight at 350–400 °C was indicative of decomposition of carboxyl groups and complete breakdown of HKUST-1 was observed at above 400 °C. The FTIR spectrum (ESI, Fig. S5<sup>†</sup>) showing peaks at 1300–1700 cm<sup>-1</sup>, was indicative of the coordination of trimesic acid with Cu. More precisely peaks at 1646 cm<sup>-1</sup>, 1599 cm<sup>-1</sup> and 1450 cm<sup>-1</sup>, 1374 cm<sup>-1</sup> corresponded to asymmetric and symmetric vibration of coordinated carboxyl groups.

The degradation kinetics was studied by exposing HKUST-1 to CEES, CEPS, DECIP and DECNP under ambient conditions.

Kinetic plots shown in Fig. 1 exhibited that initial degradation of toxicants were faster followed by a steady state reaction indicating the first order reaction. The fast initial reaction is attributed to the rapid adsorption and distribution of the toxicants within the pores and its interaction with the accessible reactive sites. The limited surface reaction occurs when the sites are exhausted, obviously, replacing the initial fast reaction by a steady state reaction. The result indicates that the degradation of CEES is faster than CEPS. The half-lives for the degradation of CEES and CEPS were found to be 16.11 and 75.27 min, respectively (Table 1). DECNP was found to degrade relatively faster



Fig. 1 Kinetics of degradation of CEES, CEPS, DECIP and DECNP.

Defence Research and Development Establishment, Jhansi Road, Gwalior 474 002, (M.P.), India. E-mail: beerbs5@rediffmail.com; Fax: +91-751-2233482; Tel: +91-9893040985

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**Table 1** Kinetics parameters for the degradation of CEES, CEPS,DECIP and DECNP on HKUST-1

Toxicants	CEES	CEPS	DECIP	DECNP
Rate constant $(k)$ (min <sup>-1</sup> )	0.043	0.009	0.007	0.011
Half life $(t_{1/2})$ (min)	16.11	75.27	60.18	42.98



Scheme 1 Reactions products of CEES and CEPS.

than DECIP with a half-life of 42.98 min (Table 1). The order for degradation of studied stimulants of sulfur mustard was: CEES > CEPS and for sarin was: DECNP > DECIP. No degradation of toxicants was observed with blank solution without MOF (Fig. 1).

Kinetic studies indicated that the degradation of CEES is faster than CEPS which is in accordance with the neighboring group participation phenomenon. The slow degradation of CEPS is because of resonance involvement of the lone pair of the sulfur atom in the phenyl ring, which in turn decreases the neighboring group participation hence decreasing the leaving group tendency of Cl<sup>-</sup>. In the case of CEES, the ethyl group attached to the sulfur atom acts as an electron releasing group which increases the electron density on the sulfur atom. The increased electron density on the sulfur atom results in an increase in neighboring group participation and makes Cl<sup>-</sup> a better leaving group as shown in Scheme 1. Kinetic studies also indicated that DECNP degraded faster than DECIP. The fast degradation of DECNP is due to the better leaving tendency of CN<sup>-</sup> as compared to Cl<sup>-</sup> of DEClP. Moreover, the order of degradation of the toxicants are in line with their vapour pressure (Table 2). Toxicants with higher vapour pressure will diffuse more rapidly and result in a faster rate of degradation.

On the other hand the effect of molecular size of the toxicant on the adsorption over MOF cannot be ruled out. The reason for the slower degradation of CEPS than CEES and DECIP than DECNP lies in the fact that the larger the size of the molecule the slower will be the adsorption (Table 2). Molecular diameter was calculated using the equation in ref. 10. The molecular size of CEPS is greater than CEES and DECIP is greater than DECNP. Therefore, toxicants having a bigger size cause slower adsorption and degradation of CEPS and DECIP relative to their counterparts due to steric hindrance. Kinetic studies also indicated that the degradation of DECNP is faster than CEPS which is not in accordance with their molecular diameter based adsorption. The fast degradation of DECNP is attributed to a better leaving tendency of  $CN^-$  which results in fast hydrolysis of the DECNP.

Table 2	Vapor	pressure	and	molecular	diameter	of	CEES,	CEPS,
DECIP an	d DEC	NP on Hk	UST	-1				

Toxicants	CEES	CEPS	DECIP	DECNP
Vapor pressure (mm Hg/25 °C)	3.789	0.043	0.100	0.158
Molecular diameter (Å)	6.98	8.6	12	10

Table 3 Reusability of HKUST-1 for degradation of CEES

No. of cycle	BET surface area $(m^2 g^{-1})$	Micropore volume $(cc g^{-1})$	% of degradation
1st	1645	0.804	92
2nd	441	0.214	70
3rd	43	0.018	50

The high surface area of the MOF was found to facilitate the faster degradation of toxicants. The role of the surface area and porosity was further confirmed by reaction of CEES with copper acetate monohydrate which has a similar coordination environment to that of HKUST-1 but a very low surface area (>5 m<sup>2</sup> g<sup>-1</sup>). Results indicated an insignificant degradation (approx. 7%) of CEES over 3 h by copper acetate monohydrate whereas MOF degraded more than 91% in 40 min (Fig. 1).

The effect of coadsorbed moisture on the degradation of sulfur mustard and sarin simulants was also studied. The degradation obtained for CEES and CEPS with HKUST-1 containing 10  $\mu$ L of water was found to be 67 and 38% only whereas, activated MOF having negligible moisture indicated 83 and 72% degradation of CEES and CEPS respectively.

The reason for the decreased degradation of CEES and CEPS by the MOF containing moisture is due to the blockage of the active sites of the MOF by the pre-adsorbed water molecules. The high moisture in MOF results in the formation of a thin film of water over the surface of the MOF, which worked as a barrier for the adsorption of lipophilic CEES and CEPS and caused the slower degradation of CEES and CEPS.<sup>11</sup> The degradation of DECIP and DECNP were found to be 60, 83% on MOF with the coadsorbed water and 48, 78% respectively on activated MOF containing negligible moisture. Here the degradation of the nerve agent simulants is enhanced on the MOF containing water is attributed to the hydrophilic character of the nerve agent simulants.

Based on the faster degradation of toxicants, CEES was selected for checking the reusability of the HKUST-1. Reusability tests indicated that the MOF can degrade CEES efficiently up to the 4th cycle. The fresh samples showed 92% degradation in 2 h whereas in 2nd, 3rd and 4th cycle degradation it was found to decrease up to 70, 50 and 45% respectively. Deactivation of MOF is attributed to the strong adsorption of products, quite evident from the reducing surface area with increased reaction cycles (Table 3) and EDAX spectra (ESI, Fig. S6†) indicating the presence of sulfur and chlorine. Another reason for the deactivation is the irreversible collapse of the structure; evident from SEM images (ESI, Fig. S2b–c†) due to the migration of the framework metal ions because of reaction with hydrochloric acid resulted from hydrolysis of CEES with the increased reaction cycles.



Scheme 2 Reactions products of DECIP and DECNP.

In order to understand the reaction pathways the reaction products were analyzed using GC-MS (Schemes 1 and 2). GC-MS data of the reaction products of CEES, CEPS (ESI, Fig. S7–S8†) indicated the formation of the hydrolysis products<sup>1,12</sup> *i.e.*, 2-hydroxyethyl ethyl sulfide (HEES) (m/z at 47, 53, 75, 96, 106) and hydroxy ethyl phenyl sulfide (HEPS) (m/z 45, 59, 73, 91, 103, 137, 167, 211, 226). A similar reaction pathway was observed for the degradation of DECIP and DECNP on HKUST-1. GC-MS data (ESI, Fig. S9†) showed the formation of diethyl phosphate (DEP) (m/z 45, 65, 81, 96, 113, 127, 147, 155, 167) as the hydrolysis product of DECIP and DECNP.

The formation of the reaction products can be explained by a detailed understanding of the structure of HKUST-1. The structure is composed of large hydrophilic type central cavities (diameter 9.0 Å) surrounded by small pockets (diameter 5.0 Å), these pores are less hydrophilic as they are encircled by four benzene rings.<sup>13</sup> The average pore diameter of the synthesized HKUST-1 was found to be 20.27 Å. Each metal corner has two copper atoms bonded to the oxygen of four BTC linkers. In the as-synthesized material, each copper atom is also coordinated to one water molecule that is, two water molecules for each paddlewheel metal corner, corresponding to 8 wt% water loading. The presence of water molecules in the first coordination sphere of Cu<sup>2+</sup> ions has suggested the possibility of obtaining a coordinative vacancy on the Cu<sup>2+</sup> species. The partial positive charge on the metal sites in HKUST-1 enhances the adsorption properties.<sup>14</sup> Therefore, toxicant molecules were attracted by the attractive forces and adsorbed in the pores of the MOF by physisorption. Thereafter adsorbed toxicant molecules reacted with chemisorbed water molecules and resulted in the formation of the hydrolysis products.

In summary, kinetic studies indicated that the degradation of CEES is faster than CEPS because of the neighboring group participation effect. DECNP degraded faster than DECIP due to a better leaving tendency of  $CN^-$  as compared to  $Cl^-$ . The molecular diameter and vapour pressure of the toxicants was also found to influence the adsorption properties of the MOF as toxicants having a bigger size and lower vapour pressure caused by steric hindrance and slow diffusion which in turn results in slow adsorption as well as degradation. The study clearly indicates that HKUST-1, is a potential material for degradation of toxicants *via* hydrolysis, therefore, HKUST-1 can be effectively used for *in situ* degradation of nerve and blister agents. This study may lead to the development of an efficient NBC filtration system and decontamination formulation based on MOFs.

Caution: Since the CW agents are highly toxic in nature, these experiments should only be performed by trained personnel using appropriate protective gear in a high-quality fuming hood.

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#### Notes and references

- 1 Y. C. Yang, J. A. Baker and J. R. Ward, Chem. Rev., 1992, 92, 1729.
- 2 S. S. Talmage, A. P. Watson, V. Hauschild, N. B. Munro and J. King, *Curr. Org. Chem.*, 2007, 11, 285.
- 3 C. T. Chen and K. S. Suslick, Coord. Chem. Rev., 1993, 128, 293.
- 4 S. Calero, A. M. Calvo, S. Hamad and E. García-Pérez, *Chem. Commun.*, 2011, **47**, 508.
- 5 F. J. Ma, S. X. Liu, C. Y. Sun, D. D. Liang, G. J. Ren, F. Wei, Y. G. Chen and Z. M. Su, J. Am. Chem. Soc., 2011, 133, 4178.
- 6 P. Krawiec, M. Kramer, M. Sabo, R. Kunschke, H. Frode and S. Kaskel, Adv. Eng. Mater., 2006, 8, 293.
- 7 O. M. Yaghi and J. L. C. Rowsell, J. Am. Chem. Soc., 2005, 128, 1304.
- 8 B. Xiao, P. S. Wheatley, X. Zhao, A. J. Fletcher, S. Fox, A. G. Rossi, I. L. Megson, S. Bordiga, L. Regli, K. M. Thomas and R. E. Morris, *J. Am. Chem. Soc.*, 2007, **129**, 1203.
- 9 U. Mueller, M. Schubert, F. Teich, H. Puetter, K. Schierle-Arndt and J. Pastre, J. Mater. Chem., 2006, 16, 626.
- 10 W. D. Harkins and G. Jura, J. Am. Chem. Soc., 1944, 66, 1366.
- 11 G. W. Wagner, G. W. Peterson and J. J. Mahle, *Ind. Eng. Chem. Res.*, 2012, **51**, 3598.
- 12 H. Tang, Z. Cheng, H. Zhu, G. Zuo and M. Zhang, *Appl. Catal.*, *B*, 2008, 79, 323.
- 13 S. S. Y. Chui, S. M. F. Lo, J. P. H. Charmant, A. G. Orpen and I. D. Williams, *Science*, 1999, 283, 1148.
- 14 L. C. Rowsell and O. M. Yaghi, Angew. Chem., Int. Ed., 2005, 44, 4670.