Highly selective adsorption of ethylene over ethane in a MOF featuring the combination of open metal site and π-complexation
Zhang, Y.; Li, B.; Krishna, R.; Wu, Z.; Ma, D.; Shi, Z.; Pham, T.; Forrest, K.; Space, B.; Ma, S.

Published in:
Chemical Communications

DOI:
10.1039/c4cc09774b

Citation for published version (APA):
The introduction of the combination of open metal site (OMS) and π-complexation into MOF for the first time, as exemplified in the context of MIL-101–Cr–SO3Ag, which demonstrates exceptional ethylene–ethane adsorption selectivity at 318 K, surpassing benchmark porous solid materials of zeolites, MOFs and PAFs. The interactions with ethylene from both OMSs and π-complexation in MIL-101–Cr–SO3Ag have been investigated by in situ IR spectroscopic studies and computational calculations, which suggest that π-complexation contributes dominantly to the high ethylene–ethane adsorption selectivity.

Due to their high surface areas, tunable pore sizes, and functionalizable pore surfaces as well as the amenability of design and modular nature, metal–organic frameworks (MOFs) have been recently explored as a new type of porous solid materials for hydrocarbon separation, including the separation of ethylene–ethane mixtures. Extensive efforts have been devoted to the creation of open metal sites (OMSSs) in MOFs to enhance the selectivity of ethylene over ethane, due to the stronger interactions of ethylene with OMSs compared with ethane. Recently, we demonstrated that a Ag(I) ion functionalized porous aromatic framework (PAF) exhibited exceptional ethylene–ethane adsorption selectivity as a result of the formation of π-complexation between ethylene molecules and Ag(I) ions. We speculate that if such a kind of π-complexation can be coupled with OMSs into MOFs, the adsorption selectivity of ethylene over ethane can be further enhanced in MOFs because of the strong interactions with ethylene from both π-complexation and OMSs. In this contribution, we report the introduction of the combination of OMSs and π-complexation into MOF for the first time, as exemplified in the context of MIL-101–Cr–SO3Ag, which demonstrates exceptional ethylene–ethane adsorption selectivity at 318 K, surpassing benchmark porous solid materials of zeolites, MOFs and PAFs.
The low-pressure ethylene–ethane sorption isotherms were collected at 296 K and 318 K. Compared with the pristine MIL-101–Cr–SO3H, the introduction of Ag(I) ion into MIL-101–Cr–SO3H results in a significant enhancement of ethylene adsorption capacity despite the decrease in surface area. Under 1 atm pressure, the ethylene uptake amounts increase from 42 cm\(^3\) g\(^{-1}\) at 296 K and 37 cm\(^3\) g\(^{-1}\) at 318 K for MIL-101–Cr–SO3H to 73 cm\(^3\) g\(^{-1}\) at 296 K and 63 cm\(^3\) g\(^{-1}\) at 318 K for MIL-101–Cr–SO3Ag (Fig. 1). Interestingly, in contrast to the ethylene adsorption, the uptake amounts of ethane at 296 K and 318 K for two samples are comparable (Fig. S4 and S5, ESI\(^\dagger\)), suggesting that the introduction of Ag(I) ions would not increase the ethane uptake capacity.

Ethylene–ethane adsorption selectivities were calculated using ideal adsorbed solution theory (IAST)\(^1\) for MIL-101–Cr–SO3H and MIL-101–Cr–SO3Ag (Fig. 2). For an equimolar mixture of ethylene and ethane at 318 K, the adsorption selectivity \(S_{\text{ads}}\) obtained for MIL-101–Cr–SO3Ag is 9.7 at 100 kPa, far exceeding that calculated for MIL-101–Cr–SO3H \(S_{\text{ads}} = 1.2\). This result suggests the predominant contribution from Ag(I) ion in comparison with the OMS of Cr(III) to the enhancement of ethylene–ethane adsorption selectivity.

The ethylene–ethane adsorption selectivity of MIL-101–Cr–SO3Ag at 318 K and 100 kPa is also significantly higher than those of the zeolite NaX\(^8\), the MOFs\(^8\) CoMOF-74 [also known as [a.k.a.] Co\(_2\)(dobdc)], MgMOF-74 [a.k.a. Mg\(_2\)(dobdc)], CuBTC [a.k.a. HKUST-1] (Fig. 2), exhibiting ethylene–ethane selectivities of 6.8, 5.7, 4.7, and 3.8, respectively. It slightly surpasses the best performance MOF of FeMOF-74 [a.k.a. Fe\(_2\)(dobdc)] \(S_{\text{ads}} = 8.9\) and PAF of PAF-1–SO3Ag\(^9\) \(S_{\text{ads}} = 6.9\). It is worth noting that the higher ethylene–ethane adsorption selectivities of MIL-101–Cr–SO3Ag compared to PAF-1–SO3Ag indicate the possible cooperative contribution from the OMS of Cr(III) to further boosting the ethylene–ethane adsorption selectivities for MIL-101–Cr–SO3Ag.

To provide a better understanding of the exceptional ethylene adsorption properties of MIL-101–Cr–SO3Ag, the isosteric heats of adsorption \(Q_{\text{st}}\) were calculated using the Clausius–Clapeyron equation by differentiation of the dual Langmuir–Freundlich fits of the isotherms at two different temperatures,\(^7\)\(^c\)\(^\dagger\) 296 K and 318 K with \(T\)-dependent parameters. As shown in Fig. 3, close to zero loading, the \(Q_{\text{st}}\) for ethylene in MIL-101–Cr–SO3Ag is 63 kJ mol\(^{-1}\), remarkably higher than that of MIL-101–Cr–SO3H (10 kJ mol\(^{-1}\)). These results highlight the role of introducing Ag(I) ions in further boosting the interactions with ethylene molecules that stem from the formation of the π-complexation bonding between the d orbital of Ag(I) and the π* orbital of carbon–carbon double bonds in ethylene.\(^1\)\(^2\) In contrast to the high \(Q_{\text{st}}\) for ethylene, MIL-101–Cr–SO3Ag shows a significantly lower \(Q_{\text{st}}\) for ethane with a value of 16 kJ mol\(^{-1}\) (Fig. S6, ESI\(^\dagger\)).
thus validating that MIL-101–Cr–SO3Ag featuring the combination of OMS and π-complexation can selectively adsorb ethylene over ethane thereby resulting in high ethylene–ethane adsorption selectivities particularly at a relatively high temperature of 318 K.

In situ IR measurements of ethylene adsorption at room temperature gave further insight into the nature of interactions between ethylene molecules and the Ag( I) ions in MIL-101–Cr–SO3Ag. As shown in Fig. 4, the appearance of IR features at 975 cm⁻¹ corresponds to the ethylene adsorption on the surface of porous materials. MIL-101–Cr–SO3Ag exhibits a stronger ethylene interaction than that of MIL-101–Cr and MIL-101–Cr–SO3H, which is evidenced by the complete disappearance of ethylene IR features at 975 cm⁻¹ for the two compared samples after room temperature desorption in helium purge gas. The extra IR features at 1952 cm⁻¹ (combination mode of –CH2 wagging), not observed on the MIL-101–Cr and MIL-101–Cr–SO3H, further confirm stronger ethylene interactions on MIL-101–Cr–SO3Ag. The blue-shift of the –CH2 wagging mode can be attributed to the combinative d–π and d–π* interaction between Ag and ethylene,13–16 as a result of the formation of π-complexation between the ethylene and Ag( I) ions in MIL-101–Cr–SO3Ag.

To further understand the interactions of ethylene–Ag(I) ion and ethylene–Cr(III) OMS, we used electronic structure calculations to estimate the bond length between ethylene and Ag(i) as well as the bond length between ethylene and Cr(III). A (C6H3(CO2)2)SO3Ag cluster was considered for this calculation since it is expected that MIL-101–Cr–SO3Ag contains this moiety. Starting with the sulfonyl terephthalate unit, a silver ion was placed in proximity to the oxygen atoms of the sulfonate group. The Ag(i) ion was optimized to an energetically favorable position within the cluster. Afterwards, an optimized ethylene molecule was placed in proximity to the Ag(i) ion in the (C6H3(CO2)2)SO3Ag cluster. The optimization of the C2H4–Ag(i) interaction was executed using the DFT method. It was observed that the distances between the Ag(i) ion and the carbon atoms of the C2H4 molecule were found to be 2.18 and 2.19 Å (Fig. 5a). A similar calculation was performed between the ethylene molecule and the Cr(III) OMSs, and the optimized C2H4–Cr(III) distances were observed to be 2.54 and 2.55 Å (Fig. 5b). These results suggest that the interactions between ethylene and Ag(i) are much stronger than those between Cr(III) OMSs and they should contribute dominantly to the high adsorption selectivity of MIL-101–Cr–SO3Ag for ethylene–ethane.

Given the reasonable accuracy of simulated breakthrough characteristics as validated by recent investigations,13–16 we carried out breakthrough simulations for C2H4–C2H6 mixtures in a fixed bed to demonstrate the feasibility of producing 99.95% + pure C2H4 in a Pressure Swing Adsorption (PSA) operation. The simulated breakthrough curves of Fig. S9 (ESI†) show transient breakthrough of an equimolar C2H4–C2H6 mixture in an adsorber bed packed with MIL-101–Cr–SO3Ag. During the adsorption cycle, C2H4 at purities >99% can be recovered for a certain duration of the adsorption cycle as indicated by the arrow in Fig. S10 (ESI†). In addition, ethylene of 99.95% + purity, required as feedstock to the polymerization reactor, can also be recovered during the time interval indicated by the arrow in Fig. S11 (ESI†) in the desorption cycle.

In summary, we have demonstrated the introduction of open metal site (OMS) and π-complexation into MOF, affording MIL-101–Cr–SO3Ag as an efficient adsorbent for separation of ethylene–ethane. MIL-101–Cr–SO3Ag exhibits significantly higher ethylene–ethane adsorption selectivity at 318 K than benchmark zeolites, MOFs and PAFs reported in the literatures. The high ethylene–ethane adsorption selectivity of MIL-101–Cr–SO3Ag are mainly attributed to the π-complexation between Ag(i) ions and the double bond of ethylene molecules, which is reflected in the high isosteric heats of adsorption of C2H4 and evidenced using in situ IR spectroscopy studies and computational calculations. In addition, the possible cooperative contribution from the OMS of Cr(III) to further enhancing the ethylene–ethane adsorption selectivities have been proved by the higher ethylene–ethane adsorption selectivities of MIL-101–Cr–SO3Ag compared to PAF-1–SO3Ag. The feasibility of MIL-101–Cr–SO3Ag for producing 99.95% + pure C2H4 in a PSA operation has also been demonstrated by breakthrough simulations. Our strategy of introducing dual functional sites into
MOF to afford high ethylene–ethane adsorption selectivities particularly above room temperature paves a new way for developing MOFs for energy-saving ethylene–ethane and other olefin/paraffin separations.

The authors acknowledge the University of South Florida and the National Science Foundation (DMR-1352065) for financial support of this work. A portion of this research including the in situ IR work was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility. B.S. acknowledges the National Science Foundation (Award No. CHE-1152362), the computational resources that were made available by a XSEDE Grant (No. TG-DMR090028), and the use of the services provided by Research Computing at the University of South Florida.

Notes and references