VIP **Adsorption** *Very Important Paper*

Deutsche Ausgabe: DOI: 10.1002/ange.201500251
Internationale Ausgabe: DOI: 10.1002/anie.201500251

High Ethene/Ethane Selectivity in 2,2′-Bipyridine-Based Silver(I) Complexes by Removal of Coordinated Solvent**

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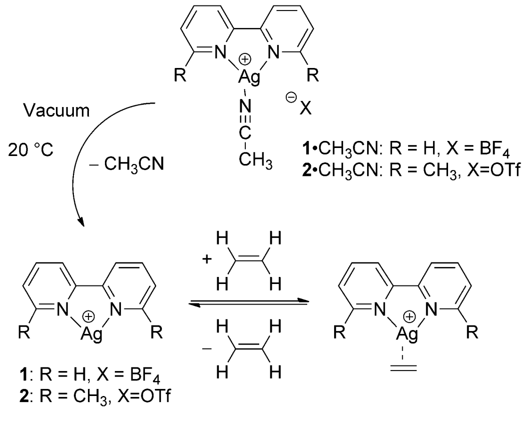
Abstract: *Following removal of coordinated CH_3CN, the resulting complexes $[Ag^I(2,2'\text{-bipyridine})][BF_4]$ (**1**) and $[Ag^I(6,6'\text{-dimethyl-}2,2'\text{-bipyridine})][OTf]$ (**2**) show ethene/ethane sorption selectivities of 390 and 340, respectively, and corresponding ethene sorption capacities of 2.38 and 2.18 mmol g^{-1} when tested at an applied gas pressure of 90 kPa and a temperature of (20 ± 1) °C. These ethene/ethane selectivities are 13 times higher than those reported for known solid sorbents for ethene/ethane separation. For **2**, ethene sorption reached 90 % of equilibrium capacity within 15 minutes, and this equilibrium capacity was maintained over the three sorption/desorption cycles tested. The rates of ethene sorption were also measured. To our knowledge, these are the first complexes, designed for olefin/paraffin separations, which have open silver(I) sites. The high selectivities arise from these open silver(I) sites and the relatively low molecular surface areas of the complexes.*

The separation of olefins from paraffins is an industrially important process required for the production of pure olefin feedstocks. In particular, worldwide ethene production exceeded 74 million metric tons in 2004, thus making it the most widely produced organic chemical.[1] The steam-cracking process used to produce olefins results in an olefin/paraffin mixture which is typically separated by cryogenic distillation, and is both energy and capital intensive.[2] In the search for more-energy-efficient separation methods, both solid sorbents and facilitated-transport membranes have been investigated.[2,3] Both technologies commonly rely on the use of olefin-complexing agents which contain a transition-metal ion, typically silver(I) or copper(I), and are capable of selective ethene adsorption.[3a] The sorbents developed include silver(I) salts,[4] silver(I) salt solutions,[5] silver(I) or copper(I) polymers,[6] and metal–organic frameworks (MOFs).[7] Silver(I)-containing porous polymers and MOFs have large surface areas and high densities of silver(I) sites, thus resulting in high ethene uptakes.[7a] However, the large non-active surface areas that often comprise aromatic groups also allow significant ethane uptake and therefore limit ethene/ethane selectivities.[7a]

The use of mononuclear silver(I) coordination complexes for ethene/ethane separations is a relatively unexplored research area, and to our knowledge, has not received dedicated attention.[6b] The benefits of using such materials for this application are increased synthetic control over the ligand design, with no need to control secondary reactivity, as is the case for silver(I)-containing polymer or MOF formation. Manipulation of ligand design can allow more precise control over the strength of ethene binding and the active/inactive surface area ratio. The inclusion of coordinated solvent molecules is widely used to produce molecules with masked reactive metal ion sites which can be activated upon removal of the coordinated solvent.[8] To our knowledge, this approach has not been combined with silver(I) ions as a strategy for producing ethene/ethane separation materials. Herein, we show that room-temperature in vacuo removal of coordinated CH_3CN from the known complexes $[(Ag^I(2,2'\text{-bipyridine})(CH_3CN)][BF_4]$[9] ($\mathbf{1}\cdot CH_3CN$) and $[Ag^I(6,6'\text{-dimethyl-}2,2'\text{-bipyridine})(CH_3CN)][OTf]$[10] ($\mathbf{2}\cdot CH_3CN$)] produces the unreported activated complexes **1** and **2** with open silver(I) sites which display ideal ethene/ethane sorption selectivities one order of magnitude higher than previously reported materials, as well as good ethene sorption capacities (Scheme 1).



Scheme 1. The mild activation of $\mathbf{1}\cdot CH_3CN$ and $\mathbf{2}\cdot CH_3CN$ to form the solid-state materials **1** and **2**, which exhibit reversible and selective ethene versus ethane binding. Tf = trifluoromethanesulfonyl.

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[**] We thank the Membrane Applied Science and Technology Center for partially funding this research. We also thank Prof. R. K. Shoemaker at CU Boulder for performing the solid-state NMR studies and S. M. Dischinger for performing the PXRD work.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201500251.

To investigate the effectiveness of activating silver(I) sites in solid-state materials by removal of coordinated solvent, we prepared the complexes **1**·CH_3CN and **2**·CH_3CN,[9,10] which have been previously synthesized and structurally characterized by single-crystal X-ray diffraction, and showed CH_3CN coordinated to the silver(I) center.[9,10] Since no bulk characterization has been reported for these two complexes, we employed thermogravimetric analysis (TGA), FT-IR spectroscopy, solid-state ^{13}C NMR spectroscopy, and elemental analysis to ensure that coordinated CH_3CN was present in the bulk materials **1**·CH_3CN and **2b** (see Section S2 in the Supporting Information).

We also examined the TGA, FT-IR, and ^{13}C NMR profiles of $[Ag^I(2,2'\text{-bipyridine})][NO_3]$ (**3**) and $[Ag^I(2,2'\text{-bipyridine})][OTf]$ (**4**) to confirm the absence of coordinated CH_3CN in these materials (see Section S2). The crystal structures of **3** and **4** do not contain CH_3CN and show that the anions are coordinated to the silver(I) ions.[11] Consequently, **3** and **4** were not expected to form open silver(I) sites upon evacuation or selectively bind with ethene, and thus served as control samples. Precautions were taken to limit exposure of the complexes to light. However, all the samples were stable enough to be handled in open air prior to characterization and ethene/ethane testing.

Table 1 summarizes the ethene gas uptake and ethene/ethene sorption selectivity for complexes **1**–**4**. Samples of **1** and **2** were obtained by evacuating (< 13 Pa) **1**·CH_3CN and **2**·CH_3CN at 20 °C for 3 hours. The loss of coordinated CH_3CN was confirmed by FT-IR spectroscopy (see Section S2.3). The ethene uptake of the activated materials **1** and **2** was 2.38 and 2.18 $mmol_{ethene}/g_{sorbent}$, respectively, with corresponding ethene/ethane selectivities of 390 and 340. For consistency, **3** and **4** were pre-treated and tested using the same procedures.

Figure 1 shows how the equilibrium capacity and selectivity of **1** and **2** compare against those of other solid sorbent materials in the literature which have been used for ethene/ethane separations. Since the mononuclear complexes are not porous, they have surface areas of less than or equal to $10\ m^2\,g^{-1}$ (dependent on crystal size), and the ethane uptake is relatively low compared to that of silver(I)-containing polymers and MOFs, which often have surface areas in the hundreds of $m^2\,g^{-1}$. Therefore, limiting the inactive/active surface area ratio is an excellent method to increase ethene/ethane selectivity. In comparison, samples of **3** and **4** [which do not have open silver(I) sites] have ethene uptakes of less than $0.01\ mmol\,g^{-1}$ and ethene/ethane selectivities of less than 4 (Table 1).

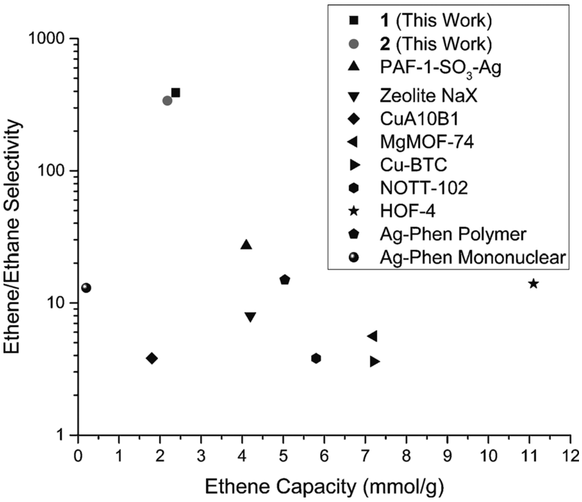

Figure 1. The ethene sorption capacity and ethene/ethane selectivity values of **1** and **2** compared with leading materials for ethene/ethane sorptive separations in the literature. The detailed values and references can be found in Table S4.

Table 1: The equilibrium ethene uptake and ethene/ethane selectivities of the solid-state materials **1**–**4**.[a]

Complex	$mmol_{ethene}/g_{complex}$	$cc_{ethene}/g_{complex}$	$mol_{ethene}/mol_{silver(I)}$	Ethene/ethane selectivity
1	2.38 (0.006)	53.4 (0.136)	0.934 (0.002)	390
2	2.18 (0.006)	48.8 (0.143)	0.962 (0.003)	340
3	0.008 ± 0.003	0.19 ± 0.06	0.004 ± 0.001	4
4	0.005 ± 0.004	0.28 ± 0.09	0.002 ± 0.001	0.3

[a] The uptakes and selectivities of **1** and **2** at 90 kPa were measured using a Quantachrome Autosorb AS1-C instrument. Ethane uptakes are reported within parentheses. The ethene and ethane uptake values of **3** and **4** were measured using the pressure drop method as described in Section S2.9.

It is known that the counterion has a significant effect on the olefin uptake capacity of silver(I)-containing ionic materials.[3a] Therefore, the comparison of **2** and **4**, which both contain the OTf^- anion and have been structurally characterized,[10,11] demonstrates that a coordinated solvent can be used to mask the silver(I) centers from undesirable interactions. The coordinated solvent can later be removed, resulting in "open" silver(I) centers that are highly active for ethene binding. As the ethene sorption capacity is retained over several sorption/desorption cycles, we infer that the anion is unable to rearrange and bind to the silver(I) center in the solid state. It should be noted that **1** has been recrystallized as a coordination polymer with the formula $([Ag^I(2,2'\text{-bipyridine})][BF_4]\cdot CH_2Cl_2)_\infty$ following dissolution. However, we assume that the structure rearranges during the recrystallization process.[9]

The ethane sorption isotherms of **1** and **2** (see Section S2.10) show very low capacities that are consistent with surface adsorption. In contrast, the ethene loadings (see Figure 2 and Sections S2.9 and S2.10) are low at low pressure, but sharply increase over a range of only a few Pa. The pressure at which the sharp increase in loading was observed increased with temperature. The ethene isotherms also showed significant hysteresis during desorption. Similar sorption isotherms have been observed for hydrocarbons in a MOF.[12] In that case, a gate-opening effect was attributed to hydrogen-bonding interactions. Stepwise isotherms have also been observed in MOFs in which a phase change is induced by guest binding.[13] The underlying cause of the stepwise adsorption in **1** and **2** (which do not have obviously flexible structures), is currently unclear and remains under investigation. For **2**, van't Hoff analysis of the ethene adsorption isotherms collected at 21, 40, and 60 °C resulted in an

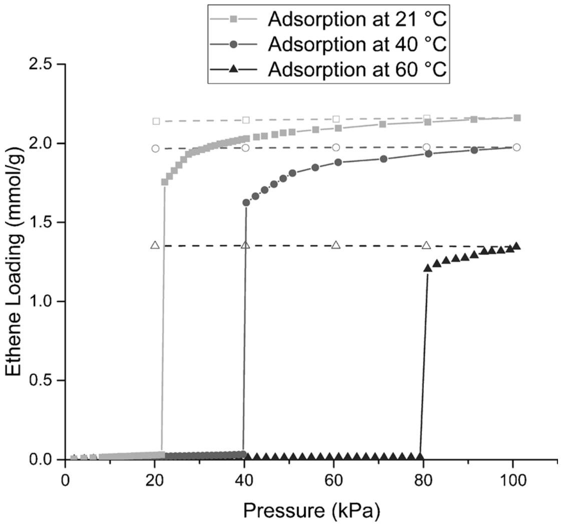

Figure 2. The ethene adsorption (solid line) and desorption (dashed line) isotherms of **2** at 21, 40, and 60 °C.

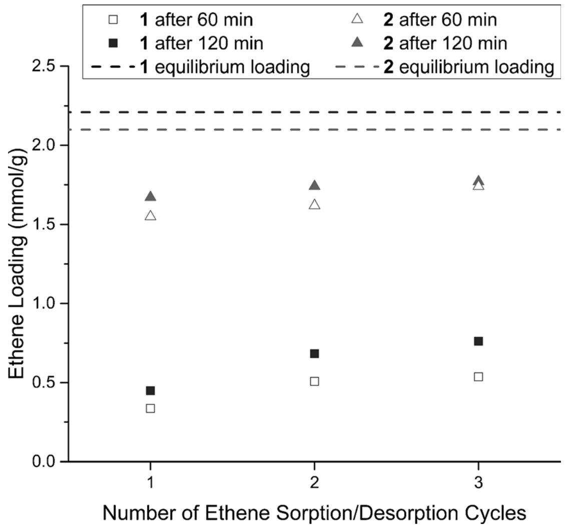

Figure 3. The ethene uptake of **1** and **2** after 1 and 2 h over multiple sorption/desorption cycles at an equilibrium pressure of 46 kPa. The detailed data are tabulated in Table S2.

estimated isoteric heat of adsorption of $-57\,\mathrm{kJ\,mol^{-1}}$. This value is significantly lower than that reported for ionic RSO_3^-–Ag^+ interactions ($-106\,\mathrm{kJ\,mol^{-1}}$).[7a] The estimated energy of desorption was estimated from differential scanning calorimetry (DSC) to be $56\,\mathrm{kJ\,mol^{-1}}$. Through ligand design, open silver sites in coordination complexes may offer more precise control over the silver(I)–ethene interaction relative to silver(I)–anion interactions. This control would allow optimization of the silver(I)–ethene interactions for industrial separations.

That **1** and **2** are not porous, yet achieve molar ethene uptake capacities of about 1 $\mathrm{mol_{ethene}/mol_{silver(I)}}$, shows that ethene can diffuse into the materials within the 18 hour duration of the isotherm measurements. The 1 $\mathrm{mol_{ethene}/mol_{silver(I)}}$ loading capacity also shows that the high surface areas are not necessary for achieving high (and selective) ethene capacities. However, we anticipate that the porous nature and therefore high surface areas of porous materials should result in higher rates of ethene uptake. Unfortunately, we have been unable to find comparative uptake rate data in the literature for other silver(I)-based solid sorbent materials and therefore cannot verify this hypothesis at this time.

For use in commercial olefin/paraffin separations, consideration of the ethene adsorption and desorption rates is also important. The single-gas sorption of ethene and ethane were tested at 46 kPa over three sorption/desorption cycles using a pressure-drop method[6b,14] (see Figure 3 and Table S1). During the first cycle of **1**, the capacity only reached 15 and 20 % of the equilibrium capacity after 1 and 2 hours, respectively. In the third cycle, those numbers increased to 24 (1 h) and 34 % (2 h). In contrast, the ethene adsorption kinetics of **2** were faster with loadings of 73 (1 h) and 80 % (2 h) as measured during the first cycle, and then increasing to 83 (1 h) and 84 % (2 h) in the third cycle. Gas desorption between cycles was achieved by evacuation (<0.1 Pa) at 21 °C for 24 and 6 h for **1** and **2**, respectively. The powder X-ray diffraction (PXRD) profiles of **2** before and after ethene sorption/desorption show very little change, thus indicating that its solid-state structure is effectively maintained (see Section S2.12 in the Supporting Information).

The difference in ethene uptake rate between **1** and **2** appears to be related to the molecular structures of the materials, which we assume remain intact after the removal of coordinated solvent. In the crystal structure of **1**·CH_3CN, only one-third of the silver(I) sites are completely open, with two-thirds of them connected by Ag^I–Ag^I bonds, (3.089 Å).[9] This structure is consistent with the complex reaching a 0.37 $\mathrm{mol_{ethene}/mol_{silver(I)}}$ uptake relatively rapidly, followed by slow uptake to about 1 $\mathrm{mol_{ethene}/mol_{silver(I)}}$. In contrast, the crystal structure of **2**·CH_3CN reveals no close contacts to the silver(I) centers, apart from the coordinated ligands, and reaches full loading comparably quickly.[10] Therefore, the accessibility of the silver(I) site may play a key role in the rate of ethene adsorption.

The rate of desorption is also important for recovering the product and reusing the sorbent. Complete desorption of **1** and **2** was achieved by application of a vacuum (≤ 0.01 kPa) at 20 °C. However, direct measurement of the desorption rate was complicated by the hysteresis in the sorption isotherms. For example, the desorption rate could not be measured using the reverse of the pressure drop method (see Section S2.9). The heat of desorption measured by DSC ($56\,\mathrm{kJ\,mol^{-1}}$) is approximately equal to the estimated heat of adsorption ($-57\,\mathrm{kJ\,mol^{-1}}$). However, temperature-induced desorption is relatively slow, so we infer that the rate of ethene desorption through the crystalline material is relatively slow. Studies to elucidate the desorption mechanism are currently underway.

In contrast to the often relatively high activation temperatures used for MOFs with open metal sites,[15] **1**·CH_3CN and **2**·CH_3CN can be activated and regenerated by application of high vacuum at room temperature. Furthermore, the CH_3CN remains coordinated during dissolution in recrystallization solvents such as THF and CH_2Cl_2.[9,10] This feature may allow processing advantages in silver(I)-based materials designed to contain a removable coordinated solvent.

In summary, the two new silver(I)-based molecular materials **1** and **2** have ethene/ethane sorption selectivities over one order of magnitude higher than other solid materials studied for ethene/ethane separations. The ethene binding in these solid-state complexes were obtained by removing a protective, coordinated solvent molecule from a precursor species to activate the silver(I) centers. This design strategy could be employed in the future to prepare materials with ethene binding energies optimized to industrial olefin/paraffin separations. High $\text{mol}_{\text{ethene}}/\text{mol}_{\text{silver(I)}}$ loadings were obtained without the need for highly porous or high surface area materials, thus allowing much higher ethene/ethane sorption selectivities to be obtained. While ethene uptakes of $0.8\ \text{mol}_{\text{ethene}}/\text{mol}_{\text{silver(I)}}$ can be reached relatively rapidly, the nonporous nature of the materials appears to significantly limit the rate of ethene desorption. The compounds **1** and **2** are promising new solid sorbents for ethene/ethane separation. We are currently working to optimize both the molecular design and engineering considerations associated with the sorption/desorption rates towards industrially relevant parameters. Future work will also focus on measuring the mixed-gas ethene/ethane isotherms of these materials.

Keywords: adsorption · alkenes · coordination modes · silver · solvent effects

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 5740–5743
Angew. Chem. **2015**, *127*, 5832–5835

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Received: January 11, 2015
Revised: February 14, 2015