Chem

CellPress

Preview

An All-Purpose Porous Cleaner for Acid Gas Removal and Dehydration of Natural Gas

Vepa Rozyyev[1] and Cafer T. Yavuz[1,*]

In this issue of *Chem*, Mohamed Eddaoudi and co-workers report a novel but simple crystalline porous superstructure that effectively removes all acidic gases and water from natural gas without taking any damage from the reactive guests.

Raw natural gas is predominantly methane (up to 95%) but also contains larger hydrocarbons such as ethane and propane, acidic gases such as H_2S and CO_2, and considerable amounts of water.[1] In some reserves, H_2S can reach up to 20%, and water content can be as much as 5%. CO_2 in natural gas, from ppm levels up to 0.5%, is less significant but noteworthy. Natural gas treatment starts with the removal of sludge and gas condensate, followed by acid gas removal (mostly H_2S) by amine scrubbing. Regenerated H_2S is converted to elemental sulfur via the Claus process or sulfuric acid by the wet sulfuric acid process. Sweet (H_2S- and CO_2-free) natural gas is then dehydrated with the use of glycols and then separated from higher alkanes (Figure 1).

Among the contaminants in the natural gas, H_2S is the worst and can never be allowed in natural gas streams because it is highly toxic to living organisms and can irreversibly and strongly coordinate to the metals in the human body, and even low concentrations of H_2S are not allowed (the Occupational Safety and Health Administration permissible limit is 5–10 ppm) because of leakage or long-term exposure risks. H_2S is an acidic gas (pK_{a1} = 7) and is often removed by amine solutions through chemical binding. H_2S can react with metal ions to form stable metal sulfides, which is partly why metal-based structures are not preferred for H_2S removal.

In the adsorption of H_2S, high selectivity is required because natural gas cannot afford to contain any H_2S gas. At the same time, regeneration energy for the spent sorbent should not be high, which adds extra cost to the gas processing. When solid adsorbents are considered for the natural gas sweetening process, competitive adsorption of water should be accounted for because untreated natural gas contains significant amounts of water.

Water in natural gas can be up to 5%. However, additional water is introduced from acid gas removal processes, given that they use water-based solutions, such as aqueous amines and aqueous K_2CO_3 solutions (Benfield process). If natural gas is not dehydrated, even trace amounts of water can cause problems in downstream processing and transportation.

One particular problem from water contamination is gas hydrates. Natural gas is usually handled under high pressure regardless of whether it is converted to other chemicals, transported, or stored. At high pressure, gas hydrates are formed, and they grow on the walls of pipelines, clog the flow, and decrease the performance of engines by pressure buildup. Because of this, methanol is constantly administered to upstream natural gas pipelines, adding significant cost to the overall refining.

Natural gas dehydration is done with liquid glycols in a temperature swing operation. Glycols are repeatedly heated up to 200°C for the regeneration of high-purity dry liquids. Similar to aqueous amines, glycols are not recovered with 100% purity, and decomposition is almost always observed. Solid desiccants such as silica gel and zeolites are also used, but they require even higher temperatures for full regeneration.

To battle the regeneration problems of liquid sorbents, solid-state porous adsorbents have long been considered for acid gas removal and dehydration of natural gas. CO_2 in particular has been thoroughly studied both for its dominant role in global warming and for its safe handling in research laboratories. Most recently, research has been focused on nanoporous materials, such as metal-organic frameworks (MOFs)[2] and porous organic polymers.[3] Key attributes in porous sorbent design are high capacity, recyclability, selectivity, chemical and thermal stability, kinetics, and cost.[4] In the case of highly selective CO_2 removal from flue gas systems, for example, three different structural motifs are effective: (1) MOFs with open metal sites (e.g., MOF-74[5]), (2) small pores with a molecular sieving effect (e.g., SIFSIX-3-M[6] and

---

[1] Graduate School of Energy, Environment, Water, and Sustainability, Korea Advanced Institute of Science and Technology, Daejeon 34141, Korea

*Correspondence: yavuz@kaist.ac.kr

https://doi.org/10.1016/j.chempr.2017.10.014

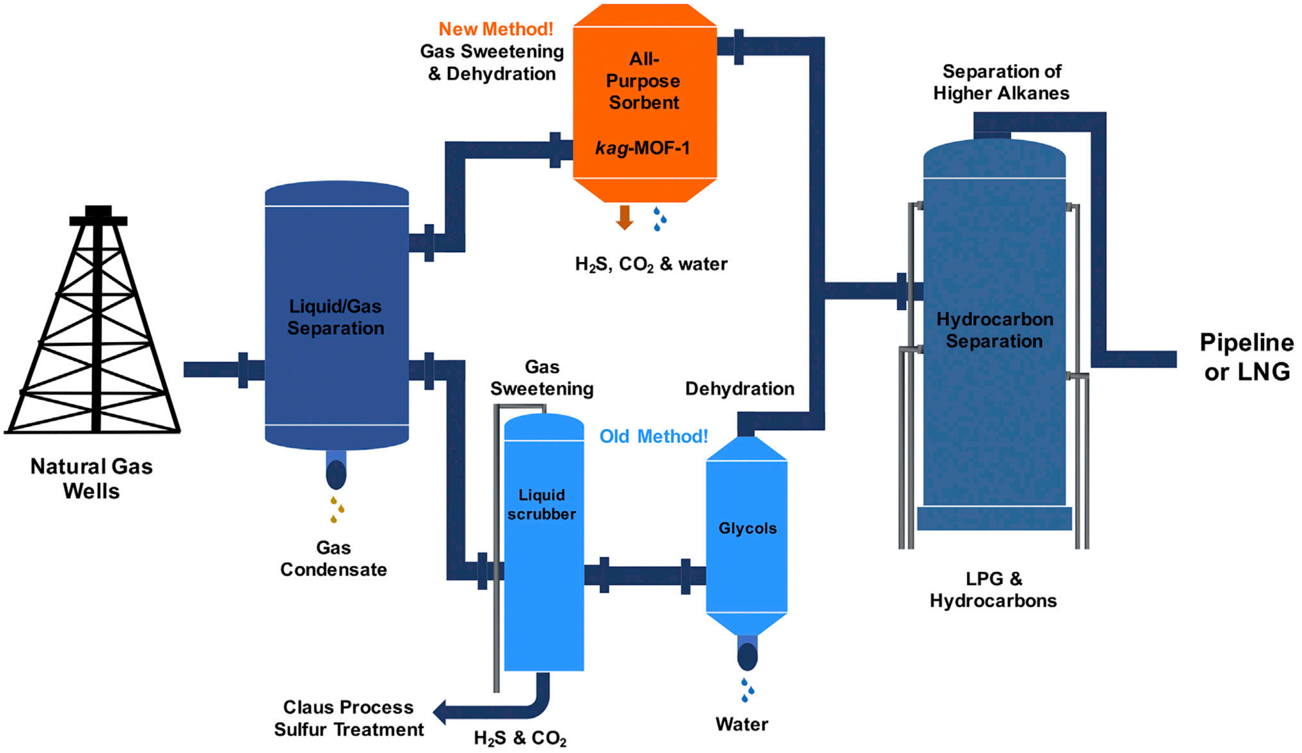

Figure 1. Simplified Natural Gas Processing Using kag-MOF-1

NbOFFIVE-1-Ni[7]), and (3) aliphatic amine-containing porous solids (e.g., COP-122 and mesoporous silica with tethered amines[8]).

Chemisorptive CO_2 capture competes with water given that water is found everywhere that CO_2 exists and always has a greater binding energy for the same reactive sites.[4] Especially at the open metal sites of MOFs, water molecules can coordinate more strongly to the metal center than CO_2. Amine-containing porous solids are not affected by the presence of water, and in some cases, CO_2 capacity is even increased as a result of the formation of ammonium carbonate.[9] However, the drawbacks of amine-containing porous solids include high regeneration energy (Q_{st} = 60–80 kj/mol) and urea formation. In molecular sieving, CO_2 cannot be selectively removed over water molecules given that H_2O has a smaller kinetic diameter (2.65 Å) than CO_2 (3.3 Å). Against all odds, however, Eddaoudi and co-workers recently demonstrated the adsorptive removal of both CO_2 and H_2O simultaneously without a decrease in CO_2 adsorption capacity by using distinct adsorption sites for CO_2 and H_2O.[10] This marked a highly promising, new, and unified approach for removing contaminants from natural gas. In this issue of *Chem*, the Eddaoudi group precisely did this by carefully tuning molecular sieving through pore apertures and creating distinct adsorption sites for H_2S, H_2O, and CO_2.[11]

The design of a new MOF that can carry out a wholesome cleaning of acid gases and water from natural gas led Eddaoudi's team to a zinc tetrazolate system with the correct pore openings and a more affordable nature. Indeed, **kag**-MOF-1 is synthesized from zinc and tetrazole carboxylate ester, both of which are more widely available than other previously reported ultramicroporous building blocks. The synthesis also involves a unique ligand preparation path through the decarboxylation of tetrazole ester. BET analysis using N_2 and Ar probes confirmed that hydrothermal synthesis yielded non-porous crystals. Surface-area analysis with a smaller CO_2 molecule showed reasonable porosity, 210 m^2/g. It is important to note the limitations of probe molecules in surface-area analysis, particularly if the intended application demands molecular sieving dimensions for small gases.

The new structure, **kag**-MOF-1, was found to be stable at pH 4 and 10, in boiling water, and in different organic solvents for 24 hr. H_2S sorption also didn't change the crystallinity. Mixed-gas CO_2/N_2 breakthrough experiments under dry and humid conditions showed the same retention time with high selectivity, indicating the stability of CO_2 adsorption under humid conditions.

More importantly, **kag**-MOF-1 is ultramicroporous and has a uniform pore size centered at 3.6 Å. It shows very high water uptake (7 mmol/g at 1.4 kPa, 298K), high adsorption heat (Q_{st} = 60 kj/mol), and considerable affinity for CO_2 (Q_{st} of 37 kj/mol). The binding energy for CO_2 is high enough for it to have higher selectivity over N_2 and CH_4 but low enough for it to regenerate with minimal energy. It has been reported that the ideal binding energy for CO_2 would be 35–50 kJ/mol.[4] Interestingly enough, CO_2 uptake of **kag**-MOF-1 under humid conditions did not change at all. The presence of water did not affect the performance of CO_2 removal, which can be explained only by the different adsorption sites for H_2O and CO_2 and the fact that they did not interfere with each other. The material showed chemical and thermal stability, which is a crucial factor in flue gas scrubbing.[4] Similarly, **kag**-MOF-1 showed high uptake for H_2S (0.9 mmol/g at 298K and 0.1 bar; 2.2 mmol/g at 298K and 1 bar), which is highly selective over nitrogen, methane, and larger hydrocarbons such as pentane and benzene. **kag**-MOF-1 could then be easily activated at 393K and 1 bar. It's remarkable that a MOF structure captures acid gases and water and is regenerated at elevated temperatures without any detectable decomposition.

If one looked deeper, one would not expect both dry and humid CO_2 removal to show the same retention time and CO_2 capacity. An adsorbent that shows higher affinity toward water (Q_{st} = 60 kj/mol) than toward CO_2 (37 kJ/mol) should capture less CO_2 when humid flue gas is treated. This indicates that CO_2 and water do not compete and bind to different adsorption sites—the only reasonable explanation for why CO_2 adsorption is not affected by water. However, Eddaoudi and co-workers assumed that both H_2O and CO_2 would bind to tetrazoles.[11] Whereas CO_2 binds to uncoordinated nitrogens of tetrazolate, water might interact with the Zn ions. Zn ions are coordinatively saturated (hexagonally coordinated to nitrogens), so H_2O binding is not as strong as open-metal-site binding (e.g., MOF-74 and HKUST-1), which explains why water can be easily recovered at lower temperature and its structure stays intact after the water adsorption cycle. CO_2 probably cannot interact with metal centers because of its larger size (3.3 Å) and the hexa-coordinated bulky environment around Zn ions. The same effect can be observed in the adsorption of H_2S, which shows only 2.2 mmol/g at 1 bar and 298K, much less than H_2O. Although H_2S has a strong affinity toward transition-metal ions (similarly to H_2O) because of its larger kinetic diameter (3.6 Å as opposed to 2.65 Å for H_2O), it cannot approach the metal center to bind strongly. Instead, H_2S binds to uncoordinated nitrogen atoms of tetrazolate ions through acid-base chemistry in the same way that CO_2 binds. This also explains why **kag**-MOF-1 shows stability during H_2S cycles.

Despite the phenomenal activity of **kag**-MOF-1 for acid gas removal and dehydration of natural gas, there are a few areas where it can be improved. First, mixed-gas breakthrough experiments and field testing are needed to show the feasibility of **kag**-MOF-1 against the mechanical impact of handling equipment and trace contaminants such as sulfur and nitrous oxides. Second, the cost and scalability are still not low enough to warrant widespread application. And lastly, the capacities for CO_2 and H_2S are not high enough for economic viability. **kag**-MOF-1, however, changes the design principles of porous sorbents for natural gas treatment, and this work will certainly lead the way in the quest for developing the next breakthrough material.

1. Li, B., Wen, H.-M., Zhou, W., Xu, J.Q., and Chen, B. (2016). Chem *1*, 557–580.
2. Wang, H., Zhu, Q.-L., Zou, R., and Xu, Q. (2017). Chem *2*, 52–80.
3. Je, S.H., Buyukcakir, O., Kim, D., and Coskun, A. (2016). Chem *1*, 482–493.
4. Patel, H.A., Byun, J., and Yavuz, C.T. (2017). ChemSusChem *10*, 1303–1317.
5. McDonald, T.M., Mason, J.A., Kong, X., Bloch, E.D., Gygi, D., Dani, A., Crocellà, V., Giordanino, F., Odoh, S.O., Drisdell, W.S., et al. (2015). Nature *519*, 303–308.
6. Shekhah, O., Belmabkhout, Y., Chen, Z., Guillerm, V., Cairns, A., Adil, K., and Eddaoudi, M. (2014). Nat. Commun. *5*, 4228.
7. Bhatt, P.M., Belmabkhout, Y., Cadiau, A., Adil, K., Shekhah, O., Shkurenko, A., Barbour, L.J., and Eddaoudi, M. (2016). J. Am. Chem. Soc. *138*, 9301–9307.
8. Dogan, N.A., Ozdemir, E., and Yavuz, C.T. (2017). ChemSusChem *10*, 2130–2134.
9. Patel, H.A., and Yavuz, C.T. (2015). Faraday Discuss. *183*, 401–412.
10. Cadiau, A., Belmabkhout, Y., Adil, K., Bhatt, P.M., Pillai, R.S., Shkurenko, A., Martineau-Corcos, C., Maurin, G., and Eddaoudi, M. (2017). Science *356*, 731–735.
11. Mohideen, M.I.H., Pillai, R.S., Adil, K., Bhatt, P.M., Belmabkhout, Y., Shkurenko, A., Maurin, G., and Eddaoudi, M. (2017). Chem *3*, this issue, 822–833.