

# ARE ZEOLITES AND RELATED MATERIALS REALLY USABLE AS ADSORBENTS FOR BIOGAS PURIFICATION?

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Searching for new sources of energy as an alternative to oil is one of the main challenges of our times, involving many scientists from all over the world. In particular hydrogen, because of its high energy content, has been identified as one of the most efficient environment-friendly fuel to be used in fuel cells to power electric motors or burned in internal combustion engines. Biogas, produced by the anaerobic digestion of biodegradable materials such as biomass, is one of the potential alternative media to provide hydrogen for fuel cells operations [1].

Biogas is typically composed by CH<sub>4</sub> (about 45-75% by volume), CO<sub>2</sub> (about 25-55%) and other compounds including H<sub>2</sub>S (whose concentration usually is in the order of magnitude of 10<sup>2</sup> ppm).

Biogas can be used directly to generate power, but the large volume of CO<sub>2</sub> reduces the heating value of the gas, increasing compression and transportation costs and limiting economic feasibility to use that occur at the point of production. Hydrogen sulfide (H<sub>2</sub>S) is extremely toxic and flammable gas; furthermore, it has corrosive effects on the very expensive, noble-metal-based equipment required for catalytic conversion operations and on the other several mechanical components.

Although in the literature there are many papers on the use of zeolites (especially 13X) as adsorbents for the removal of H<sub>2</sub>S from biogas, simple characterization experiments on such materials after H<sub>2</sub>S adsorption runs seem to reveal that this process is not quite reversible, *i.e.* the adsorbent structures undergo radical changes from which there is no turning back.

These considerations lead to the demand for new types of adsorbent materials that are able to unfold good capture performances towards both CO<sub>2</sub> and H<sub>2</sub>S without the need to be replaced after very few adsorption runs. Interesting insights related to CO<sub>2</sub> or H<sub>2</sub>S adsorption on functionalized mesoporous silicas are reported in literature [2-4]. Recently, a considerable interest has also been shown for adsorbents based on metal organic frameworks (MOFs). The choice of suitable metal groups and/or organic linkers allows to obtain many different chemical structures, sometimes with very large pores and surface areas, thus improving the adsorption affinity towards acidic compounds such as CO<sub>2</sub> and H<sub>2</sub>S. As an example, Aprea *et al.* [5] compared the CO<sub>2</sub> adsorption behavior of a copper-bearing MOF (namely, Cu-BTC) with that of a commercial 13X zeolite. Results showed that the selected MOF had better performances in terms of adsorption capacity at ambient temperature, and furthermore released less heat during the adsorption phase. The modeling and experimental results reported by Peluso *et al.* [6] indicated that MIL-101 (Cr-containing) showed a high H<sub>2</sub>S adsorption capacity at near-ambient temperature and a low heat release during the adsorption phase, suggesting a potential use of the selected metal-organic framework for fixed-bed adsorption operations.

**References.** [1] Weixin Y., Bandosz, T. J., (2007): *Fuel* **86**, 2736; [2] X. Ma, X., Wang, X., C. Song, C., (2009): *J. Am. Chem. Soc.* **131**, 5777; [3] Gargiulo, N., Pepe, F., Caputo, D. (2012) *J. Colloid Interf. Sci.* **367**, 348-354; [4] Gargiulo, N., Caputo, D., Colella, C., (2007) *Stud. Surf. Sci. Catal.* **170**, 1938-1943; [5] Aprea, P., Caputo, D., Gargiulo, N., Iucolano, F., Pepe, F. (2010): *J. Chem. Eng. Data*, **55**, 3655–3661; [6] Peluso, A., Gargiulo, N., Aprea, P., Pepe, F., Caputo, D., (2013): *Sci. Adv. Mater.*, submitted.