Novel vacuum pressure swing adsorption for green hydrogen recovery from natural gas grids using carbon molecular sieve

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Green hydrogen (GH), produced via water electrolysis, is widely recognized as a cost-effective fuel, and it plays a key role in the transition to a sustainable energy economy [1]. GH is a promising fuel for long-distance transportation, powering fuel cells in the mobility sector, and it helps to decarbonize heavy industries [2]. After GH production, it can be co-transported into the existing natural gas grids (NGG), thereby avoiding the need for extensive infrastructure investments [3]. However, upon blending GH into the NGG, it becomes important to recover and purify it to a high degree of purity to enable, for instance, fuel cell applications (H_2 > 99,97%). One problem concerning the separation and purification of GH from NGG relates to the H_2 feed concentration (< 20%), which differs greatly from conventional H_2 purification processes (> 70%) [4]. Moreover, the high CH_4 concentration and its relatively weak adsorption affinity on commonly used adsorbents further complicate achieving high-purity H_2 and high recovery rates through conventional approaches.

In this work, we report a novel conceptual vacuum pressure swing adsorption (VPSA) process to separate H_2 from CH_4 by exploiting the kinetic selectivity of H_2 over CH_4 on CMS-3K-172, as shown in Figure 1A. To develop the conceptual VPSA cycle, a series of single and multicomponent breakthrough curves for H_2 and CH_4 were performed on CMS-3K-172 between

195 and 273 K, and pressures up to 18 bar. These experiments were performed in a cryogenic fixed-bed adsorption unit specially designed to work at lower temperatures (until 77 K) by using cryogenic baths [5]. The example shown in Figure 1B refers to single breakthrough curves of H_2 and CH_4 on CMS-3K-172 compared to a blank experiment (glass spheres inside the column) performed at 195 K and 12 bar, where a clear kinetic separation can be seen. CH_4 has a limited diffusion, and it is blocked from entering the CMS-3K-172 for the short breakthrough time, which results in its early breakthrough compared to the blank experiment. On the other hand, the H_2 breakthrough curve shows a delay compared to the blank experiment due to H_2 being adsorbed on CMS-3K-172.

A fixed-bed adsorption mathematical model was validated through the fitting of binary experimental breakthrough curves (H_2/CH_4 - 20/80%), and, after that, it was used for the VPSA process simulations. The conceptual VPSA developed consists of 1 bed with 5 steps, namely (1) pressurization with feed, (2) feed, (3) H_2 purge, (4) cocurrent depressurization (COD), and (5) countercurrent vacuum blowdown. The VPSA performance, i.e., H_2 purity and recovery, was evaluated by changing the process variables such as step time, intermediate-to-high pressure ratio, purge-to-feed ratio, and VPSA type configuration. Figure 1C shows three VPSA types that were simulated: type I with the five steps mentioned above, type II without the COD step, and type III without the H_2 purge step. The H_2 purity-recover trade-off for the three VPSA types can be seen in Figure 1D. From a feed of 20% H_2, the VPSA type II allows obtaining an H_2 purity of up to 68% with a recovery of up to 92%, and the best trade-off between purity and recovery was 83% and 85%, respectively.

This work shows for the first time that an adsorbent that adsorbs preferentially H_2 and blocks CH_4 from entering its pores can be useful to enrich H_2 from a low feed concentration. Moreover, this work provides insights for developing new materials with the same CMS characteristics but with higher H_2 capacity, which could be beneficial to improve the VPSA process. In conclusion, the developed VPSA process is useful for increasing the H_2 molar fraction from 20% to 60 - 70% with a high recovery. We are currently working on a second stage to be incorporated into the VPSA process to purify H_2 for fuel cell applications (>99.97%).

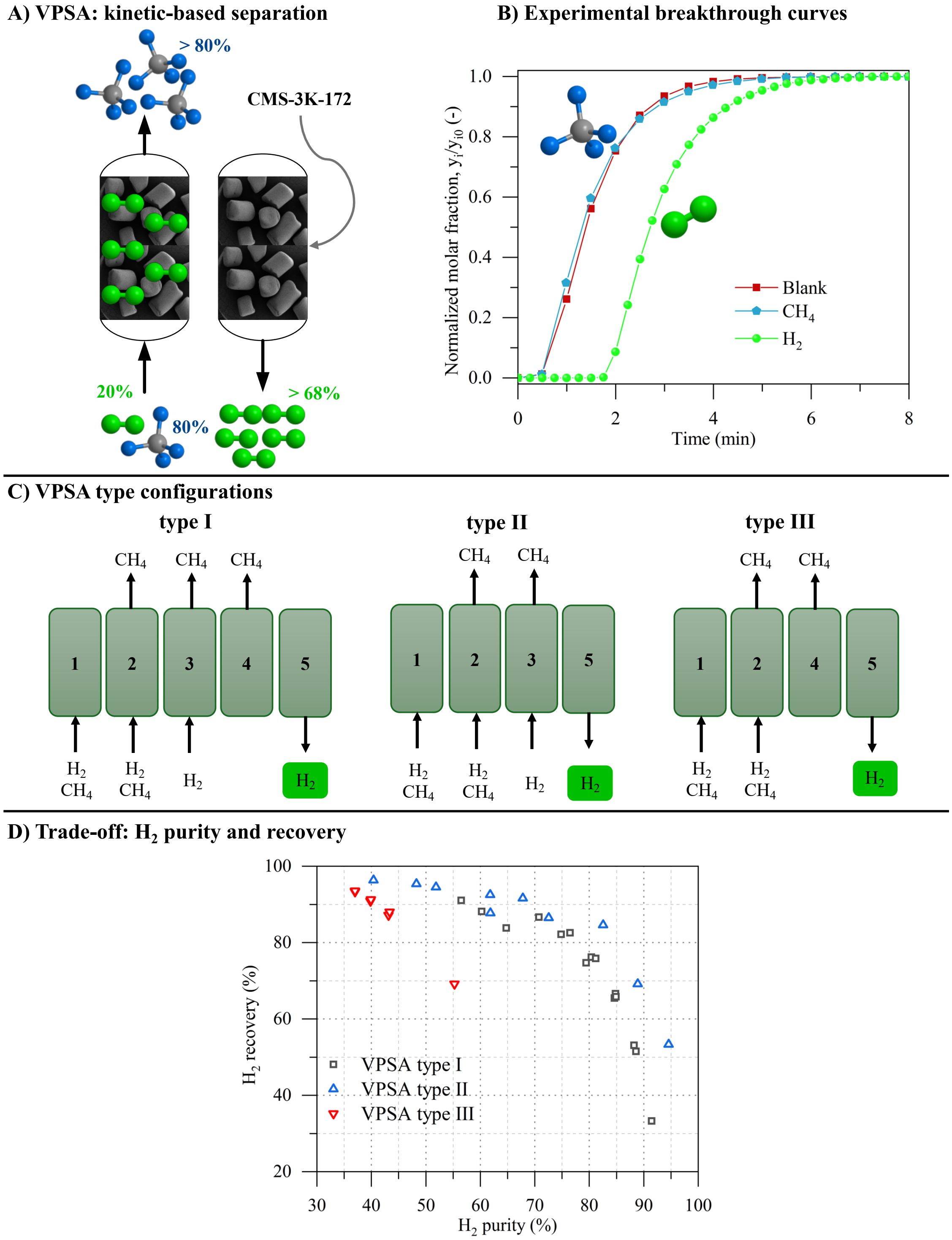

Figure 1. A) VPSA based on the kinetic selectivity of H_2 over CH_4 on CMS-3K-172; B) Experimental single breakthrough curves of H_2 and CH_4 on CMS-3K-172 compared to the blank experiment at 195 K and 12 bar; C) VPSA type configurations; and D) Trade-off between H_2 purity and recovery for different VPSA types and sets of process variables. VPSA steps: (1) pressurization with feed, (2) feed, (3) H_2 purge, (4) cocurrent depressurization (COD), and (5) countercurrent vacuum blowdown.

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