



Exploring the Impact of NaX and AgX Zeolite Additions on Mixed-Matrix Carbon Membranes

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Abstract

Carbon membranes exhibit limited selectivity for separating paraffins and olefins like ethane and ethylene. To improve this selectivity, mixed-matrix carbon membranes are proposed, with silver cations facilitating olefin transport. However, these cations tend to reduce to inactive metallic silver. To address this issue, stabilizing them within zeolites via ion exchange could be a solution. This study aims to identify differences in the separation properties of carbon membranes incorporating Zeolite X Faujasite (NaX) and silver-modified Zeolite X Faujasite (AgX), elucidating their correlation with the resulting carbon microstructure [1].

NaX zeolite was synthesized following the method proposed by Zhan et al. [2]. Sodium hydroxide (34 g) was dissolved in deionized water (50 g), followed by the addition of sodium aluminate (2.42 g) and Aerosil silica (3.43 g). The reaction mixture was agitated at 250 rpm for 96 hours and then centrifuged, with subsequent washing until achieving a supernatant pH of 7 to 8. Ion exchange was conducted by combining 20 ml of 0.18 M silver nitrate solution per gram of zeolite, followed by agitation at 250 rpm for 10 hours at 25 °C. The resulting solution was filtered, and excess silver was washed away with deionized water.

A polymeric solution was prepared by mixing 33 % (w/w) poly(ether imide) (PEI) in N-methyl-2-pyrrolidone (NMP) at 60 °C. Zeolites suspended in NMP (0.25 % w/w) were added to a quarter of the polymeric solution, followed by agitation and ultrasonication. This process was repeated until complete consumption of the PEI solution, yielding a solution containing 20 % PEI and 0.1 % zeolites. For comparison, a solution containing only 20 % PEI in NMP was prepared.

Alumina supports were coated with the solutions using spin coating method, while unsupported films were prepared by casting. The films were then pyrolyzed in a horizontal furnace under a nitrogen atmosphere. After pyrolysis, all unsupported carbon films were ground into a fine powder for X-ray diffraction (XRD) and Raman spectroscopy analysis. Carbon membranes (CM) were denominated as CM-PEI, without zeolites, CM-NaX, with NaX zeolites, and CM-AgX, with AgX zeolites. Pure gas permeation tests were performed with CO₂, N₂, and ethylene.

The XRD analysis of the CMs is shown in Fig. 1. For all samples, two broad bands around 20° and 45° are observed. This outcome suggests that the formed material is predominantly amorphous since there aren't sufficient crystalline planes to induce the formation of narrow peaks. However, it's worth noting that a turbostratic structure, characterized by containing crystalline nanodomains, typical of CMs, is also present. This finding aligns with previous observations by Hamm (2018) [3], who noted a similar diffraction pattern in pyrolyzed PEI films at 600 °C. A comparable diffractogram was reported by Zhang et al. (2014) [4] and Tseng, Shiu, and Lin (2011) [5], who produced MCs pyrolyzed at 650 °C and 600 °C, respectively. A shift in the observed peak position towards the band around 20° is noticeable. This band corresponds to the spacing between *quasi*-graphitic layers present in the turbostratic material, situated within regions of higher order. Perfectly graphitic layers exhibit a spacing of 3.36 Å. The carbon membranes produced display spacings greater than graphite, indicative of turbostratic structure formation. These findings suggest that the addition of zeolitic material increased the spacing between graphitic layers, leading to the development of a more open structure, potentially conducive to enhancing the permeance of gas species.

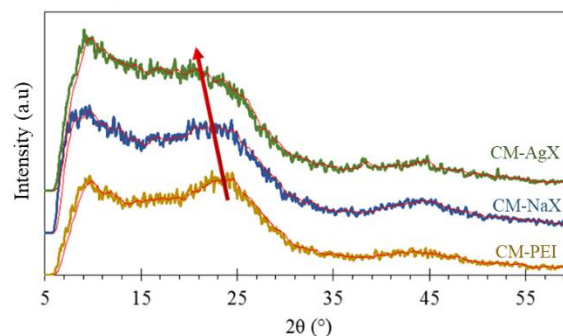


Fig. 1 – Diffratograms of CM-PEI, CM-NaX, and CM-AgX membranes



In Fig. 2, the presence of two broad bands centered at 1355 cm^{-1} and 1580 cm^{-1} is noticeable, corresponding to the D and G bands, respectively. The D band originates from the vibrational mode of "breathing" of 6-membered carbon rings, with A_{1g} symmetry. This vibrational mode is absent in defect-free graphite and only becomes active in the presence of system disorder. The G band is associated with the vibrational mode of E_{2g} symmetry, found in graphitic structures, and is associated with the stretching of pairs of carbon atoms with sp^2 hybridization correlated with organized regions within the turbostratic structure [6]. All analyzed samples exhibit these two broad bands, suggesting the essentially amorphous nature of the formed material. Additionally, around 1110 cm^{-1} , a pronounced shoulder is observed, particularly in the MC-PEI and MC-NaX samples. This shoulder is related to the presence of heteroatoms in the carbon structure [7], indicating the presence of imide group remnants in the carbon film structure.

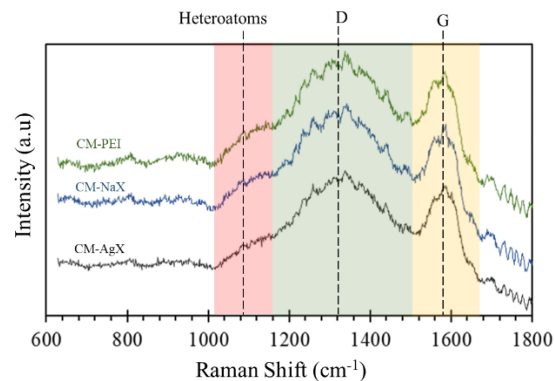


Fig. 2 – Raman spectroscopy of CM-PEI, CM-NaX, and CM-AgX membranes

No significant changes in the intensity of the D and G bands are observed. In fact, the ratio between the band intensities, I_D/I_G , was quite similar across the samples, ranging from 1.64 to 1.67. This outcome suggests the addition of NaX and AgX zeolites, at the proportion used in this study, did not affect the degree of organization of the final carbonaceous structures.

The gas permeation test results (Table 1) reveal an increase in CO_2 permeability upon the addition of NaX and AgX zeolites, while N_2 permeability decreases. This behavior is attributed to the microstructure observed via XRD analysis. The reduced interplanar distance between graphitic layers in the turbostratic structure facilitates the passage of gases with a smaller kinetic diameter (such as CO_2) while hindering the passage of gases with a larger kinetic diameter (like N_2). Similar trends are observed for ethylene, with permeability decreasing upon the addition of NaX zeolites but increasing with AgX zeolites, indicating a mechanism of facilitated diffusion due to the affinity of silver cations and olefin double bonds.

	Permeability (Barrer)			Selectivity	
	CO_2	N_2	Ethylene	N_2/CO_2	Ethylene/ CO_2
CM-PEI	1.7	2.0	2.3	1.2	1.2
CM-NaX	2.5	0.64	0.15	3.9	0.2
CM-AgX	3.5	0.13	1.2	26.4	9.5

Table 1 – Permeability and selectivity of CM-PEI, CM-NaX, and CM-AgX

It can be concluded that the presence of zeolites in the carbon matrix reduces the d-spacing of the carbon structure, restricting the passage of gases that do not have affinity with the zeolites. However, the addition of zeolites does not influence the degree of order of the turbostratic structure, as evidenced by Raman spectroscopy.

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