Evaluation of gas sorption performances of iron oxide and nickel oxide doped ZIF-8 materials

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Highlights

- Fe_3O_4 and NiO successfully inserted into ZIF-8 structure
- Fe_3O_4 and NiO expanded pores and reduced crystal size
- Fe_3O_4 and NiO insertion slightly decreased H_2 sorption of ZIF-8

1. Introduction

Energy storage and usage of hydrogen has grown in importance globally since it is a clean, renewable energy source. Because of their large specific areas, high porosity, and abundance of active metal sites, metal-organic frameworks (MOFs) have been exploited recently as hydrogen storage materials, catalysts, or catalyst carriers during hydrogenation and dehydrogenation processes. Surface area, pore volume and size, low bulk density, and significant adsorption enthalpy are the main parameters affecting hydrogen affinity towards materials [1–3]. It was reported that pore size had a greater impact on hydrogen storage than surface area and surface chemistry. It was shown that tiny holes less than 1 nm are more effective in absorbing H_2, whereas pores greater than 1.5 nm barely little contribute [1]. According to research, the ideal carbon pore widths range for high pressure and 77 K are between 0.6 and 0.7 nm [1], > 0.56 nm for applications at 77 K under any pressure, and around 0.6 nm for applications at 300 K under at least 100 bar [2].

Based on the aforementioned information, it can be deduced that the combination of hierarchically porous Zeolitic imidazolate framework (ZIF-8) and metal oxides (Fe_3O_4 and NiO) was combined during synthesis of ZIF-8 in order to improve adsorption properties of ZIF 8 toward hydrogen gas. ZIF-8 and metal-oxide doped ZIF-8 were characterized using XRD, XRD, XPS, Raman, FTIR and STEM.

2. Methods

ZIF-8 sample was prepared according to our previous study [4]. The molar ratio of metals was kept at 5% to avoid disrupting the polyhedron structure of ZIF-8. To prepare metal/ZIF-8 nanocomposites, firstly, 80 mL methanol containing 3.284 g 2-MIM and 20 ml methanol solution containing 2.125 mmol $Zn(NO_3)_2.6H_2O$ and 0.125 mmol metal oxide (Fe_3O_4 and NiO) were prepared. The mixture was stirred well at room temperature for 2 h, and metal/ZIF-8 nanocomposites were obtained by washing the solution with methanol three times, centrifuging, and drying at 60 °C overnight.

All samples were caharecterized using XRD (Panalytical –Empyrean), XRF (Thermo Scientific Niton XL3t Goldd+), XPS(Specs-Flex XPS), Raman(WITec/Alpha M+), FTIR (Bruker Alpha II) and STEM (TESCON-Mira III XMU). Nitrogen and hydrogen physorption experiments were done using gas sorption analyzers (AUTOSORB 1C, Quantachrome Corp., USA and Micromeritics) were performed at 77 K bath temperature after degassing at 60 °C.

3. Results and discussion

The results of the XRF analysis of the synthesized samples are shown in Table 1. The Zn content of the samples varied between 33.5 and 37.3 % depending on the metal oxide loading. Although the molar

percentage of metal oxide is 5% in all samples, the percentage of metal loaded into the structure varies depending on the metal oxide and metal oxide mixture. Both Fe_3O_4 and NiO loadings reduce the crystal size calculated from the XRD patterns. This structure may result from the incorporation of metal oxides into the structure of ZIF-8. STEM images of ZIF-8 showed the polyhedral structure of ZIF-8 preserved by doping with Fe_3O_4 and NiO. The interaction of Fe_3O_4 and NiO with ZIF-8 is confirmed by XPS results.

The H_2 and N_2 sorption results in Table 1 show that the highest surface area was found for ZIF-8. When Fe_3O_4 and NiO were used individually or mixed in ZIF-8, the surface area decreased slightly with increasing average pore diameter. The H_2 sorption performance of Fe_3O_4 is higher than that of NiO and the highest H_2 sorption was obtained for 3.3 % Ni and 1.6 % Fe. The specific surface area determined with N_2 was almost 10 times larger than that of H_2, which is due to the sorption of hydrogen in pore diameters less than 1 nm [1]. In fact, almost 10 % of the pores in ZIF-8 and metal oxide/ZIF-8 can adsorb H_2 and almost 90 % of the pores have a pores larger than 0.7 nm.

Table 1. Composition and crystallinity and hydrogen sorption characteristics of ZIF-8, single and binary metal oxide doped ZIF-8 samples

Samples	Composition wt.%			Crystal size	H_2			N_2		
	Zn	Fe	Ni	nm	S_{BET} m^2/g	VT cm^3/g	D nm	S_{BET} m^2/g	VM cm^3/g	D nm
ZIF-8	37.27	-	-	43.48	231.63	0.156	2.69	2088	0.840	2.10
Fe/ZIF-8	35.64	0.93	-	18.18	225.89	0.154	2.74	2069	0.771	3.38
Ni/ZIF-8	36.63	-	2.35	20.09	219.02	0.154	2.82	2016	0.724	2.66
Fe-Ni/ZIF-8 (R1)	35.69	1.57	3.31	19.80	222.46	0.152	2.74	2016	0.799	3.50
Fe-Ni/ZIF-8 (R2)	33.49	1.40	0.75	18.34	210.09	0.142	2.70	2046	0.755	3.54
Fe-Ni/ZIF-8 (R3)	35.08	0.55	2.65	18.74	201.17	0.137	2.72	2111	0.785	2.89

4. Conclusions

Fe_3O_4 and NiO were loaded into the ZIF-8 structure without damaging the polyhedral structure. The loading of metal oxides led to a reduction in crystal size and particle size as well as an expansion of the pores. The expansion of the pores slightly reduced the H_2 sorption and surface area of ZIF-8 .

References

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