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### **Supplementary Data File**

# Nano-Gate Opening Pressures for the Adsorption of Isobutane, n-Butane, Propane, and Propylene Gases on bimetallic Co-Zn Based Zeolitic Imidazolate Frameworks

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#### S1. XRD analysis

The mixed metal CoZn-ZIF-8 (termed Zn/Co-ZIF-8) has been successfully prepared rapidly via a microwave-assisted in-situ technique. Two cobalt mixed ZIF-8 samples were prepared with 50 and 100% Co, termed Zn/Co-ZIF-8 and Co-ZIF-8, respectively, and their properties are compared to pristine ZIF-8. Powder X-ray diffraction (XRD) patterns of ZIF-8, Zn/Co-ZIF-8 and Co-ZIF-8 nanocrystals are exposed in Fig.S1. Both of the two mixed metal CoZn-ZIF8exhibited similar XRD patterns to that of the ZIF-8, indicating the preservation of crystal lattice in the  $I\bar{4}3m$  space group. These observations are in a good agreement with the previous literature and refer to the formation of pure phase ZIF-8 nanocrystals.<sup>1,2</sup> Noticing well-shaped peaks, especially the very sharp peak of (001) at 7.36° declares a high crystallinity of the prepared nanoparticles. For the three samples, the crystals exhibited a body-centered cubic crystal lattice.<sup>3</sup> Further, the (011) peak intensity rises by increasing the Co mixing ratio into the reaction solution. Fig. S1 affirms that the presence of  $Co^{2+}$  in the matrix of ZIF-8 did not make any structure changes, and that ZIF-8 samples have preserved their crystalline integrity even after being mixed with  $Co^{2+}$ . The mixing of  $Co^{2+}$  does not distort the crystal lattices of ZIF-8 materials since the ionic size of  $Co^{2+}$  (0.65 Å) is smaller than that of  $Zn^{2+}$  (0.74 Å) in the tetrahedral coordination structure.<sup>4,5</sup>

#### S2. Raman spectra

**Figure S2** illustrates the Raman spectra of three prepared ZIF-8, Zn/Co-ZIF-8 and Co-ZIF-8. It is seen that the characteristic peaks of these samples are of 282, 683, 834, 945, 1023, 1143, 1182, 1312, 1385, 1460, 1507, 2932, cm<sup>-1</sup>. These peaks refer, respectively, to Zn-N (stretching), imidazolium ring puckering,  $\delta$  H (out of plane), bending C–H (out of plane) (C4–C5), bending C–H (out of plane) (C2–H), bending C–H (out of plane), stretching C5–N, stretching C–N, N–H wag, ring expansion, N–H wag, bending of CH<sub>3</sub>, stretching of C2–N1, stretching of C5–N1, wag of N–H and stretching of C–H (methyl). Further, the two peaks at 3111 and 3136 cm<sup>-1</sup> refer to the stretching C–H (imidazolium ring).



Figure S1. XRD patterns of ZIF-8, Zn/Co-ZIF-8 and Co-ZIF-8 samples.



Figure S2. Raman spectra of ZIF-8, Co-ZIF-8 and Zn/Co-ZIF-8 samples.

#### **S3. TGA and DSC analyses**

**Figure S3(a, b)** exposes the TGA and DSC thermogram curves of ZIF-8, Zn/Co-ZIF-8 and Co-ZIF-8. Overall, it was observed form **Figure S3 (a)** that the presence of Co<sup>2+</sup> ion into the Zn-ZIF-8 structure decreases its thermal stability. Through the results embedded in **Fig. S3a**, it was observed that at 150 °C, the pristine ZIF-8 has almost no weight loss; whereas Co-ZIF-8 and Zn/Co-ZIF-8 have weight losses of 0.27% and 1%, respectively. At 514 °C, the thermal decompositions of ZIF-8, Zn/Co-ZIF-8 and Co-ZIF-8 are 3.16, 5.09 and 4.11 %, respectively. The thermal decompositions of ZIF-8, Zn/Co-ZIF-8 and Co-ZIF-8 at 700 °C are 48.67, 58.57 and 60.27%, respectively. **Figure S3(b)** exposes the DSC thermogram curves of ZIF-8, Zn/Co-ZIF-8 and Co-ZIF-8 is greater than Co-ZIF-8 and Co-ZIF-8, which indicates that some processes occurred such crystallization and/or oxidation.<sup>6</sup>

#### S4. XPS analysis

**Figure S4** illustrates full XPS survey spectra of the three samples; ZIF-8, Zn/Co-ZIF-8 and Co-ZIF-8. The results of the ZIF-8 reveal the presence of O, C, N, and Zn; whereas those for Co-ZIF-8 are Co, O, C, and N, and for Zn/Co-/ZIF-8 are Co, O, C, N, and Zn. The spectrum of Zn-ZIF-8 sample has a dominant peak of the binding energy of Zn at 1021.2 eV,<sup>7</sup> which is assignable to N-coordinated metal (Zn-Nx). On the other hand, the samples of Co-ZIF-8 and Zn/Co-/ZIF-8 have a dominant peak of Co at 781.2 eV, which is ascribed to N-coordinated metal (Co–N<sub>X</sub>),<sup>7, 8</sup> which serves as an effective activity center. It can be noticed from these results that the presence of Co<sup>2+</sup> into complexation with 2-methylimidazole shifted the peak to lower energy. It was noticed that this spectrum of N is found in the three adsorbents. It was seen that N1s of ZIF-8 appeared at 398.4 eV, while for Co-ZIF-8 and Zn/Co-ZIF-8 appeared at 396.61 eV. Consequently, the binding energy of N1s peak was shifted to a lower energy due to the entrance of Co<sup>2+</sup> into matrix. Furthermore, it was seen from **Fig.S4** that the peaks of O1s and C1s in the three samples appeared at 531.5 and 284.6 eV, respectively.



Figure S3. (a) TGA and (b) DSC thermograms of ZIF-8, Co-ZIF-8 and Zn/Co-ZIF-8 samples.



Figure S4. Full XPS survey scan spectra of (a) ZIF-8, (b) Zn/Co-ZIF-8 and (c) Co-ZIF-8 adsorbents.

#### **S5. EDX analysis**

**Figure S5** shows the elemental analysis by using the EDX of three adsorbent of ZIF-8, Zn/Co-ZIF-8 and Co-ZIF-8. The spectrum of Zn appeared at the two peaks of 1.01 and 8.60 eV, whereas that of Co appeared at the two peaks of 0.32 and 6.91 eV. These analyses indicate that there are variations in outcome values of C, N, O, Zn and Co form each sample. Sample of ZIF-8 contains C, N, O and Zn, while the sample of Zn/Co-ZIF-8 contains C, N, O, Zn and Co. In addition, the sample of Co-ZIF-8 contains C, N, O and Co.

#### S6. Variation of $p_0$ values

**Figure S6 (a, b)** exposes that  $p_0$  values of propane and propylene gases onto the ZIF-8, Zn/Co-ZIF-8 and Co-ZIF-8. It was seen that  $p_0$  values mostly decreases by increasing cobalt composition into the composition of ZIF. On the other hand, the  $p_0$  value of n-butane gas onto ZIF-8, Zn/Co-ZIF-8 and Co-ZIF-8 showed s a small variation when increasing cobalt percentage into the composition of ZIF, with an observable decrement for ZIF-8 and constant value by increasing the cobalt composition into the of ZIF. Moreover, the isobutane gas exhibited variable values of the  $p_0$  when being adsorbed onto ZIF-8, Zn/Co-ZIF-8 and Co-ZIF-8.



Figure S5. EDX spectra of (a) ZIF-8, (b) Zn/Co-ZIF-8 and (c) Co-ZIF-8 adsorbents.



**Figure S6.** Variation of nanogate opening pressure ( $p_0$ ) values exhibited in the adsorption of different gases at 25°C onto ZIF-8, Co-ZIF-8 and Zn/Co-ZIF-8 samples.

## **S7. References**

- 1 T. Zhang, L. Lin, X. Zhang, H. Liu, X. Yan, J. Qiu, K. L. Yeung, Mater. Lett., 2015, 148, 17-21.
- 2 T.-T. Han, Y.-Y. Liu, G.-C. Yang, J.-F. Ma. Micropor. Mesopor. Mater., 2017, 247, 177-183.
- M. Ghani, S. Masoum, S. M. Ghoreishi, V. Cerdà, F. Maya, J. Chromatogr. A, 2018, 1567, 55-63.
- 4 C. Sámano-Alonso, J. Hernández-Obregón, R. Cabrera, J. A. I. Díaz-Góngora, E. Reguera, *Colloid. Surface. A*, 2016, **506**, 50-55.
- 5 D. Al-Masri, M. Dupont, R. Yunis, D. R. MacFarlane, J. M. Pringle, *Acta*, 2018, **269**, 714-723.
- 6 W. S. Chi, S. O. Hwang, S.-J. Lee, S. Park, Y.-S. Bae, D. Y. Ryu, J. H. Kim, K. Jinsoo, J. Membrane Sci., 2015, 495, 479-488.
- 7 A. Morozan, P. Jegou, B. Jousselme, S. Palacin, *Phys. Chem. Chem. Phys.*, 2011, **13**, 21600–21607.
- 8 M. Yuasa, A. Yamaguchi, H. Itsuki, K. Tanaka, M.Yamamoto, K. Oyaizu*Chem. Mater.*, 2005, 17, 4278–4281.