Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary information

Enhanced and Selective Photocatalytic reduction of CO_2 by H_2O over Strategically Doped Fe and Cr into Porous Boron Carbon Nitride

Niwesh Ojha, Abhinav Bajpai, Sushant Kumar*
Gas-Solid Interaction Laboratory, Department of Chemical and Biochemical Engineering,
Indian Institute of Technology Patna, Bihta, Patna, 801 106, Bihar, India

* Corresponding author:

(Sushant Kumar) E-mail: sushantkumar@iitp.ac.in; Tel.: +91-612-302-8670

Index Page

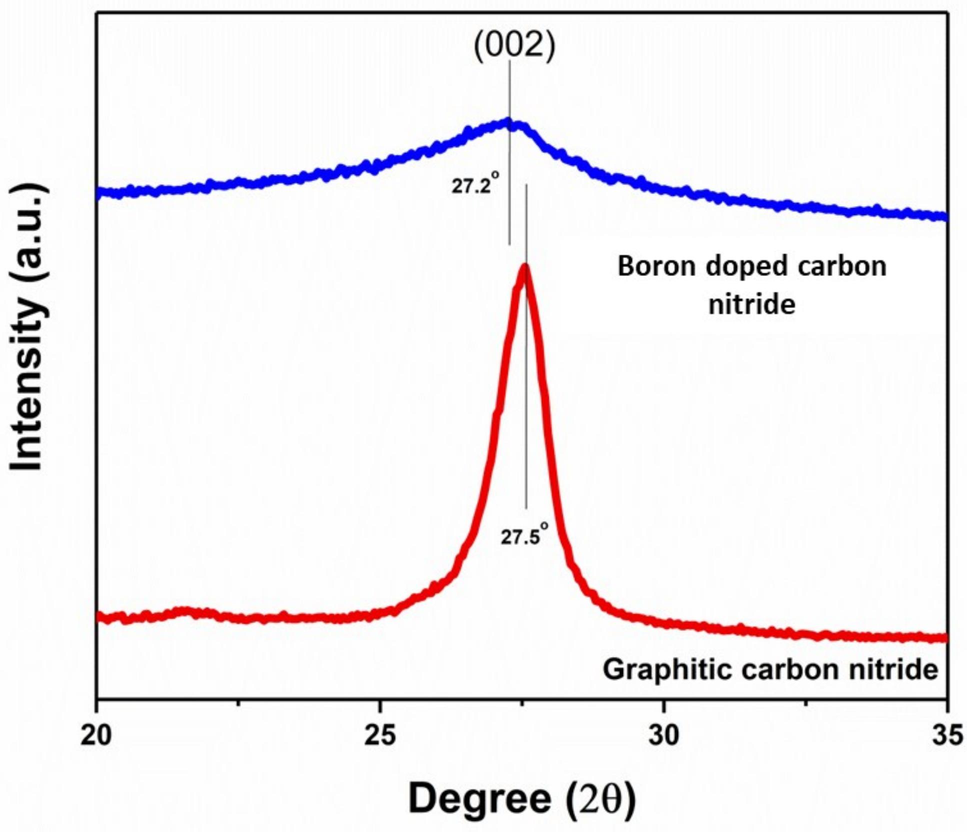

Figure S1 depicts shift in position of (002) peak towards lower scattering angle for boron-doped carbon nitride (B-CN) sample. This infers that for B-CN, void-to-void distance for in-plane structure is higher compared to that of CN which indicates that boron insertion led to an increase in inter-planar stacking distance. Also, the intensity of the peak found to be reduced, which could be due to replacement of carbon atoms by boron atoms. [1,2]

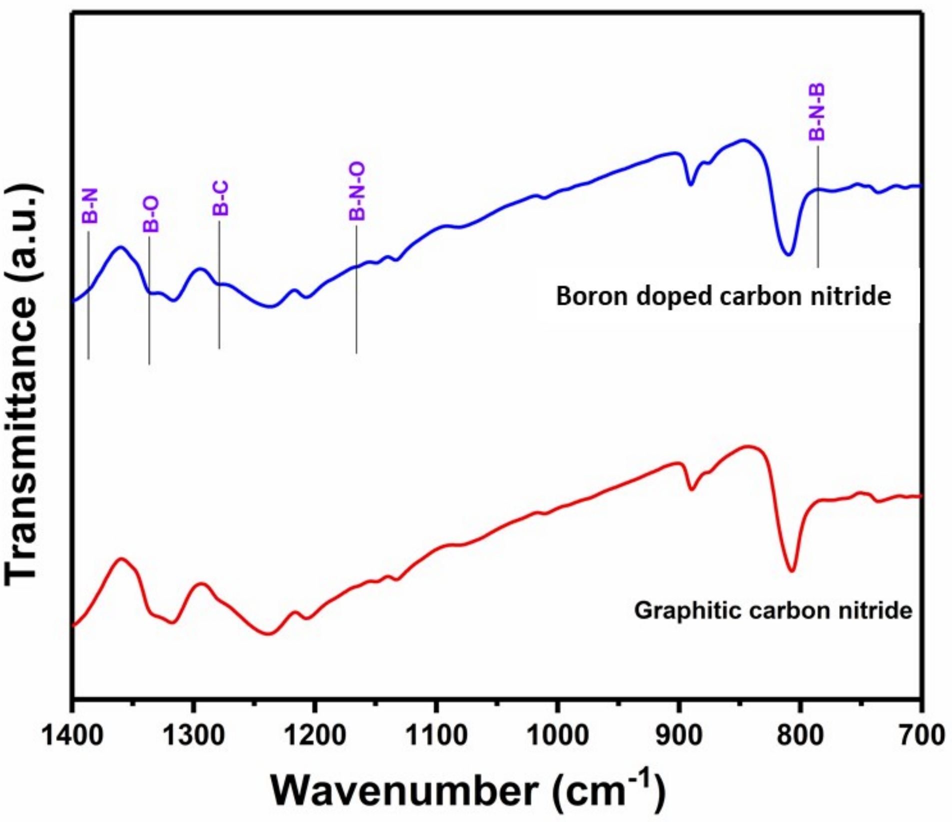

Figure S2. IR spectrum for B-CN illustrates presence of B-N-B, B-N-O, B-C, B-O and B-N. [3–6]

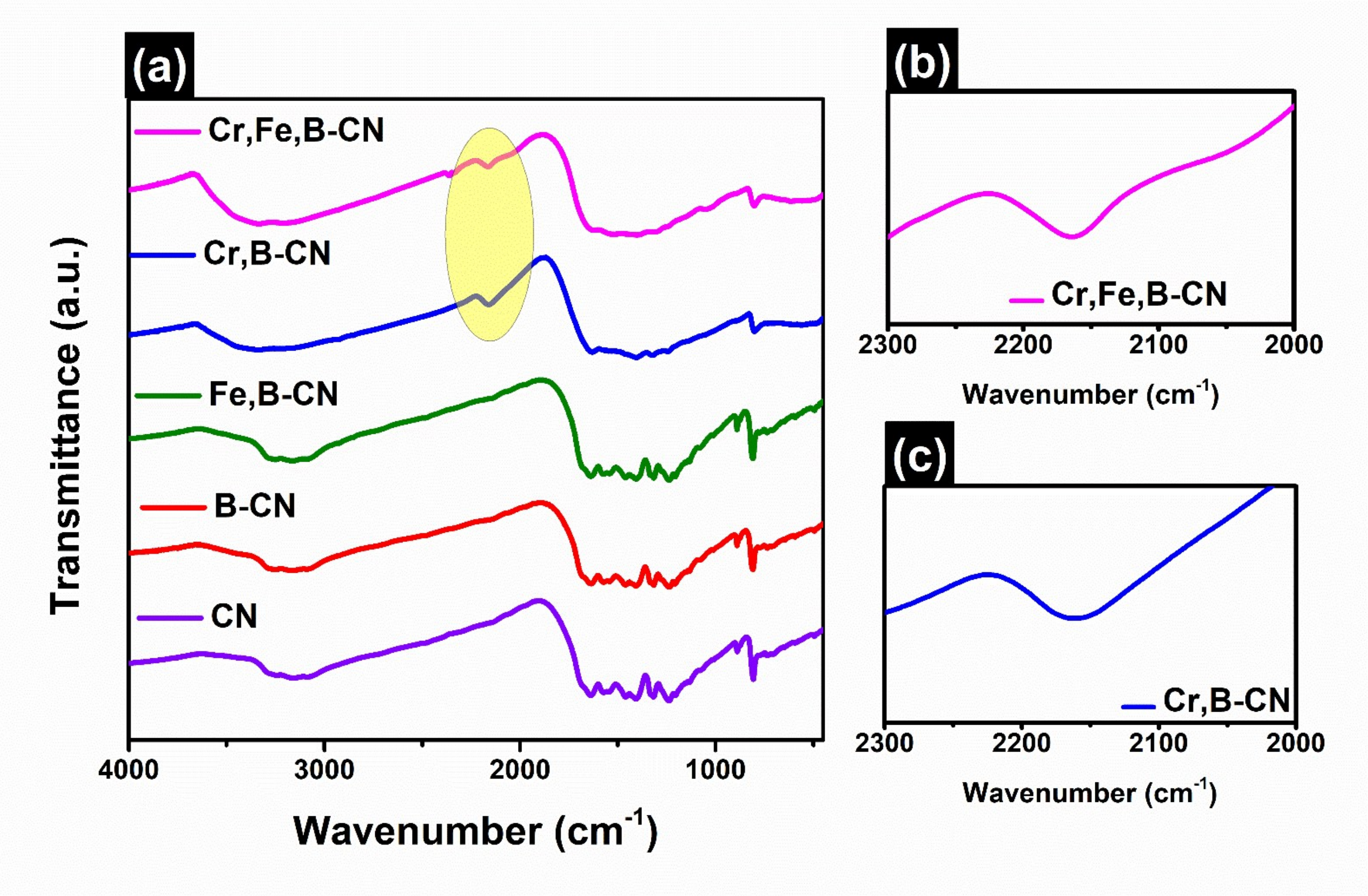

Figure S3 (a) IR spectrum of all synthesized photocatalysts, **(b)** and **(c)** showing a close-up view of the wavenumber range (2300-2000 cm^{-1}) to illustrate the presence of -CO bond stretching vibration (at 2164 cm^{-1}). [7]

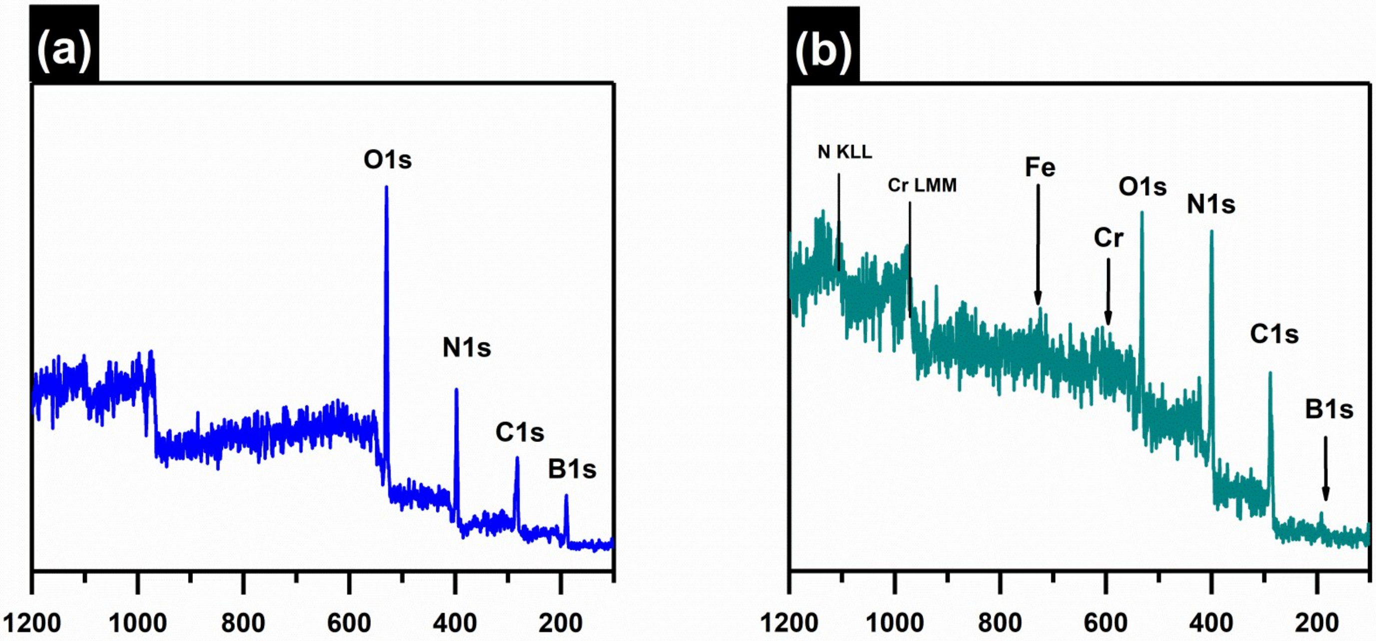

Figure S4 XPS survey spectra of **(a)** B-CN and **(b)** Cr, Fe, B-CN. Scans show the existence of B, C, N and surface oxygen in B-CN sample. Expectedly, other than these elements Fe and Cr were also present in Cr, Fe, B-CN.

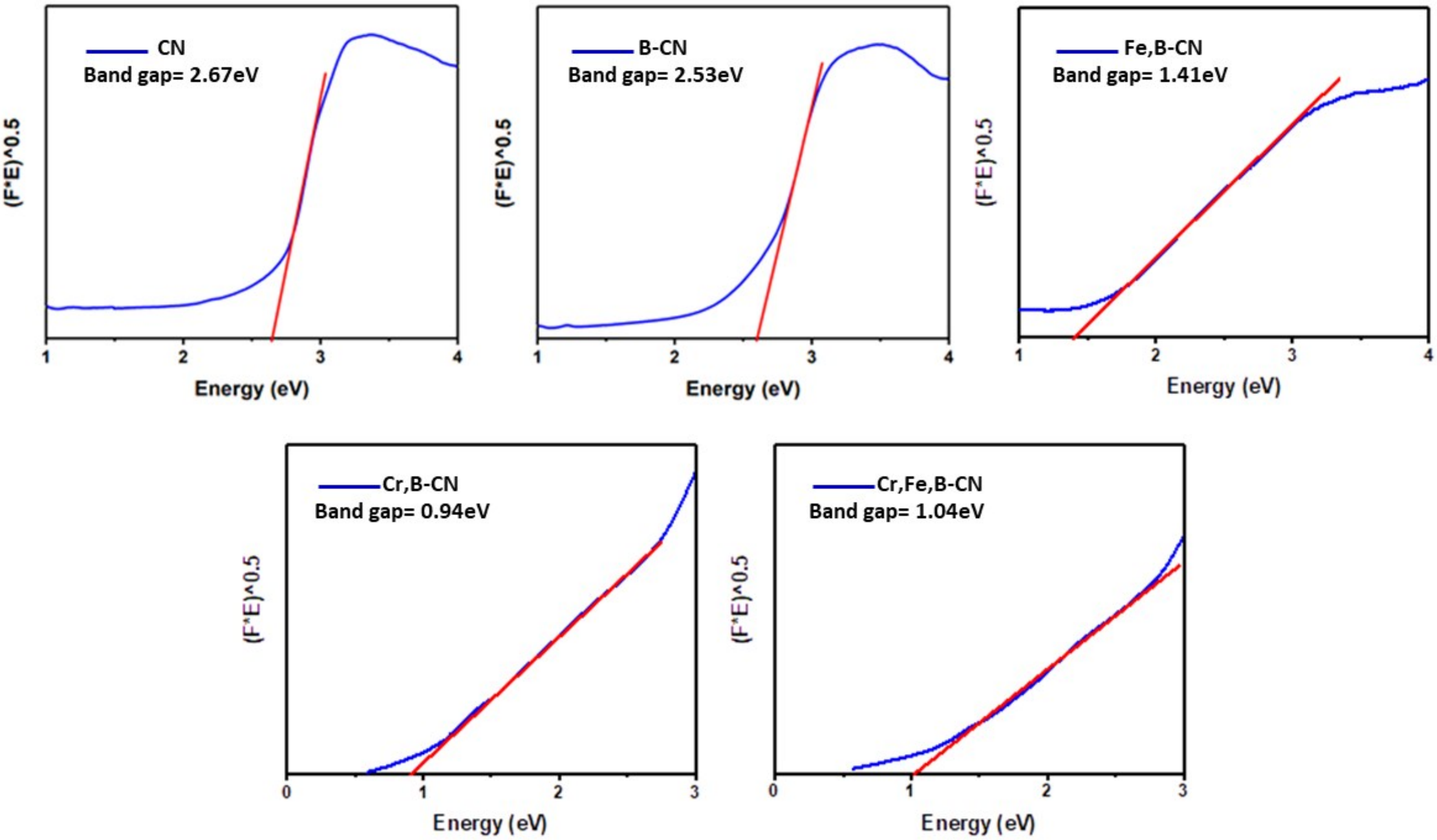

Figure S5 The Tauc Plot [$(\alpha h\nu)^{1/2}$against $h\nu$] for all as-synthesized catalysts and corresponding band gap energies (E_g) are shown. [2,8]

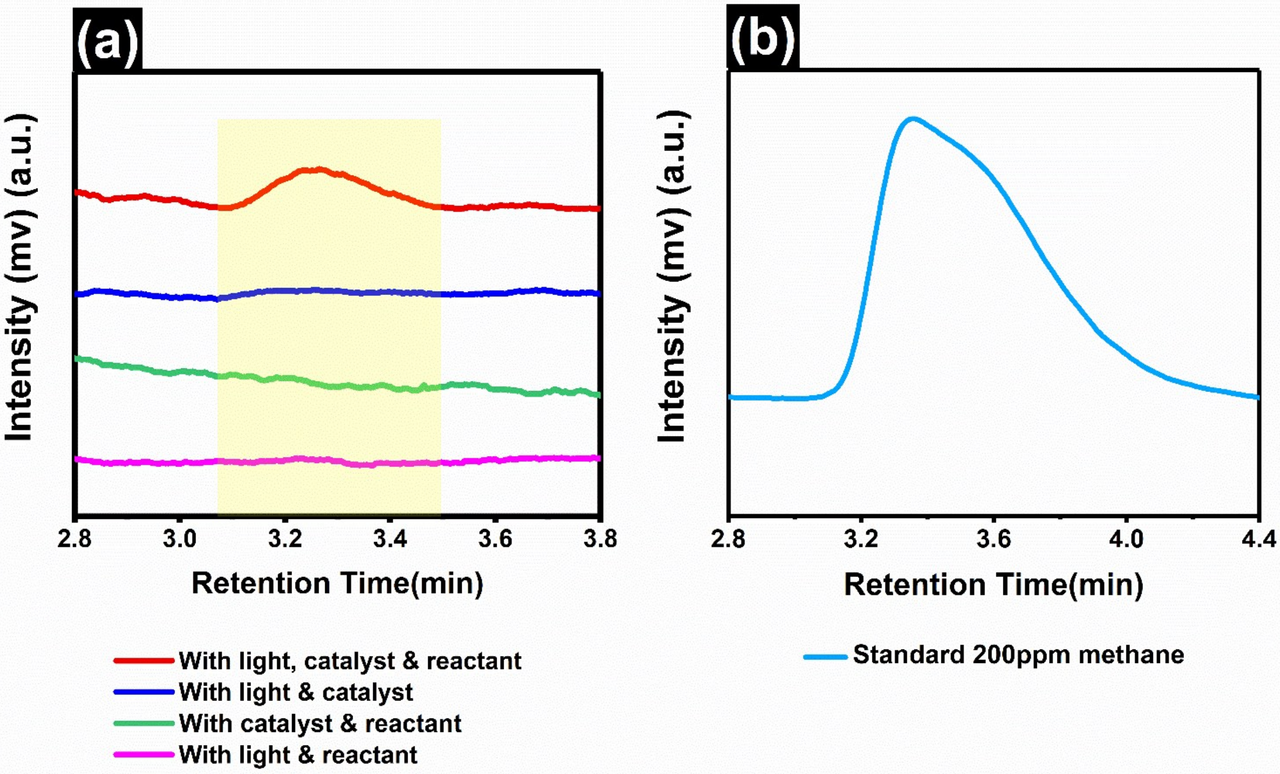

Figure S6 (a) Gas chromatograph results for different set of controlled experiments which also include experiment with light, catalyst and reactants. Notably, experiments without involving any of these three; could not result to any product formation. This also infers that the obtained reduced products are from the reactions and not from any adsorbed species on the catalysts. **(b)** The gas chromatograph result for 200ppm CH_4 in the standard gas mixture.

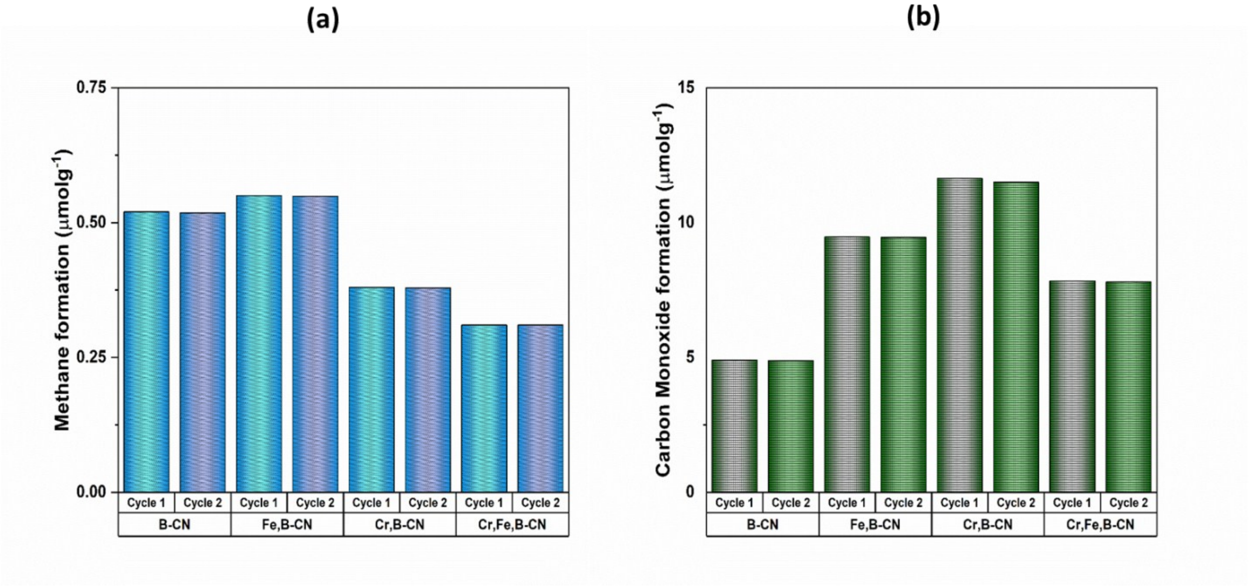

Figure S7 As-synthesized photocatalyst shows consistent reduced product formation such as (a) Methane and (b) Carbon monoxide after four hours (1st cycle) and 8hours (2nd Cycle).

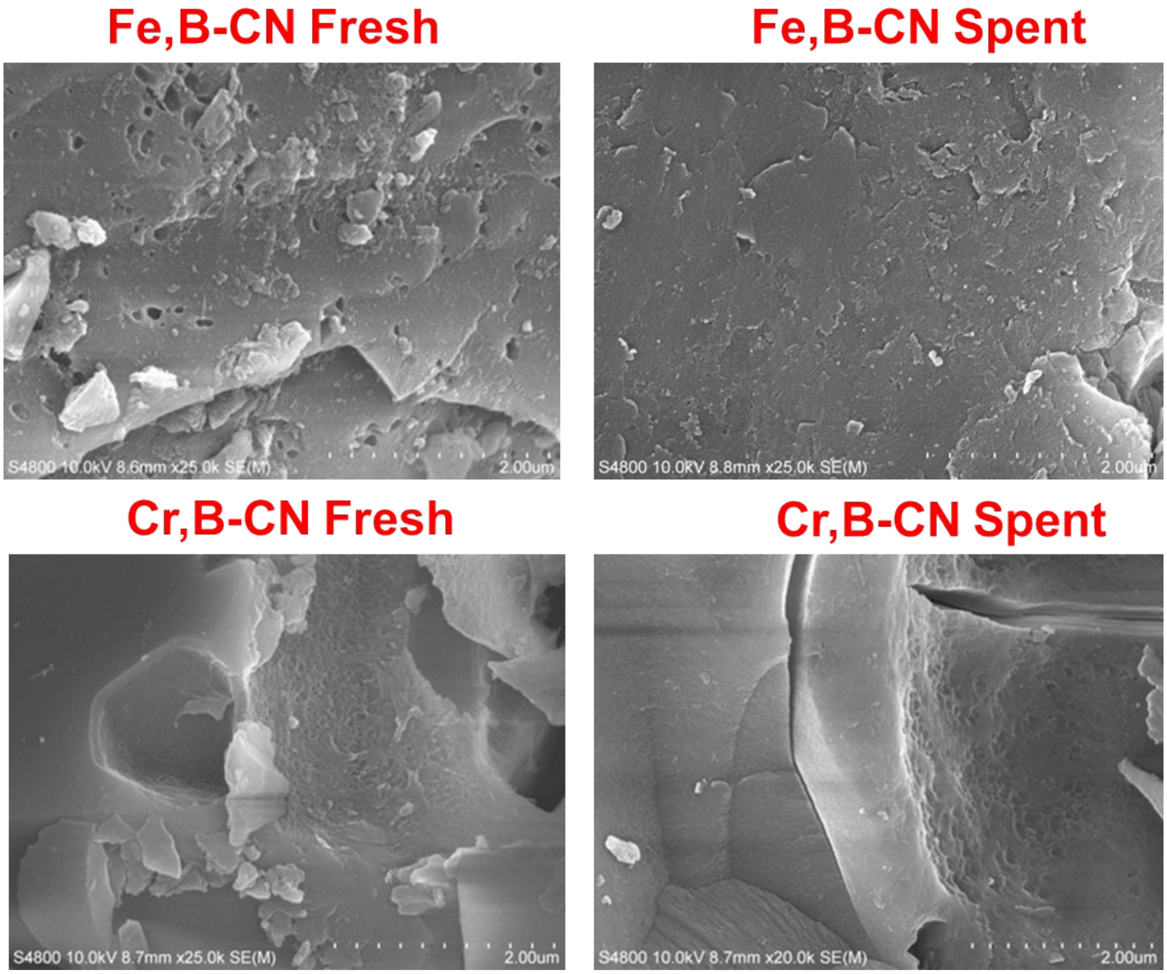

Figure S8 SEM micrographs for fresh and spent catalysts **(a)** Fe, B-CN and **(b)** Cr, B-CN. It is clearly evident that the two-dimensional structure remained intact even after post-reaction and therefore indicates higher stability for the catalysts.

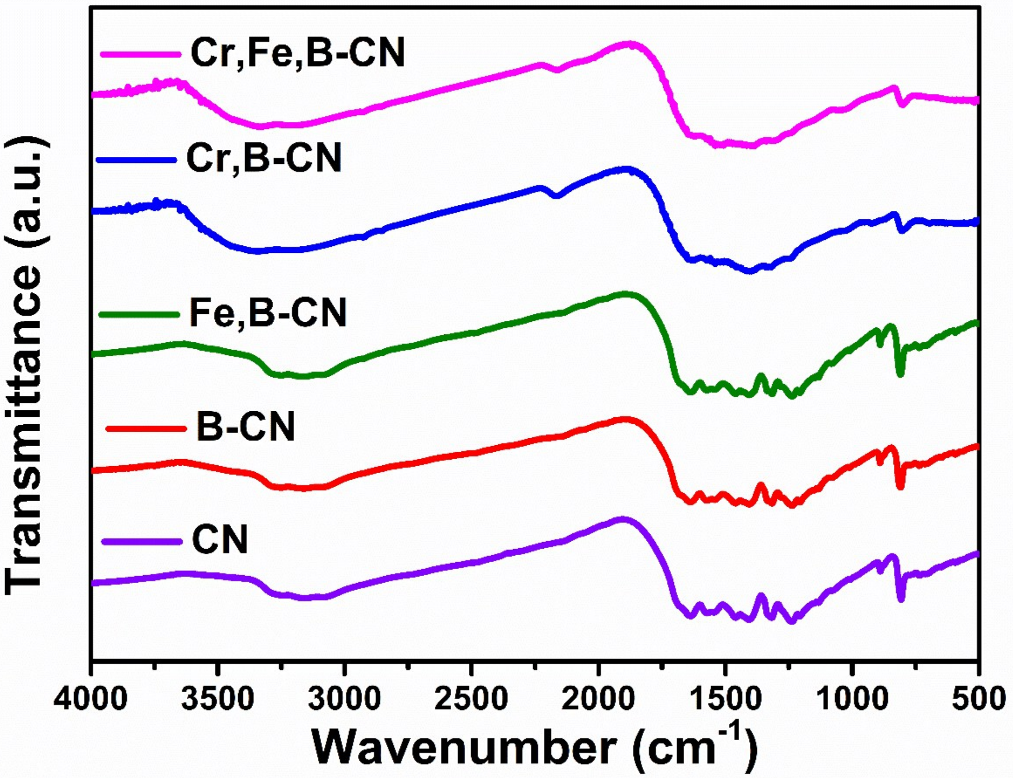

Figure S9 IR spectrum for used catalysts. Comparing pristine catalysts, no apparent changes in the spectral features of used catalysts were observed.

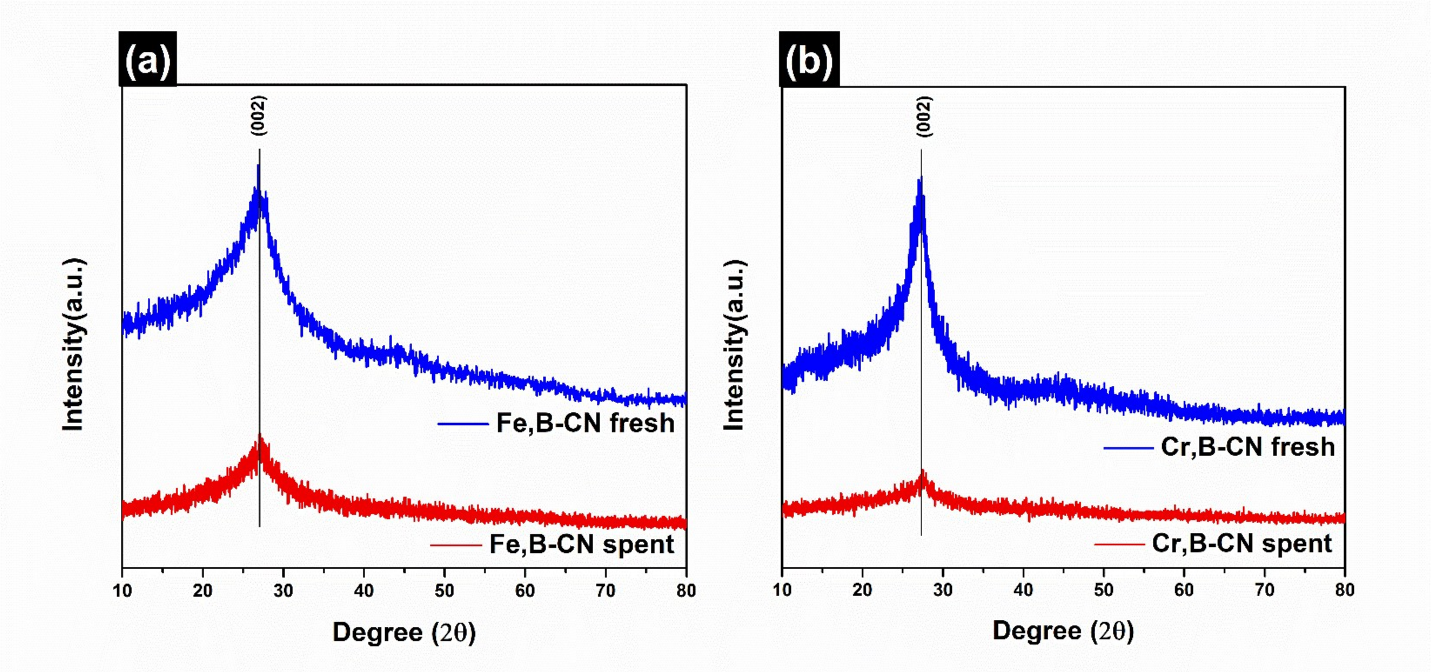

Figure S10 XRD pattern for spent catalysts **(a)** Fe, B-CN and **(b)** Cr, B-CN. No new peaks corresponding to any new phase appeared after reaction. And also, no shift in the peak position was observed. However, the peak intensity for the (002) peak diminished for the post-reaction catalysts, which could be attributed to change in the crystal structure. [9,10]

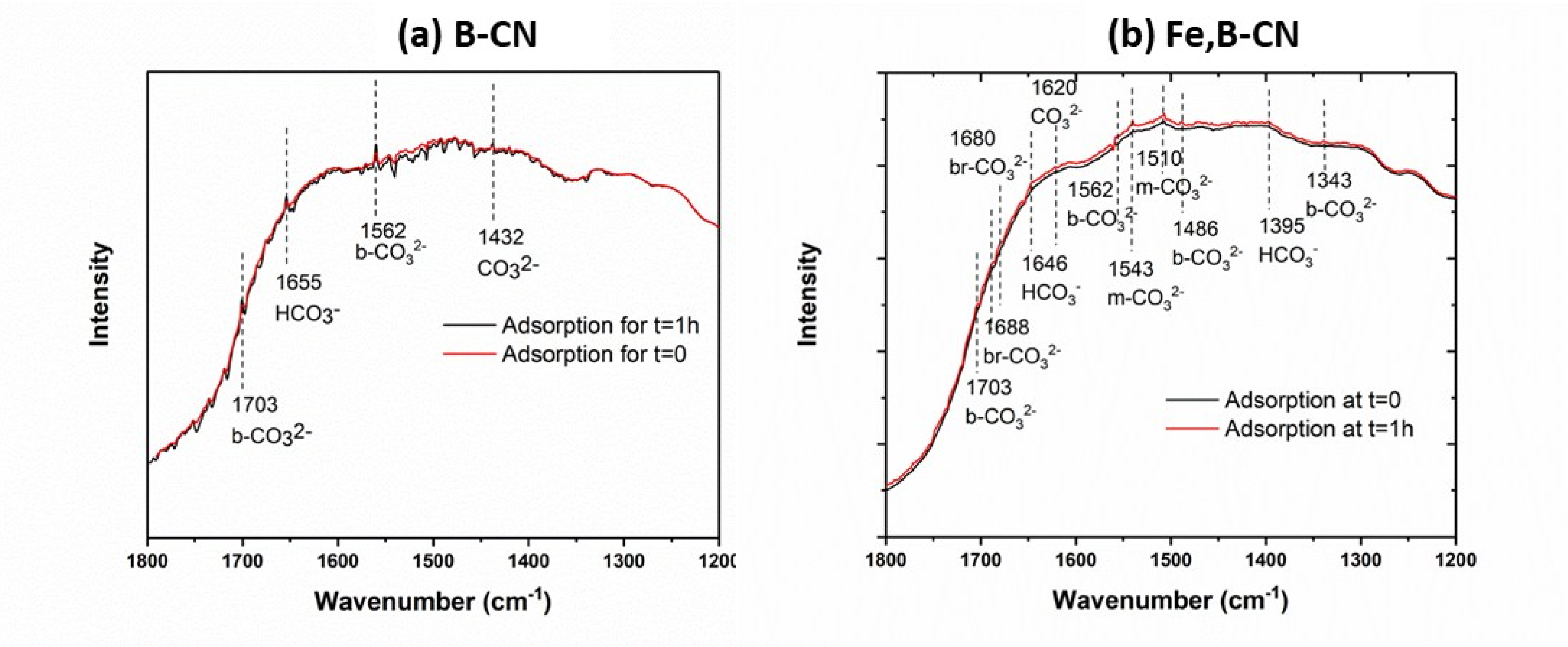

Figure S11 Changes in IR spectral features after adsorption of moist CO_2 for **(a)** B-CN and **(b)** Fe, B-CN. The data was collected for 1h exposure time at room temperature.

References

1 Q. Yan, G. F. Huang, D. F. Li, M. Zhang, A. L. Pan and W. Q. Huang, *Journal of Materials Science and Technology*, 2018, **34**, 2515–2520.

2 Q. Guo, Y. Zhang, J. Qiu and G. Dong, *Journal of Materials Chemistry C*, 2016, **4**, 6839–6847.

3 M. Zhou, S. Wang, P. Yang, C. Huang and X. Wang, *ACS Catalysis*, 2018, **8**, 4928–4936.

4 P. M. Sudeep, S. Vinod, S. Ozden, R. Sruthi, A. Kukovecz, Z. Konya, R. Vajtai, M. R. Anantharaman, P. M. Ajayan and T. N. Narayanan, *RSC Advances*, 2015, **5**, 93964–93968.

5 Y. Hang-Sheng, Z. Jian-Ying, N. An-Min and Z. Xiao-Bin, *Chinese Physics B*, 2008, **17**, 3453–3458.

6 M. J. Mendelssohn and H. J. Milledge, *International Geology Review*, 1995, **37**, 95–110.

7 Q. Zhang, M. Chen and M. Zhou, *Journal of Physical Chemistry A*, 2014, **118**, 6009–6017.

8 J. Liu, Y. Yu, R. Qi, C. Cao, X. Liu, Y. Zheng and W. Song, *Applied Catalysis B: Environmental*, 2019, **244**, 459–464.

9 M. Tahir, C. Cao, F. K. Butt, S. Butt, F. Idrees, Z. Ali, I. Aslam, M. Tanveer, A. Mahmood and N. Mahmood, *CrystEngComm*, 2014, **16**, 1825.

10 A. Kadam, M. Moniruzzaman and S.-W. Lee, *Molecules*, 2019, **24**, 450.