



Assessment of Ag Nanoparticles Interaction over Low-Cost Mesoporous Silica in Deep Desulfurization of Diesel.

Rafael V. Sales¹, Heloise O. M. A. Moura¹, Anne B. F. Câmara¹, Enrique Rodríguez-Castellón², José A. B. Silva¹, Sibeles B. C. Pergher¹, Leila M. A. Campos³, Maritza M. Urbina⁴, Tatiana C. Bicudo¹ and Luciene S. de Carvalho ^{1,*}

¹ Institute of Chemistry and School of Science and Technology, Federal University of Rio Grande do Norte, Energetic Technologies Research Group, 59078-900, Natal, Brazil.

² Dpto. de Química Inorgánica, Cristalografía y Mineralogía, Facultad de Ciencias, Universidad de Málaga, 29071, Málaga, Spain

³ Chemical Engineering Post-Graduate Program, Salvador University (UNIFACS), 40140-110, Salvador/BA Brazil.

⁴ Chemical Engineering, Center for Technology, Federal University of Alagoas, 57072-900, Maceió, AL, Brazil

* Correspondence: luciene_car@hotmail.com; Tel.: +55 84 9-8828-5261

SUPPLEMENTARY MATERIAL

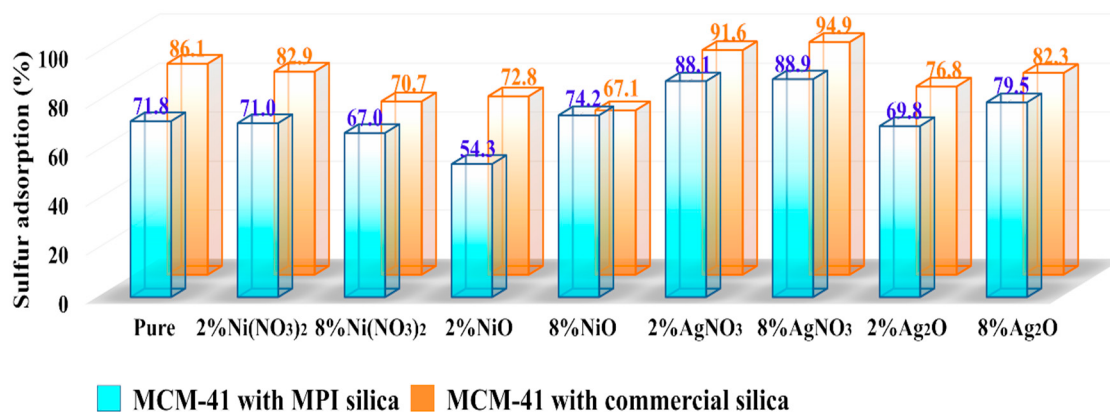


Fig. S1 Results for preliminary sulfur adsorption tests.

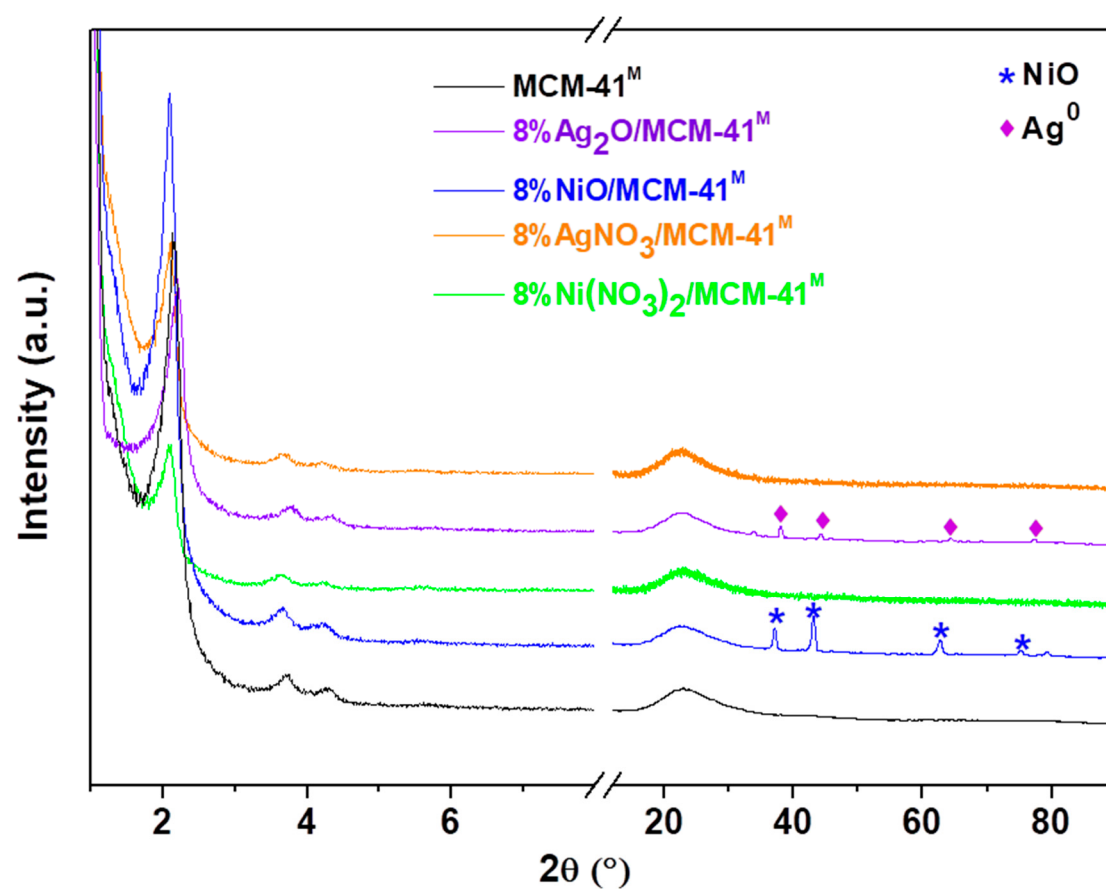


Fig. S2 XRD results for the adsorbents with 8% metal.

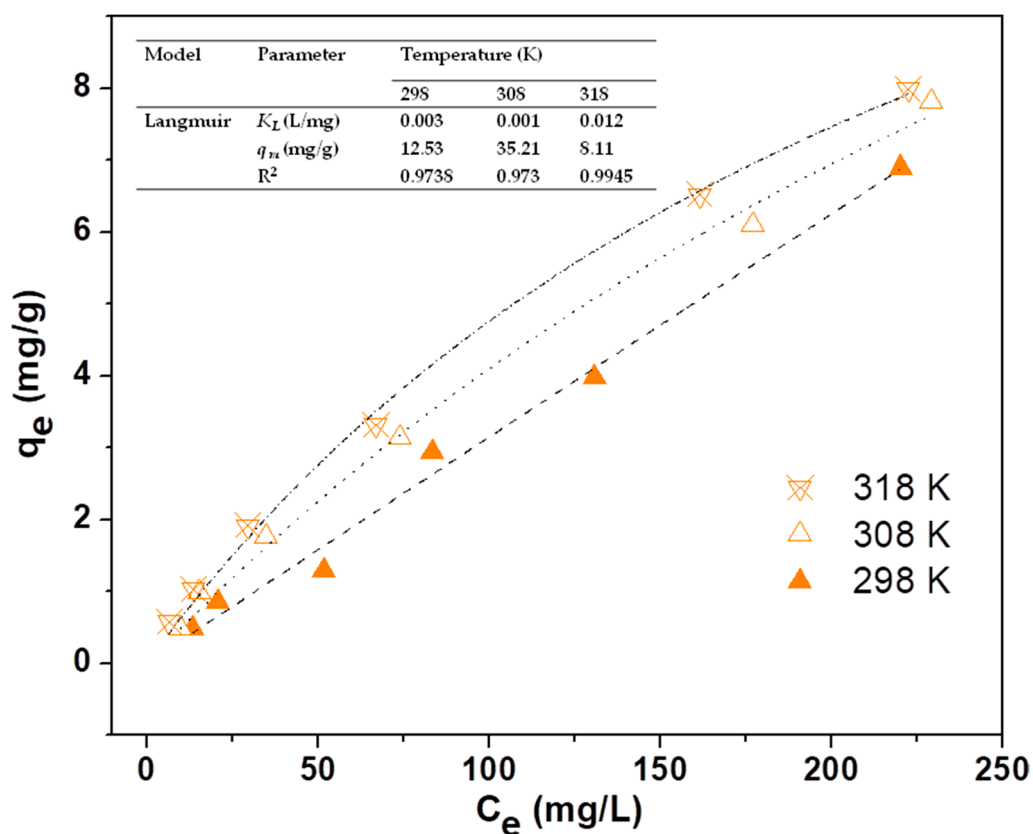


Fig. S3 Langmuir model fitting for sulfur adsorption results over $\text{AgNO}_3/\text{MCM-41}^{\text{M}}$ material at different temperatures.

Table S1 Sulfur compound distribution in a straight run diesel oil sample (Hua et al. 2003).

Sulfur compound group	Content (mg/Kg)
DBTs	37.3
4-MeDBTs	71.9
2-MeDBTs	50.8
3-MeDBTs	1.2
1-MeDBTs	38.9
4-EtDBTs	15.4
4,6-DMeDBTs	38.0
Alkyl S + TPs	550
Group BTs	1900
Group DBTs	2900
Group BNTs	20
Total S	5400

Alkyl S: thiols + sulfides + disulfides; TP: thiophenes; BT: benzothiophenes; DBT: dibenzothiophenes; BNT: benzonaphthothiophenes.

Table S2 Critical diameter data for the main aromatic organosulfurs in real diesel.

Organosulfur	Critical diameter (Å)	Reference
Thiophene	5.3	(Van der Voorde et al. 2015)
Benzothiophene	6.0	(Van der Voorde et al. 2015)
Dibenzothiophene	8.0	(Van der Voorde et al. 2015)
4,6-Dimethylbenzothiophene	9.0	(Jayne et al. 2005)
Ethyl mercaptan	5.1	(SIGMA-ALDRICH®)

Table S3 Sulfur adsorption performance of some materials studied in literature for comparison.

Adsorbent	Feedstock	Conditions	q _m (mg g ⁻¹)	Reference
Cu(I)/SBA-15(30)	Thiophene	30 °C, 6.27 % de Cu (wt%)	21.85	Kong et al. 2017
10Cu/SBA-15	Thiophene	Ambient conditions	14.33	Subhan et al. 2018a
AC/Ce/Fe	Thiophene, BT, DBT		0.33; 2.48; 3.70	Danmaliki et al. 2017
Activated boron nitride (BN)	DBT	25 °C, atmospheric pressure	42.2	Luo et al. 2018
Zn / Co @ C-800; Zn @ C-800; Co @ C-800	DBT	Room temperature	43.47; 37.93; 17.9	Huo et al. 2019
MMZ; 5Ni / MMZ; 10Ni / MMZ; UR.10Ni / MMZ; 15Ni / MMZ	Thiophene	Ambient conditions	16.96; 21.37; 23.98; 9.095; 10.87	Subhan et al. 2018b
P-4	DBT	Room temperature	52.41	Zhang et al. 2018
MCM-41 ^M	Diesel fuel	25 °C	3.06	This study
AgNO ₃ /MCM-41 ^M	Diesel fuel	25 °C, 2% Ag	31.25	This study
MCM-41 ^C	Diesel fuel	25 °C	7.25	This study
AgNO ₃ /MCM-41 ^C	Diesel fuel	25 °C, 2% Ag	15.41	This study

References

- Danmaliki, G.I., Saleh, T.A.: Effects of Ce/Fe nanoparticles on the desulfurization of thiophenes using activated carbon. *Chemical Engineering Journal*. 307, 914-927 (2017). <https://doi.org/10.1016/j.cej.2016.08.143>
- Hua, R., Li, Y., Liu, W., Zheng, J., Wei, H., Wang, J., Lu, X., Kong, H., Xu, G.: Determination of sulfur-containing compounds in diesel oils by comprehensive two-dimensional gas chromatography with a sulfur chemiluminescence detector. *J. Chrom. A*. 1019, 101-109 (2003). <https://doi.org/10.1016/j.chroma.2003.08.048>
- Huo, Q., Li, J., Liu, G., Qi, X., Zhang, X., Nig, Y., Zhang, B., Fu, Y., Liu, S.: Adsorption desulfurization performances of Zn/Co porous carbons derived from bimetal-organic frameworks. *Chemical Engineering Journal*. 362, 187-297 (2019). <https://doi.org/10.1016/j.cej.2019.01.050>
- Jayne, D., Zhang, Y., Haji, S., Erkey, C. Dynamics of removal of organosulfur compounds from diesel by adsorption on carbon aerogels for fuel cell applications. *International Journal of Hydrogen Energy*. 30, 1287-1293 (2005). <https://doi.org/10.1016/j.ijhydene.2005.03.014>
- Kong, L., Zhang, T., Yao, R., Zeng, Y., Zhang, L., Jian, P. Adsorptive desulfurization of fuels Cu (I)/SBA-15 via low-temperature reduction. *Microporous and Mesoporous*. 251, 69-76 (2017). <https://doi.org/10.1016/j.micromeso.2017.05.052>
- Luo, J., Xiong, J., Chao, Y., Li, X., Li, H., Pang, J., Zhu, F., Zhu, W., Li, H. Activated boron nitride ultrathin nanosheets for enhanced adsorption desulfurization performance. *Journal of the Taiwan Institute of chemical Engineers*. 93, 245-252 (2018). <https://doi.org/10.1016/j.jtice.2018.07.021>
- SIGMA-ALDRICH®: Molecular Sieves - Technical Information Bulletin. <https://www.sigmaaldrich.com/chemistry/chemical-synthesis/learning-center/technical-bulletins/al-1430/molecular-sieves.html>
- Subhan, F., Aslam, S., Yam, Z., Zhen, L., Ikram, M., Ullan, R., Etim, U.J., Ahmad, A. Ammonia assisted functionalization of cuprous oxide within confined spaces of SBA-15 for adsorptive desulfurization. *Chemical Engineering Journal*. 339 557-565 (2018a). <https://doi.org/10.1016/j.cej.2018.01.146>
- Subhan, F., Aslam, S., Yan, Z., Liu, Z., Etim, U.J., Wadood, A., Ullah, R. Confinement of mesopores within ZSM-5 and functionalization with Ni NPs for deep desulfurization. *Chemical Engineering Journal*. 354, 706-715 (2018b). <https://doi.org/10.1016/j.cej.2018.08.059>

Van der Voorde, B., Hezinová, M., Lannoeye, J., Vandekerkhove, A., Marszalek, B., Gil, B., Beurroies, I., Nachtigall, P., De Vos, D. Adsorptive desulfurization with CPO-27/MOF-74: an experimental and computational investigation. *Physical Chemistry Chemical Physics*. 17, 10759-10766 (2015). <https://doi.org/10.1039/c5cp01063b>

Zhang, I., Sun, S., Bian, Y., Li, W., Liu, R., Zhao, D. Adsorptive desulfurization of metal phthalocynine functionalized poly-ionic liquids grafted to sílica gel. *Fuel*. 220, 513-520 (2018). <https://doi.org/10.1016/j.fuel.2018.01.135>