

Supplementary Materials

Metal-Loaded Mesoporous MCM-41 for the Catalytic Wet Peroxide Oxidation (CWPO) of Acetaminophen

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Figure S1

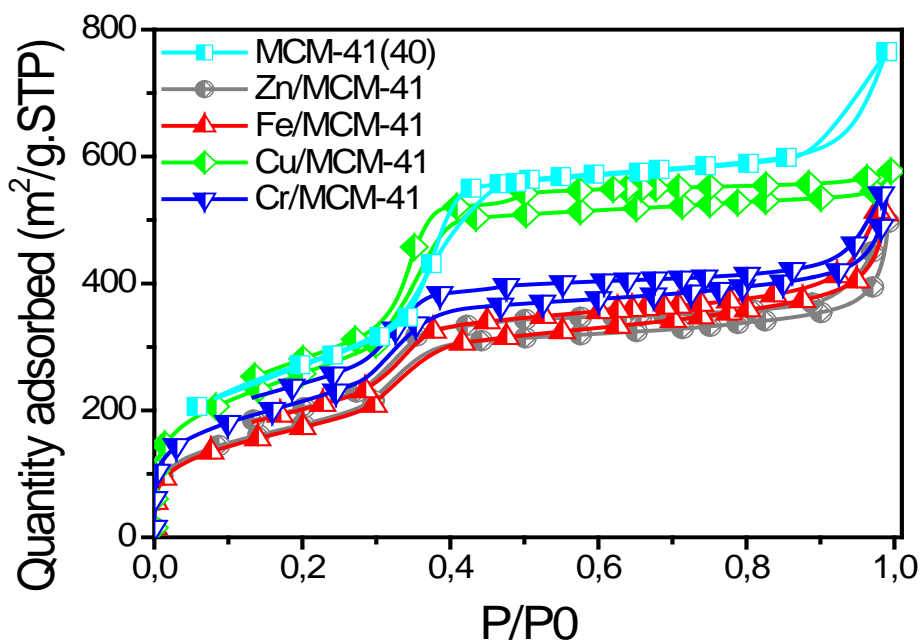


Figure S1. Nitrogen adsorption–desorption isotherms of the obtained calcined catalysts.

Figure S2

In this temperature range the mass loss in water varies in the following sequence MCM-41(5.9%) > Cr/MCM-41(4.79%) > Cu/MCM-41(4.4%) > Fe/MCM-41(4%) > Zn/MCM-41 (3.8%). In 120 and 700°C temperature range the mass loss varies in the following order MCM-41(38.4%) > Cu/MCM-41(36.42%) > Cr/MCM-41(35.21%) > Zn/MCM-41(34.7%) > Fe/MCM-41(33.05%). This also shows that a slight amount of CTA⁺ was removed during treatment with transition metals; this behavior is strongly linked to the cation exchange between a certain amount of CTA⁺ and the metal M⁺. This technique also shows that there has been an increase in the thermal stability of the metals-treated materials, suggesting that the transition metal has been reacted with the surfactant by different interactions, which subsequently gives rise to a better stability.

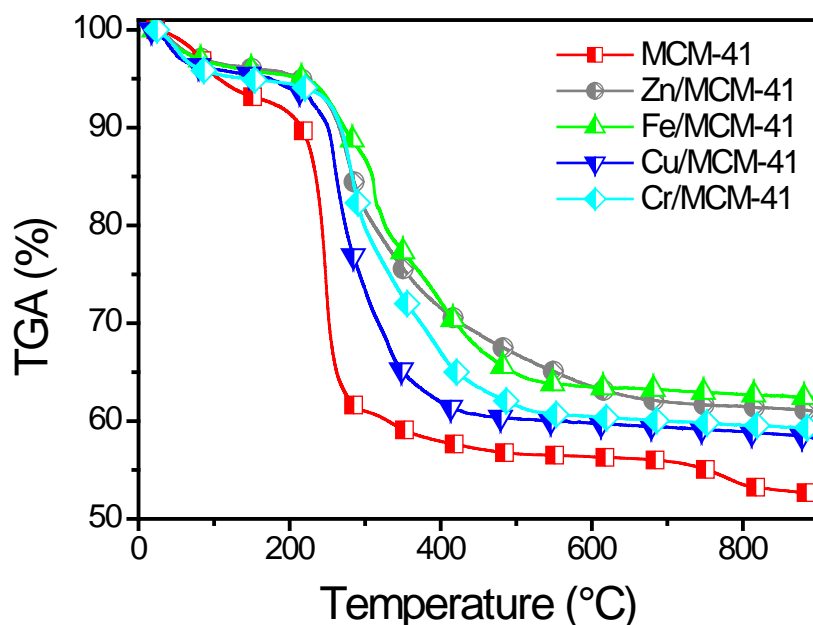


Figure S2. TGA analysis curves of obtained catalysts.

Figure S3

Figure S3a shows the FTIR spectra of MCM-41 modified by different transition metals prior calcination. All materials have a wide band at 3308 cm^{-1} mainly due to the O–H stretch of silanol groups and of the adsorbed water molecules [1–3]. There is also another band located at 1642 cm^{-1} which corresponds to the deformation vibrations of the adsorbed water molecules. The intense bands at 1221 and 1032 cm^{-1} correspond to the asymmetric stretching vibrations of the Si– or Al–O–Si bands [1–3]. The bands at 953 , 786 and 572 cm^{-1} are attributed to the asymmetric and symmetric stretching of T–O and to the deformation of T–O–T structure (T = Si, Al or transition metal), respectively. The C–H aliphatic bending vibrations overlapped with the N–H deformation vibrations can be observed at 1482 cm^{-1} . The band at 1325 cm^{-1} is assigned to the symmetrical vibration of $-\text{CH}_2$ [1–3]. The bands at 2919 and 2848 cm^{-1} are mainly due to the presence of the CTABr surfactant, which corresponds to the asymmetric and symmetrical C–H vibrations of $-\text{CH}_3$ and $-\text{CH}_2$, respectively [4].

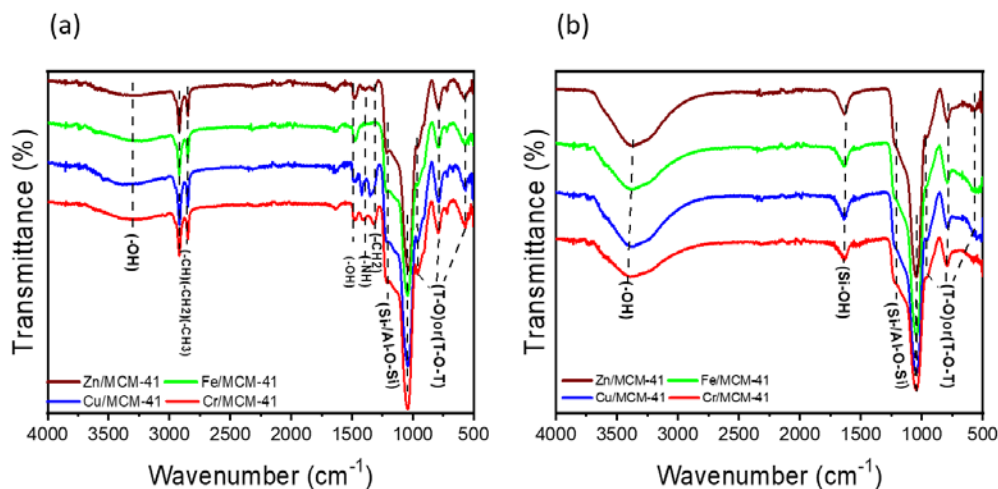


Figure S3. FTIR spectra of non-calcined (a) and calcined (b) catalysts.

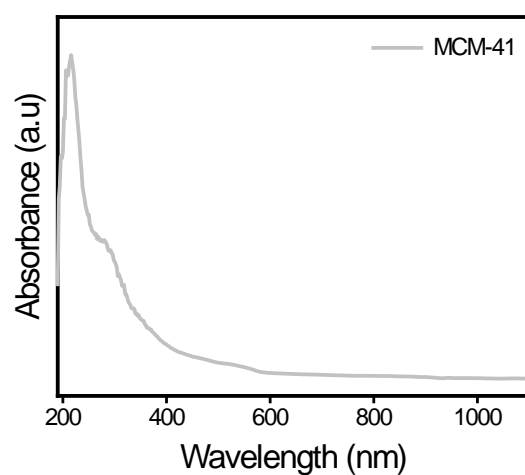


Figure S4. UV-Vis spectra of the calcined MCM-41.

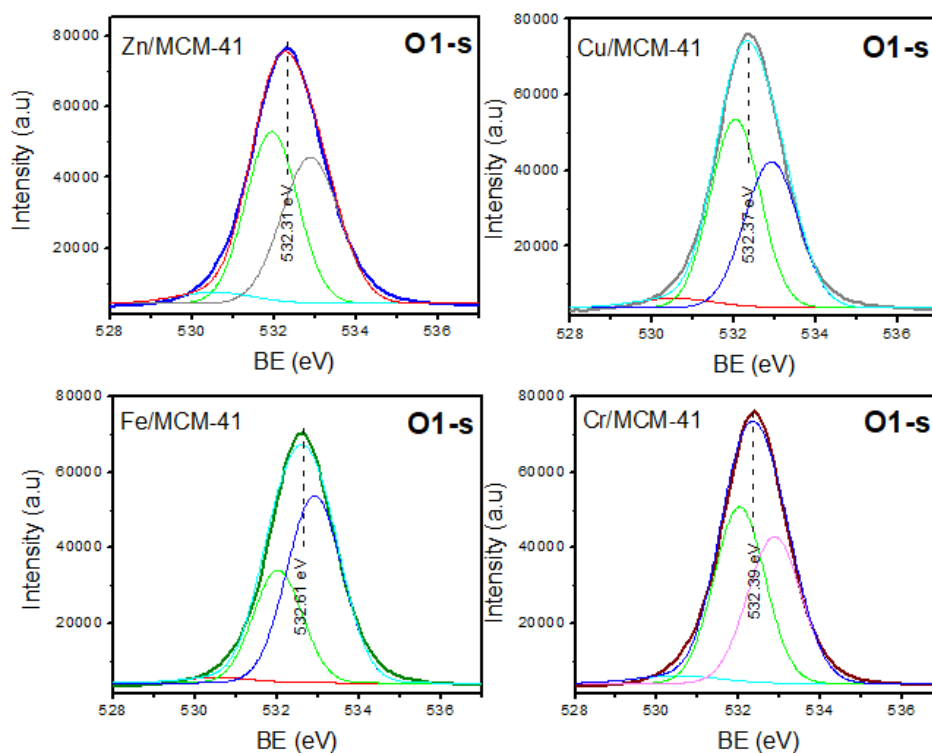


Figure S5. Typical XPS O1s spectra of the calcined catalysts Cr/MCM-41, Cu/MCM-41, Zn/MCM-41 and Fe/MCM-41.

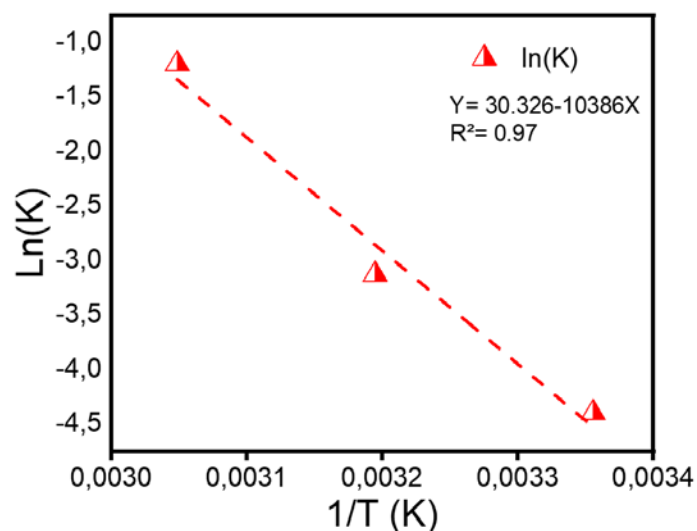
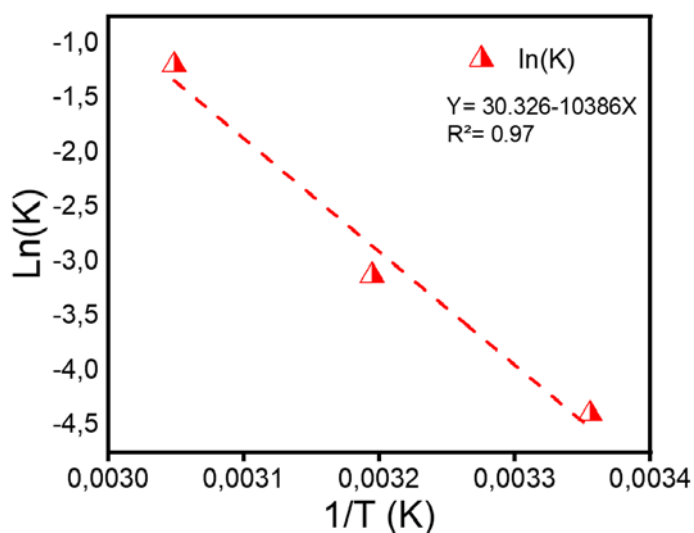


Figure S6. Adsorption tests.

Figure S7. Arrhenius plot Log K versus $1/T$ acetaminophen oxidation by Fe/MCM-41.

References

1. Boukoussa, B.; Kibou, Z.; Abid, Z.; Ouargli, R.; Choukchou-Braham, N.; Villemin, D.; Bengueddach, A.; Hamacha, R. Key factor affecting the basicity of mesoporous silicas MCM-41: effect of surfactant extraction time and Si/Al ratio. *Chem. Pap.* **2018**, *72*, 289–299, doi:10.1007/s11696-017-0279-4.
2. Boukoussa, B.; Zeghada, S.; Ababsa, G.B.; Hamacha, R.; Derdour, A.; Bengueddach, A.; Mongin, F. Catalytic behavior of surfactant-containing-MCM-41 mesoporous materials for cycloaddition of 4-nitrophenyl azide. *Appl. Catal. A Gen.* **2015**, *489*, 131–139, doi:10.1016/j.apcata.2014.10.022.
3. Boukoussa, B.; Hamacha, R.; Morsli, A.; Bengueddach, A. Adsorption of yellow dye on calcined or uncalcined Al-MCM-41 mesoporous materials. *Arab. J. Chem.* **2017**, *10*, S2160–S2169, doi:10.1016/j.arabjc.2013.07.049.
4. Su, G.; Yang, C.; Zhu, J.J. Fabrication of gold nanorods with tunable longitudinal surface plasmon resonance peaks by reductive dopamine. *Langmuir* **2015**, *31*, 817–823, doi:10.1021/la504041f.