Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

XPS results on M_MCM-41 SAMPLES

High-resolution Fe 2p spectra (Figure S1) were recorded with a large number of scans in order to increase the signal-to-noise ratio.

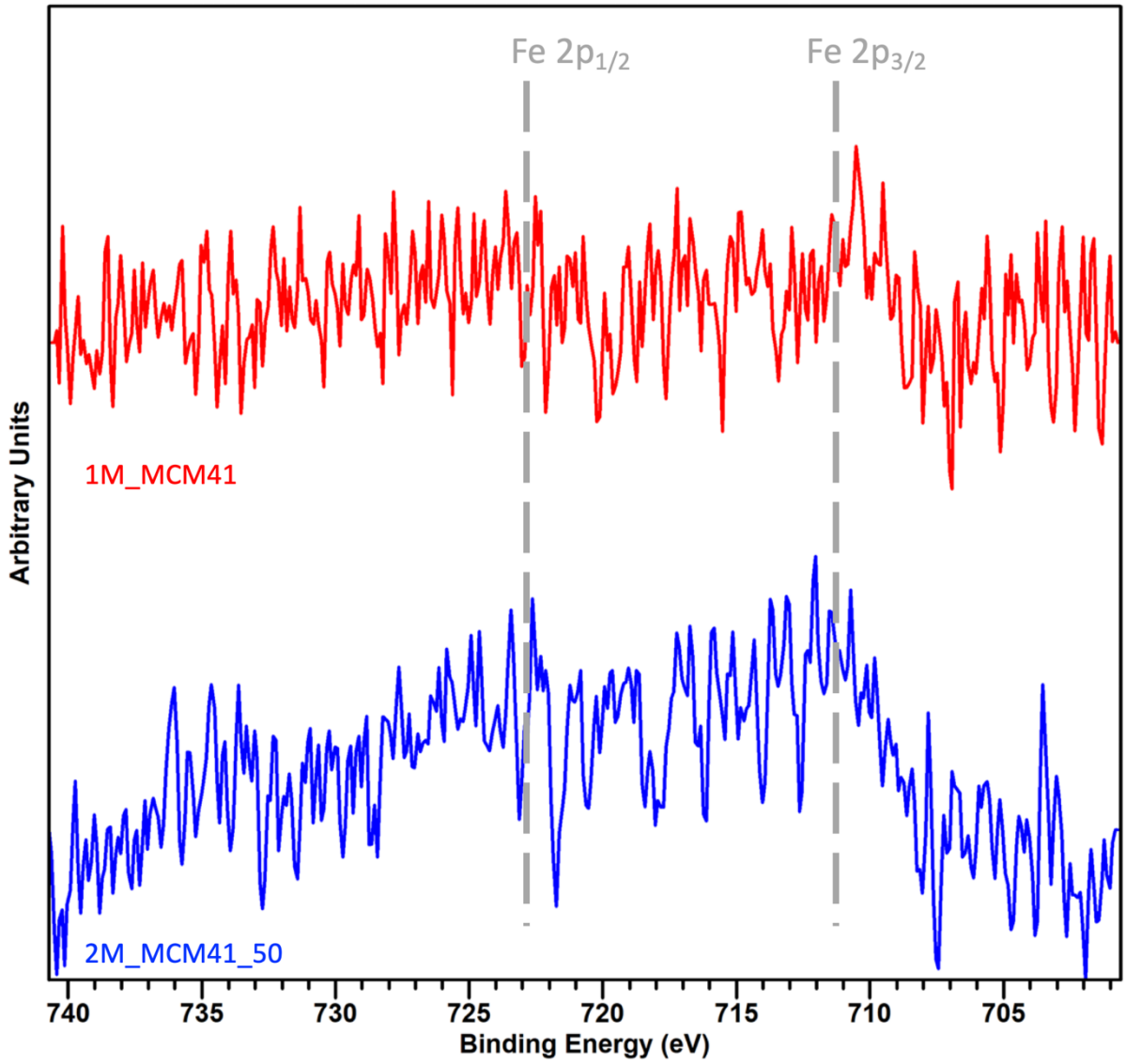

Figure S1: Fe 2p detailed spectra of 1M_MCM41 (red) and 2M_MCM41_50 (blue) samples.

Fe 2p spectra is composed of a doublet Fe $2p_{3/2}$ – Fe $2p_{1/2}$ due to the spin-orbit coupling with an energy separation of about 13 eV and with intensity ratio of 2:1.

Despite the bulk concentration of iron in the samples is expected to be high enough to provide clearly detectable Fe signals, the Fe 2p doublet is barely visible even in the case of 2M_MCM41_50 sample (13 wt%) and it is not detected for the 1M_MCM41 (4 wt%) sample.

In order to distinguish between the different chemical state of iron, curve fitting of the signals is required, thus, model curves determined on standard reference materials should be adapted to the experimental ones; due to the poor signal-to-noise ratio of the Fe 2p signal also in the case of 2M_MCM41_50 sample, no curve-fitting procedure was attempted.

The reason of such a low intensity signal might be ascribed to the XPS sampling depth, for electrons emitted from iron and travelling through an inorganic silica matrix.

The sampling depth can be estimated as $3\lambda\cos\theta$, where l is the inelastic mean free path, and θ is the emission angle (53° in our experiments). According to the semi-empirical approach proposed by Seah, M.P. and Dench W.A. (1979), Quantitative electron spectroscopy of surfaces: A standard data base for electron inelastic mean free paths in solids. Surf. Interface Anal., 1: 2-11. https://doi.org/10.1002/sia.740010103], λ (nm) can be estimated by the equation:

$$\lambda = {}^{A}/_{KE^2} + B \times \sqrt{KE}$$

where A = 641 and B = 0.096 for an inorganic matrix. A binding energy value of 711 eV for the Fe $2p_{3/2}$ signal, the resulting kinetic energy value is KE = (1486.6 – 711) eV = 775.6 eV and l is estimated to be 2.7 nm; the sampling depth, d, is estimated to be equal to 4.8 nm using the equation $d = 3\lambda\cos\theta$. Such results substantiate the hypothesis that the iron oxide is located inside the pores and that iron signals are attenuated from at least two MCM41 silica walls, considering the estimated attenuation length.