

SUPPORTING INFORMATION

Details of the determination of the chemical formula of the produced ferrites. The proposed chemical formula was determined according the following calculations, assuming both the electroneutrality and the matter conservation in the studied systems:

$$2[\text{O}^{2-}] = 2[\text{Zn}^{2+}] + 2[\text{Fe}^{2+}] + 2[\text{Mn}^{2+}] + 3[\text{Fe}^{3+}] + 3[\text{Mn}^{3+}] + 4[\text{Mn}^{4+}]$$

$$2[\text{O}] = 2[\text{Zn}] + 2 \times 0.35[\text{Fe}] + 2 \times 0.50[\text{Mn}] + 3 \times 0.65[\text{Fe}] + 3 \times 0.40[\text{Mn}] + 4 \times 0.10[\text{Mn}]$$

Where $[\text{O}^{2-}]$, $[\text{Zn}^{2+}]$, $[\text{Fe}^{2+}]$, $[\text{Mn}^{2+}]$, $[\text{Fe}^{3+}]$, $[\text{Mn}^{3+}]$, $[\text{Mn}^{4+}]$, $[\text{O}]$, $[\text{Zn}]$, $[\text{Fe}]$ and $[\text{Mn}]$ are the chemical composition per formula unit of the O^{2-} , Zn^{2+} , Fe^{2+} , Mn^{2+} , Fe^{3+} , Mn^{3+} , Mn^{4+} , O, Zn, Fe and Mn species, respectively.

$$2 \times 4 = 2[\text{Zn}] + 2 \times 0.35 \times \left(\frac{\text{wt.}_{\text{Fe}} \times 65.370}{\text{wt.}_{\text{Zn}} \times 55.847} \right) \times [\text{Zn}] + 2 \times 0.50 \times \left(\frac{\text{wt.}_{\text{Mn}} \times 65.370}{\text{wt.}_{\text{Zn}} \times 54.938} \right) \times [\text{Zn}] +$$

$$3 \times 0.65 \times \left(\frac{\text{wt.}_{\text{Fe}} \times 65.370}{\text{wt.}_{\text{Zn}} \times 55.847} \right) \times [\text{Zn}] + 3 \times 0.40 \times \left(\frac{\text{wt.}_{\text{Mn}} \times 65.370}{\text{wt.}_{\text{Zn}} \times 54.938} \right) \times [\text{Zn}] + 4 \times 0.10 \times$$

$$\left(\frac{\text{wt.}_{\text{Mn}} \times 65.370}{\text{wt.}_{\text{Zn}} \times 54.938} \right) \times [\text{Zn}]$$

Where wt._{Mn} , wt._{Fe} and wt._{Zn} are the Mn, Fe and Zn weight content determined by ICP analysis for each samples, respectively, assuming from XPS measurements that 35 and 65% of the iron atoms are in the oxidation state +2 and +3, respectively, while 50, 40 and 10% of the manganese atoms are in the oxidation state +2, +3 and +4, respectively.

We deduce then the stoichiometry coefficient of Zn (α), and then Zn^{2+} , in the general

spinel ferrite formula unit $(\text{Zn}_{\alpha}^{2+} \text{Fe}_{\beta}^{2+} \text{Mn}_{\delta}^{2+}) (\text{Fe}_{\gamma}^{3+} \text{Mn}_{\lambda}^{3+} \text{Mn}_{\omega}^{4+})_{\varepsilon} \text{O}_4$:

$$\alpha = \frac{8}{2 + (2 \times 0.35 + 3 \times 0.65) \times \left(\frac{\text{wt.}_{\text{Fe}} \times 65.370}{\text{wt.}_{\text{Zn}} \times 55.847} \right) + (2 \times 0.50 + 3 \times 0.40 + 4 \times 0.10) \times \left(\frac{\text{wt.}_{\text{Mn}} \times 65.370}{\text{wt.}_{\text{Zn}} \times 54.938} \right)}$$

From this value it is possible to determine the stoichiometry coefficient all the other cations, and that of the cation vacancies and called here l, the latter being obtained thanks to the following equation:

$$l = 3 - (\alpha + \beta + \delta + \gamma + \lambda + \omega)$$

Indeed, in a stoichiometric spinel ferrite compound AB_2O_4 , the sum of the cation content must reach 3 and then $1+\alpha+\beta+\delta+\gamma+\lambda+\omega = 3$.

Tabulated metal-oxygen distances in oxides. The metal cation oxygen distance is dependent on the oxidation state of the cations and their local symmetry. These values are tabulated in oxides and are summarized here after for Mn-O, Fe-O and Zn-O bonds:

| | R_{tetra} (Å) | R_{octa} (Å) | Reference |
|---------------------|-----------------|----------------|-----------|
| Mn ²⁺ -O | 2.04 | 2.22 | [31,32] |
| Mn ³⁺ -O | - | 2.04 | [31,32] |
| Mn ⁴⁺ -O | - | 1.84 | [31,32] |
| Fe ²⁺ -O | 2.01 | 2.13 | [33] |
| Fe ³⁺ -O | 1.89 | 2.00 | [34] |
| Zn ²⁺ -O | 1.97 | 2.05 | [31,35] |

Table S1. Tetrahedral and octahedral bond distances for cubic spinels, taken from structure refinements of dense oxides and silicates. When more than one reference is cited, the tabulated values of R_{tetra} and R_{octa} represent average values. The range of observed values is typically within $\pm 2\%$ of the average.

EXAFS Analysis. The quality of the fits performed on the inverse Fourier transform of the first peak at the K(Fe) and K(Zn) edges EXAFS signal of P8M sample is illustrated here after assuming two Fe-O distances and only Zn-O one.

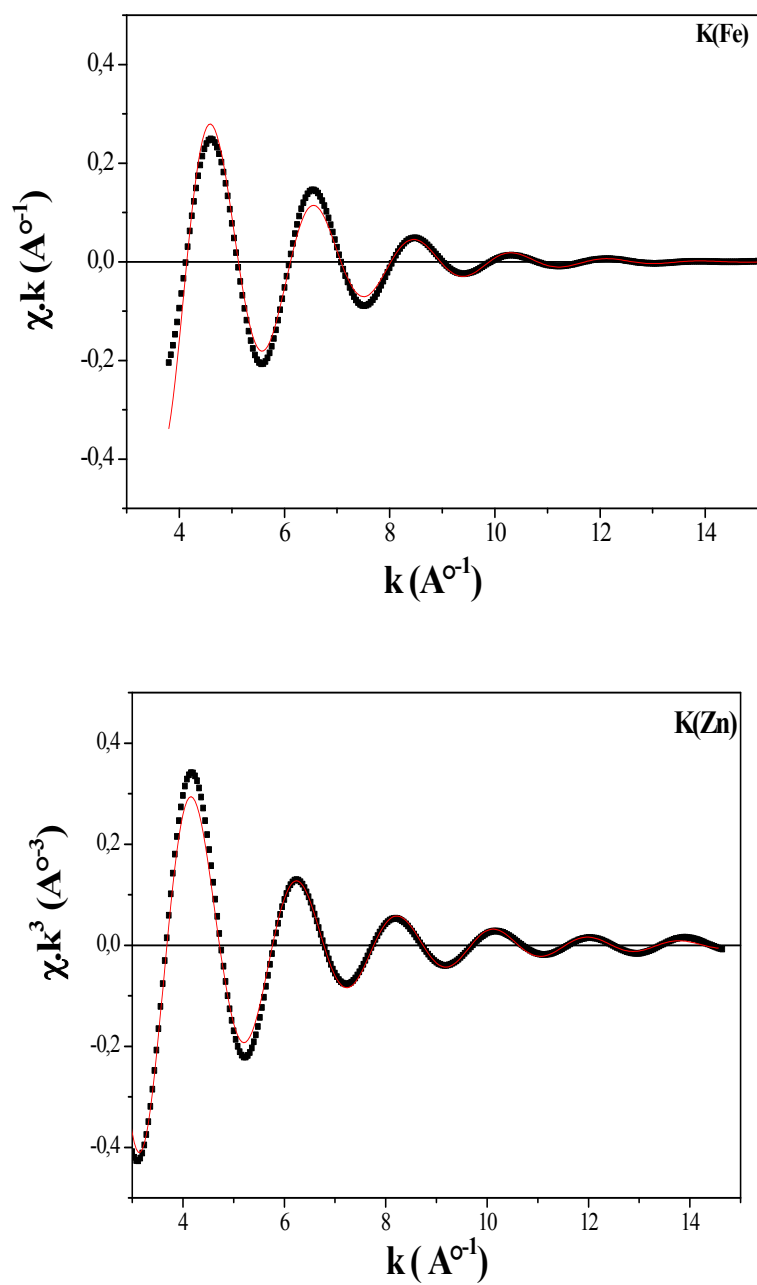


Figure S2. Inverse Fourier transform of the first peak at the K(Fe) and K(Zn) edges for P8M sample. The solid line is the fit of Eq. (2) given in the main text.

Particles size distribution. The size distribution of the particles constituting P8M and P2M samples and its statistical analysis through a lognormal law is illustrated in Figure S3

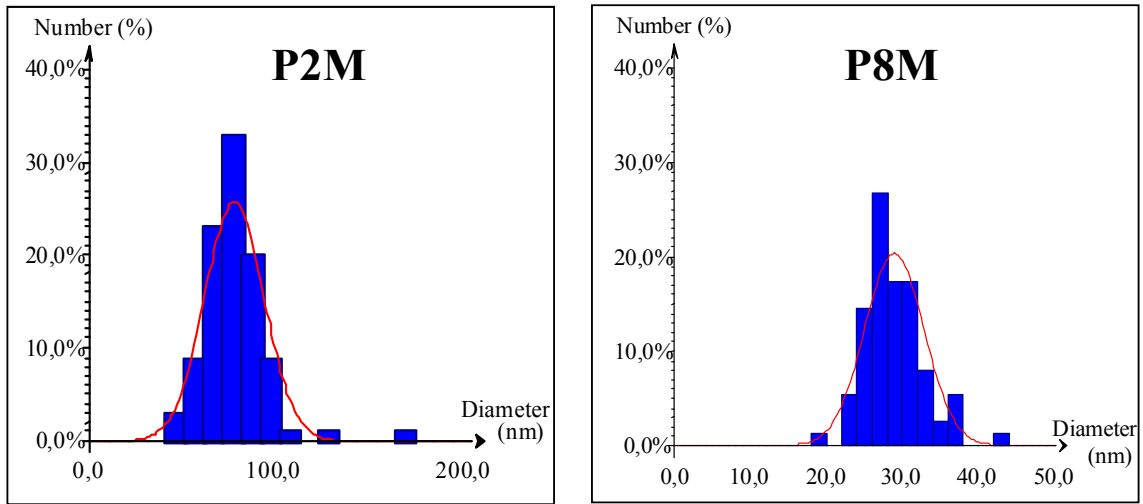


Figure S3. Size distribution of the polyol-made P2M and P8M particles as inferred from TEM observation.

Catalysis tests. To appreciate the catalytic performance of the produced ferrite nanoparticles toward DME combustion, though blank tests have been performed. The DME conversion was plotted as a function of the operating temperature in Figure S4, evidencing that the non-catalytic combustion can be achieved only at high temperatures (higher than those required for the catalytic one).

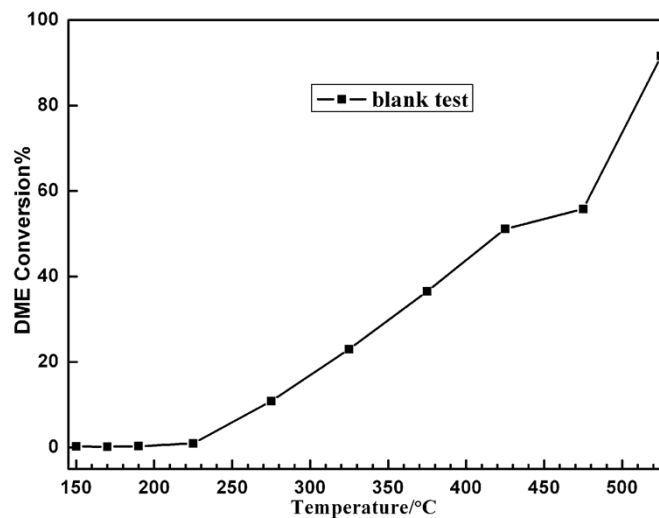


Figure S4. DEM combustion-blank test [46a] performed in the same conditions than those used with our catalysts.