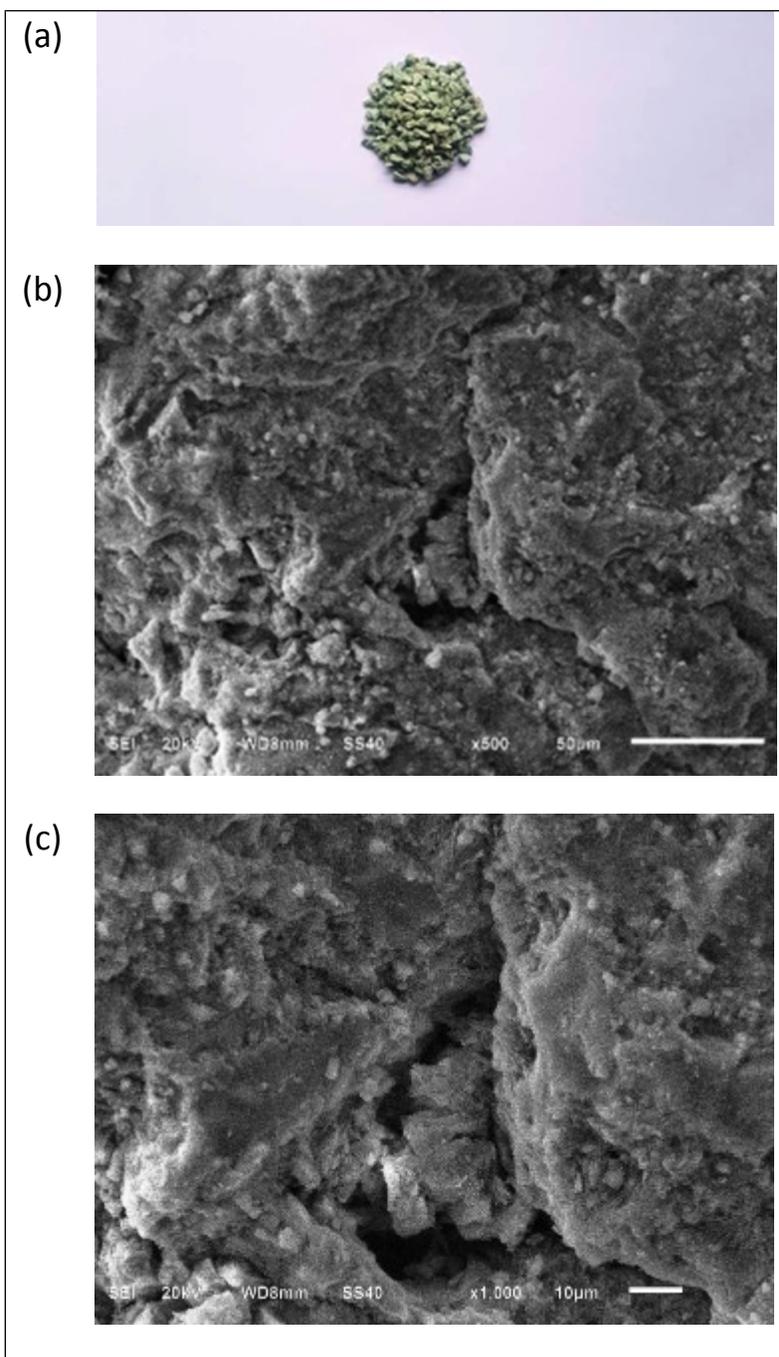
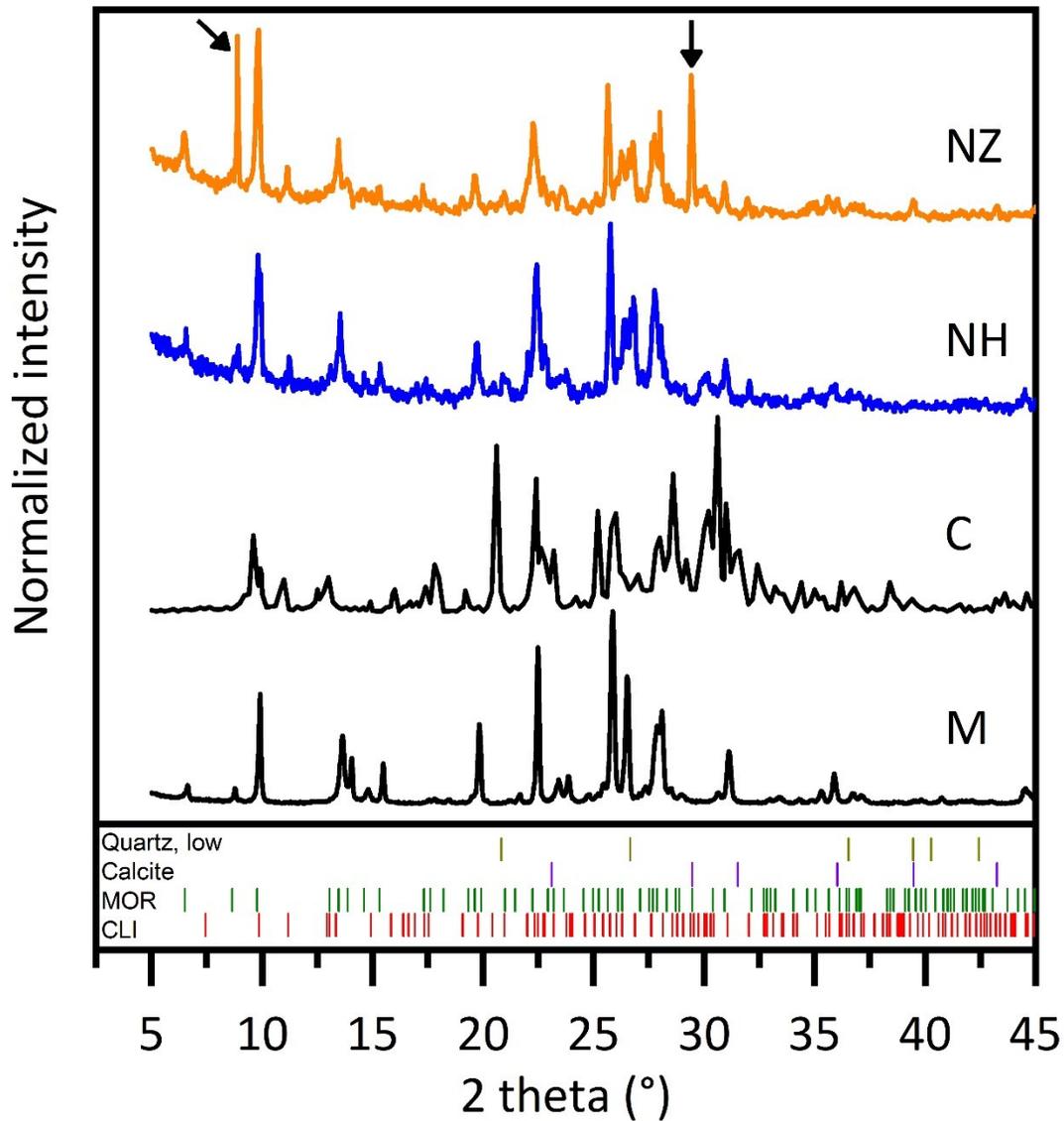


**Supplement 1**



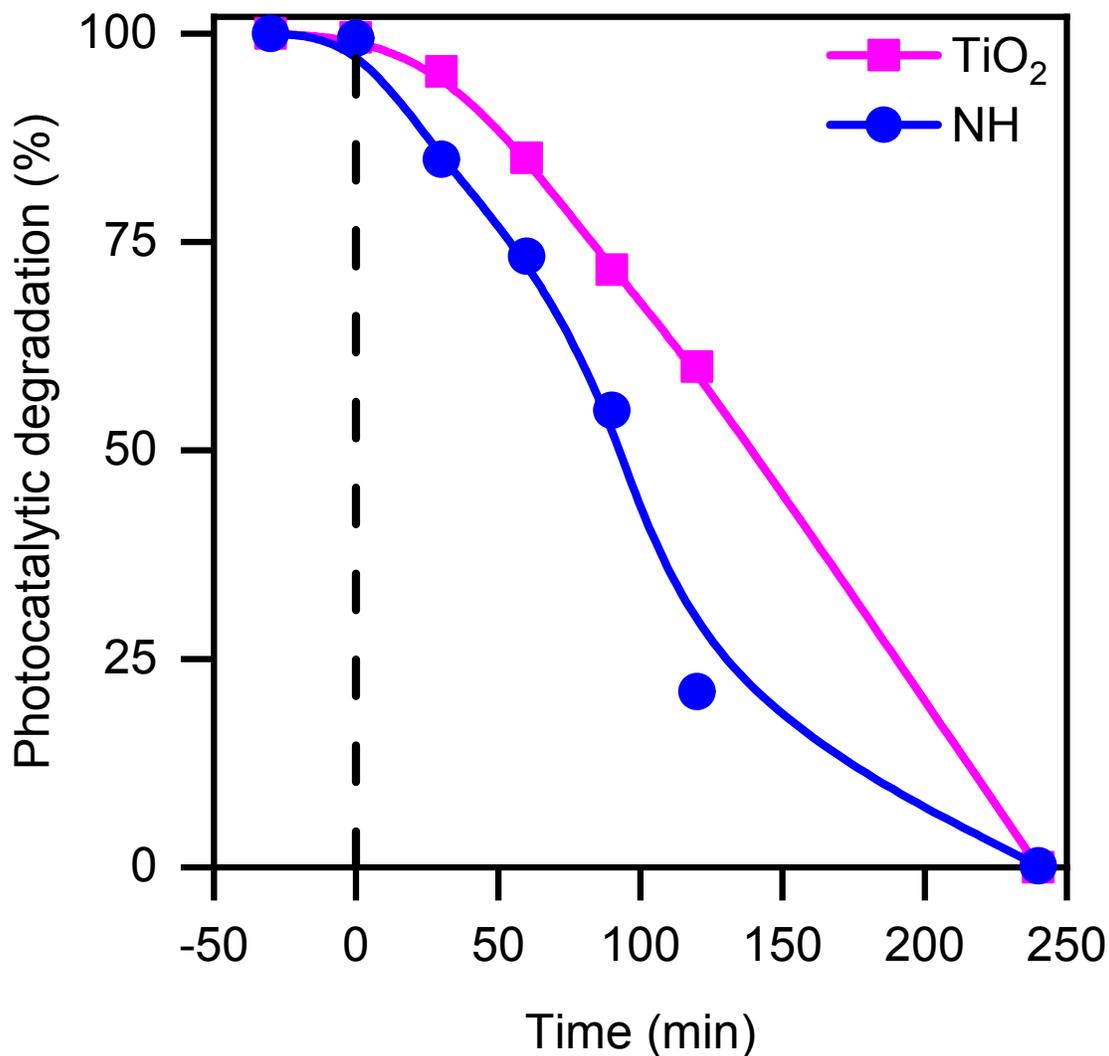
**S1.** (a) Grains and SEM images of the natural zeolite NH at magnification (b) x500 and (c) x1000.

## Supplement 2



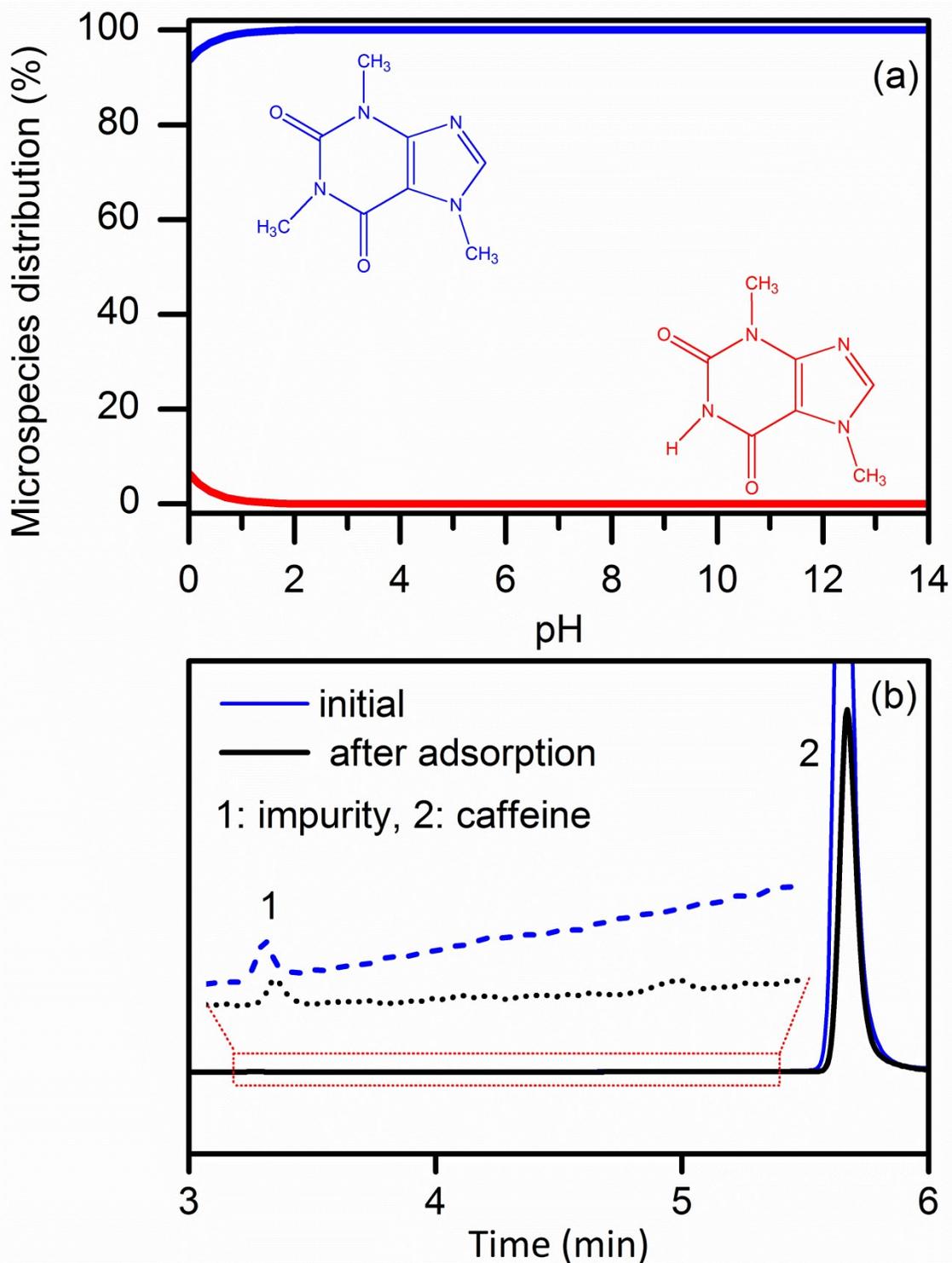
**S2.** Normalized X-ray diffraction patterns of the natural zeolitic tuff (NZ), natural zeolitic tuff treated with acid solution (NH), and the synthetic zeolites C and M. The marks at the bottom of the figure indicate different phases: low quartz (PDF: 00-005-0490), calcite (PDF: 01-085-1108), clinoptilolite (PDF: 01-080-1557), and mordenite (PDF: 04-014-3294). The peaks marked by arrows at 8.9 and 29.4 ° indicate impurities in NZ disappearing after acid treatment to yield NH.

### Supplement 3



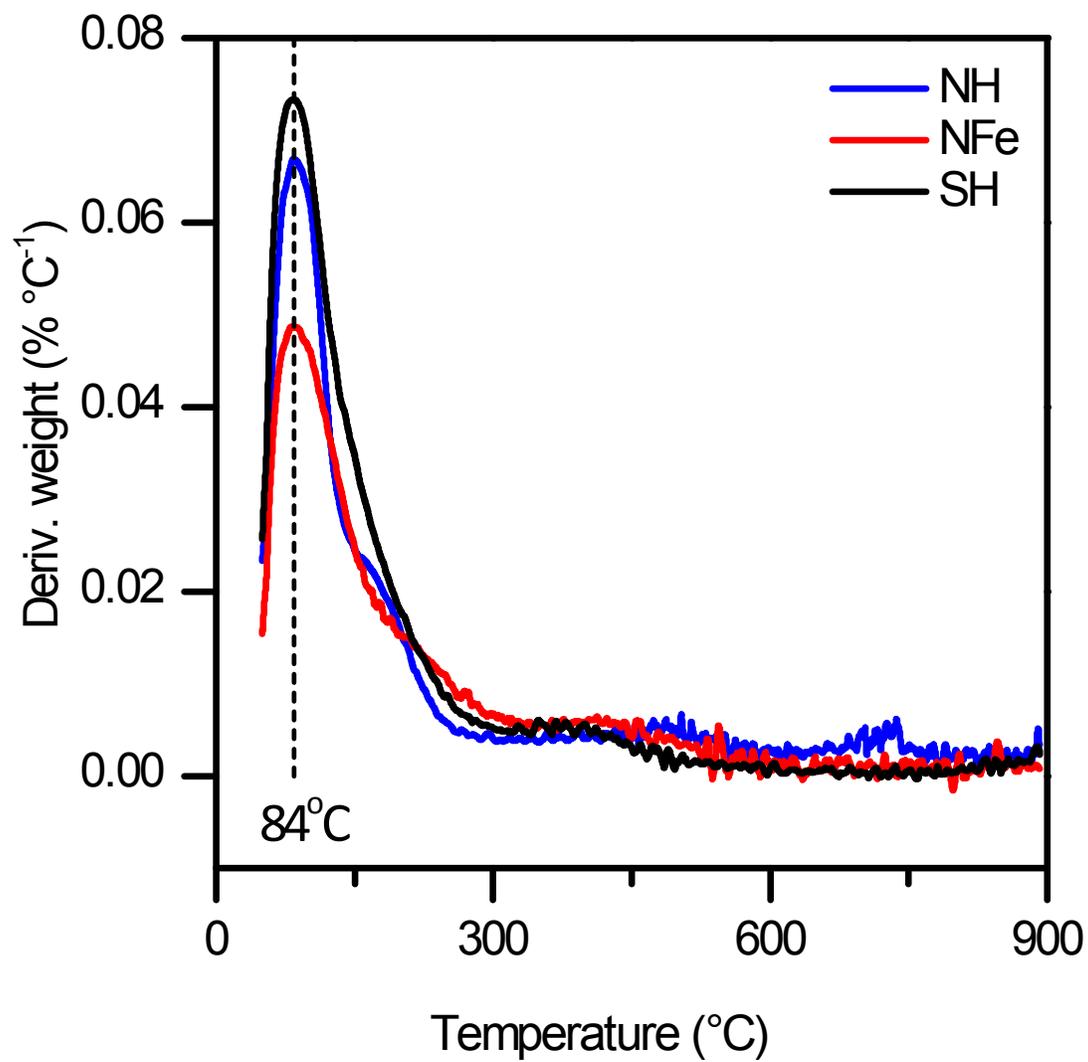
**S3.** Comparison between the photocatalytic activity of the natural zeolite NH and TiO<sub>2</sub> particles (anatase phase) in the decomposition of caffeine in aqueous solution. Mass to volume ratio 10 g L<sup>-1</sup> for NH and 4 g L<sup>-1</sup> for TiO<sub>2</sub>. Anatase (66 m<sup>2</sup>g<sup>-1</sup>) was prepared hydrothermally using TiOSO<sub>4</sub>·xH<sub>2</sub>O as precursor.

Supplement 4



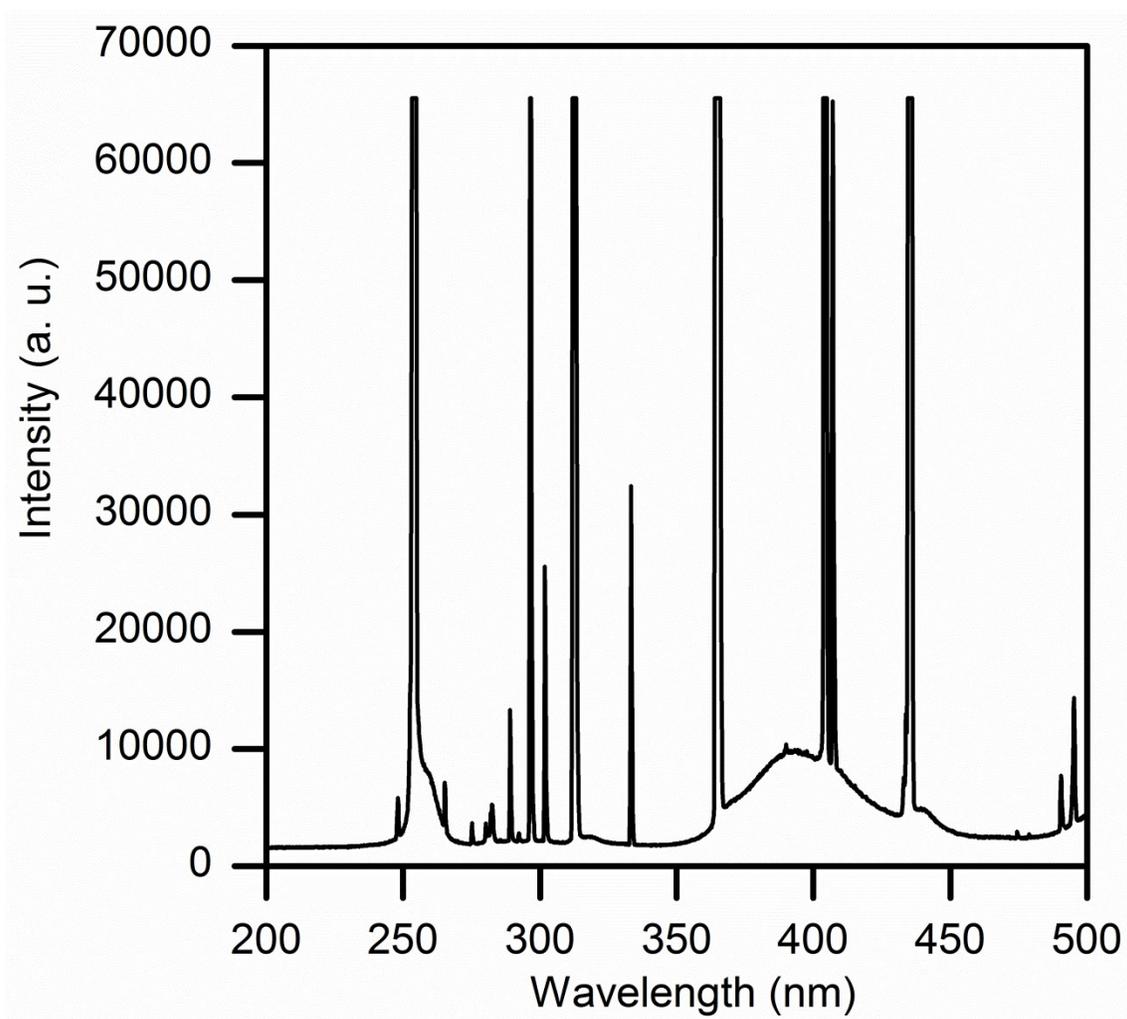
**S4** (a) Caffeine microspecies distribution diagram and (b) DAD-HPLC chromatogram of an aqueous caffeine solution ( $50 \text{ mg L}^{-1}$ ) before and after 48 hours adsorption equilibrium.

Supplement 5



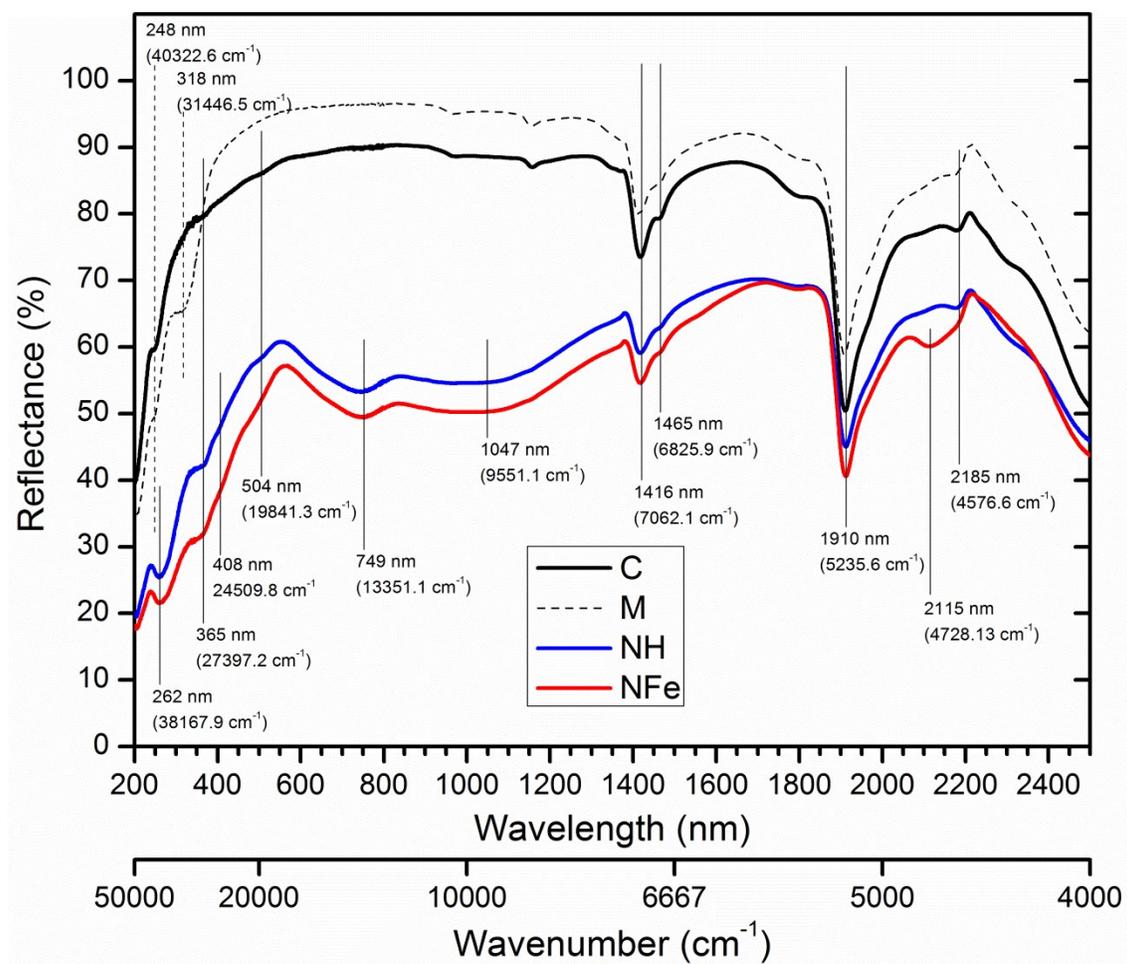
S5. DTG curves of the studied samples NH, NFe and SH.

Supplement 6



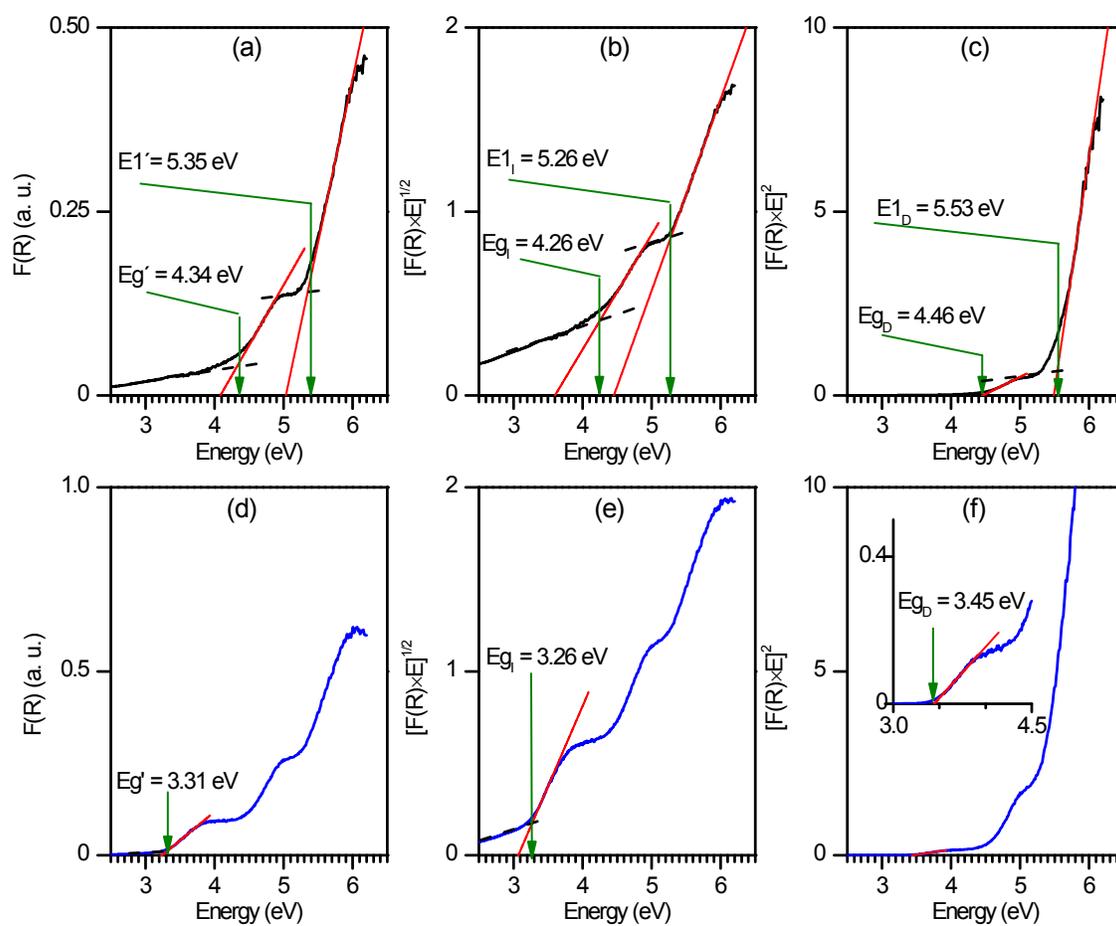
S6. Spectrum of the lamp in the UV-Vis range.

## Supplement 7



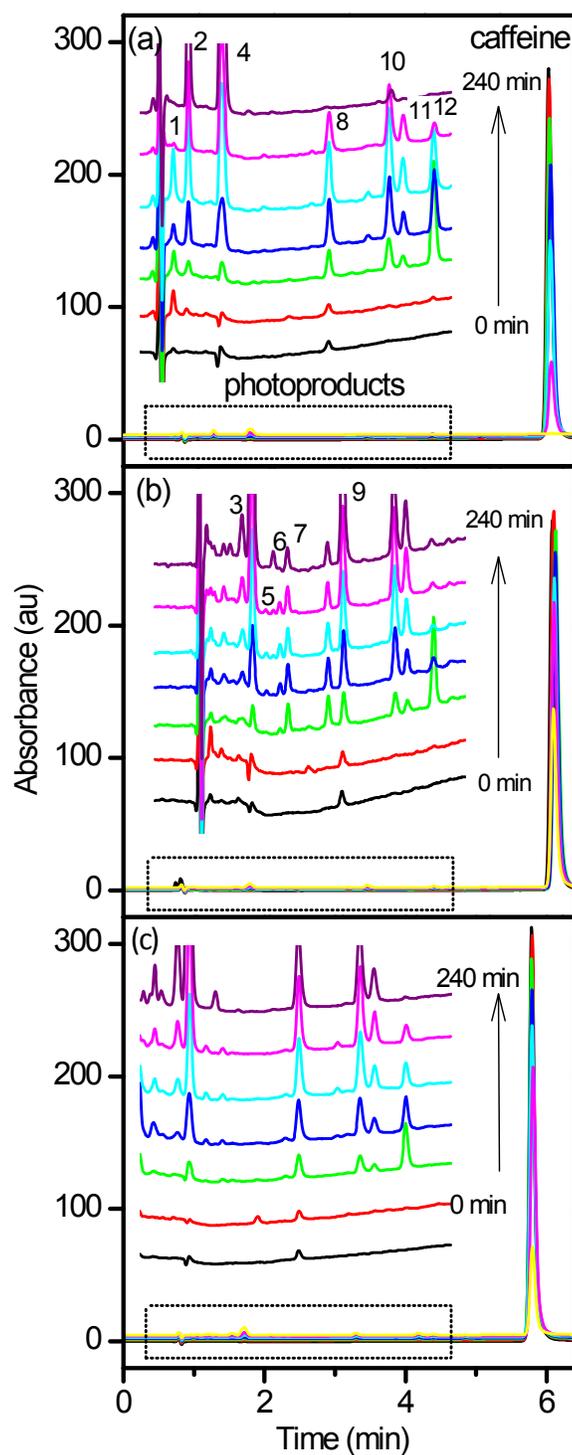
S7. UV-VIS-NIR diffuse reflectance spectra of the studied samples indicating band position.

## Supplement 8



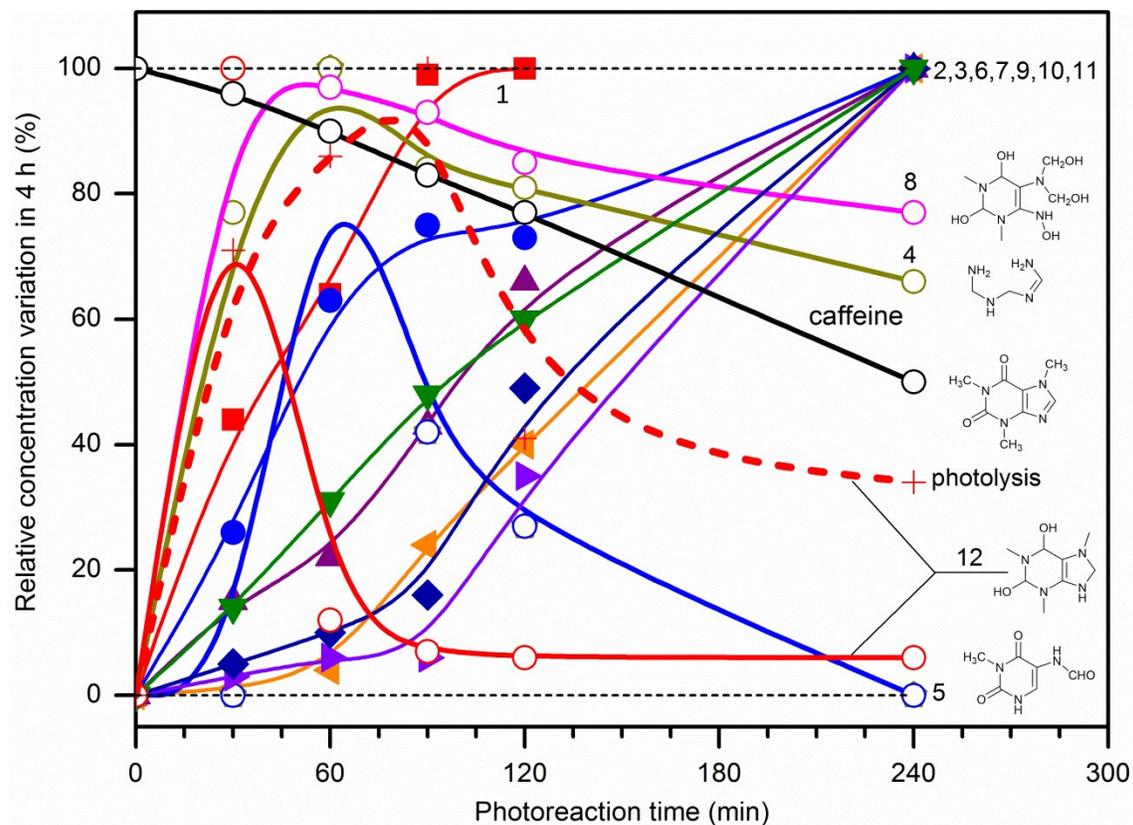
**S8.** Band gap energies of synthetic (a-c) clinoptilolite and (d-f) mordenite.

Supplement 9



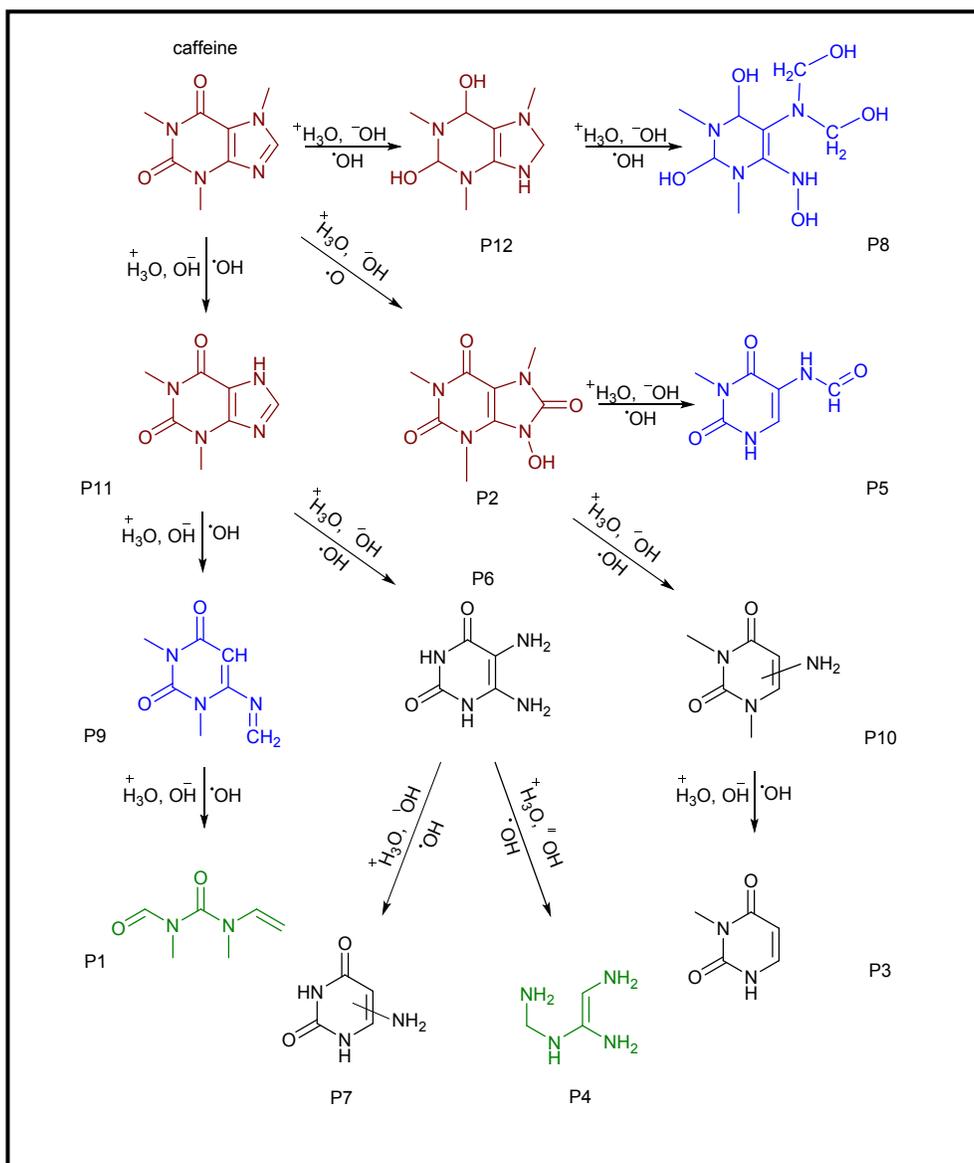
S9. DAD-HPLC chromatograms of caffeine aqueous solutions at different times of the photocatalytic reaction on (a) NH, (b) NFe and (c) SH. Detection at 236 nm.

## Supplement 10



**S10.** Evolution of the photoproducts generated over NFe during 4 hours and of the compound 1,3,7-trimethyl-2,3,6,7,8,9-hexahydro-1H-purine-2,6-diol produced by photolysis.

Supplement 11



S11. Proposed photocatalytic decomposition pathway of caffeine by natural zeolites. P indicates the peak number in Fig. 5.