Electronic supplementary information of the paper entitled " Zeolite nanoparticles with immobilized metal ion: isolation and MALDI-TOF-MS/MS identification of phosphopeptides".

Experimental details:

Protein digestion:

Bovine β -casein, 2 mg/mL in 50 mM ammonium bicarbonate buffer at pH 8.3, was incubated at 37 °C with trypsin (E:S = 1:50) for 18 h.

Isolation of phosphopeptide from β -casein digest by Fe^{3+} ion-immobilized zeolite nanoparticles (Fe^{3+} -nanozeolites):

Fe³⁺-nanozeolites suspension (10 μ L of 3 mg/mL) was added into 0.2 mL of 5ng/ μ L or 0.5 ng/ μ L β -casein peptide digests solution. Then the solution containing peptides and Fe³⁺-nanozeolites was vibrated at 37 °C for 90 min, and centrifugated at 17000 rpm for 15 min. After removing the supernate, the residual peptides/Fe³⁺-nanozeolites were redispersed into 5 μ L of 50% acetonitrile aqueous solution.

MALDI-TOF-MS process:

Peptides/ Fe³⁺-nanozeolites were deposited on the MALDI target using dried droplet method. 0.35 μ L of the above slurry was spotted onto the MALDI plate and then another 0.35 μ L of α -CHCA saturated solution (in 50% acetonitrile aqueous solution containing 0.1% trifluoroacetic acid) was introduced. Positive ion MALDI-TOF mass spectra were acquired on 4700 Proteomics Analyzer (Applied Biosystems, USA). Sample desorption was achieved using an Nd-YAG laser (355 nm) operated at a repetition rate of 200 Hz and acceleration voltage of 20 kV.



Fig. S1 SEM images of zeolite-beta nanoparticles before (a) and after (b) immobilizing metal ions. The SEM images indicate that this covalent modification has no influence on the morphology of nanoparticles. 1 bar is $1\mu m$.



Fig. S2 FT-IR spectrum of the Fe^{3+} -nanozeolites. The absorption on 1604 cm⁻¹ and 1458-1394 cm⁻¹ could be assigned to the anti-symmetric and symmetric stretching vibration of carboxylate, respectively.



Fig. S3 Energy dispersive spectrum (EDS) analyses of the Fe^{3+} -nanozeolites. The EDS analysis was carried out by means of a Philips XL30 scanning electron microscope. The appearance of Au element can be attributed to the sprinkling Au on the sample before SEM analysis.