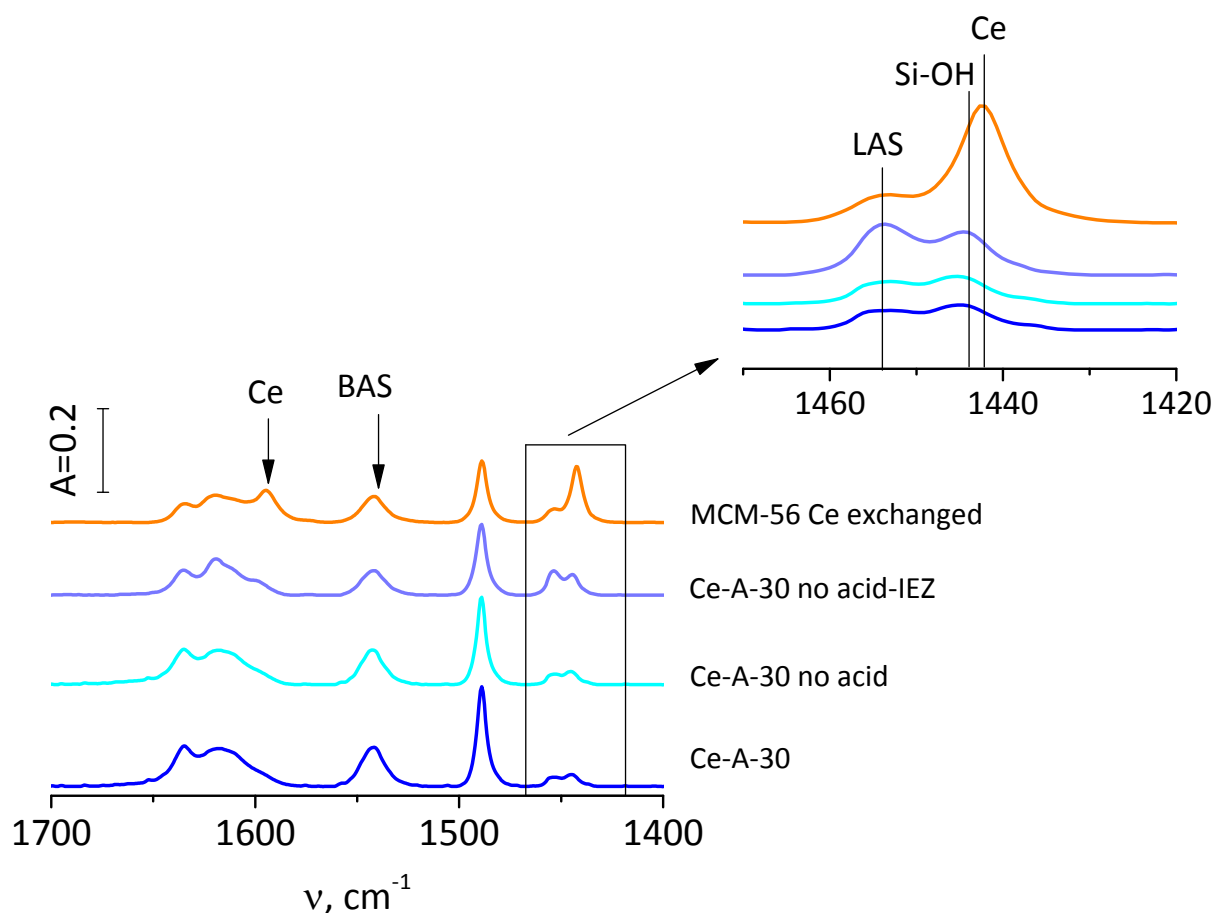


## Supplementary Information

### Framework-substituted cerium MCM-22 zeolite and its interlayer expanded derivative MWW-IEZ.

Wiesław J. Roth, Barbara Gil, Waław Makowski, Andrzej Sławek, Aleksandra Korzeniowska, Justyna Grzybek, Michał Siwek, Piotr Michorczyk

#### 1. Status of cerium in framework-substituted MWW zeolites – pyridine adsorption

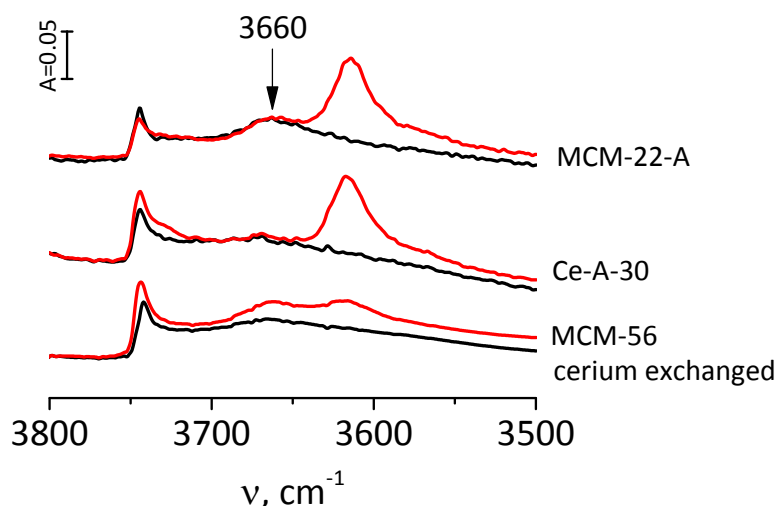


**Figure S1** IR spectra of pyridine adsorbed on framework-substituted (Ce-A-30, Ce-A-20 no acid and Ce-A-30 no acid IEZ) and cation-exchanged (MCM-56) MWW zeolites

The spectra recorded after pyridine adsorption (Figure S1) show for all framework-substituted samples only the maxima, characteristic of pyridine adsorbed on BAS ( $1545\text{ cm}^{-1}$ ), LAS ( $1454\text{ cm}^{-1}$ ) and silanol groups ( $1445\text{ cm}^{-1}$ ). Only in the case of cerium-exchanged MCM-56 sample, where cerium was introduced as the exchangeable cation two new maxima appear, characteristic of pyridine adsorbed on cerium cations – at  $1594\text{ cm}^{-1}$  (C-C stretching vibration of pyridine ring) and at  $1442\text{ cm}^{-1}$

(C-N stretching vibration of pyridine ring). This experiment shows that cerium in framework-substituted zeolites is not detected by pyridine as the extraframework cation.

## 2. Presence/absence of Ce-OH groups – pyridine adsorption.



**Figure S2** IR spectra of framework-substituted MCM-22 (Ce-A-30), cerium-exchanged MCM-56 and MCM-22-A (no cerium) before (red spectra) and after (black spectra) pyridine adsorption.

Extraframework Ce-OH groups, if present, should give rise to the specific IR maximum in the region 3660-3675  $\text{cm}^{-1}$ , as reported in the literature. Sousa-Aguiar et al. (Microporous and Mesoporous Materials 25, 1998, 25-34) discussed in details the formation of new Ln-OH groups in La-, Nd-, Sm-, Gd- and Dy-exchanged NaY zeolite. In their work the Ln-OH appeared in the region 3530  $\text{cm}^{-1}$  to 3498  $\text{cm}^{-1}$ . There are also two other bands, at higher frequency. The first one at 3680  $\text{cm}^{-1}$  was assigned there to the Al-OH species, originated (according to the authors) from framework dealumination upon ion exchange in acidic medium. Second one, at 3638  $\text{cm}^{-1}$  was present only in the LaNaY and was not discussed in the text.

C. Ramos Moreira et al. (Microporous and Mesoporous Materials 100, 2007, 276-286) observed intense and quite narrow (half-width ca. 25  $\text{cm}^{-1}$ ) band at 3674  $\text{cm}^{-1}$  after introduction of Ce into exchangeable positions of HUSY zeolite, appearing (according to the authors) due to the interaction of cerium species with extra-framework Al (EFAL) species via -OH groups. In more recent work, L.D. Borges (Applied Catalysis A: General 450, 2013, 114-119) reported a band at 3663  $\text{cm}^{-1}$  appearing after impregnation of USY zeolite with cerium salt and assigned it to OH groups associated with Ce(III) species.

According to above mentioned papers, the position of Ce-OH band should be very close to the one usually reported for non-acidic Al-OH groups (3660 to 3680  $\text{cm}^{-1}$ ), which is also present in our samples (Fig. 4 in main manuscript and SI Fig. S2). IR maximum of Al-OH groups at 3660  $\text{cm}^{-1}$ , visible for MCM-22-A and Ce-A-30, does not disappear after pyridine adsorption, confirming non-acidic character of such Al-OH groups.

The IR band at the same position (3660  $\text{cm}^{-1}$ ) is also present for cerium-exchanged MCM-56 zeolite. In this case however, this band partially disappears after pyridine adsorption. Since Ce-OH groups are

acidic and according to literature reports they interact with pyridine, this confirms that for cerium-exchanged MWW the Ce-OH groups are present and they are characterized by the maximum at  $3660\text{ cm}^{-1}$ .

On the other hand, since the band at  $3660\text{ cm}^{-1}$  for framework-substituted MWW zeolites did not disappear after pyridine adsorption, thus it should originate only from the presence of Al-OH groups.

Considering all above we can say that the properties of cerium in ion-exchanged and framework-substituted MWW samples are different, which is supporting the hypothesis that in the latter, cerium is located in the framework positions.