

Supplementary Information

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

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

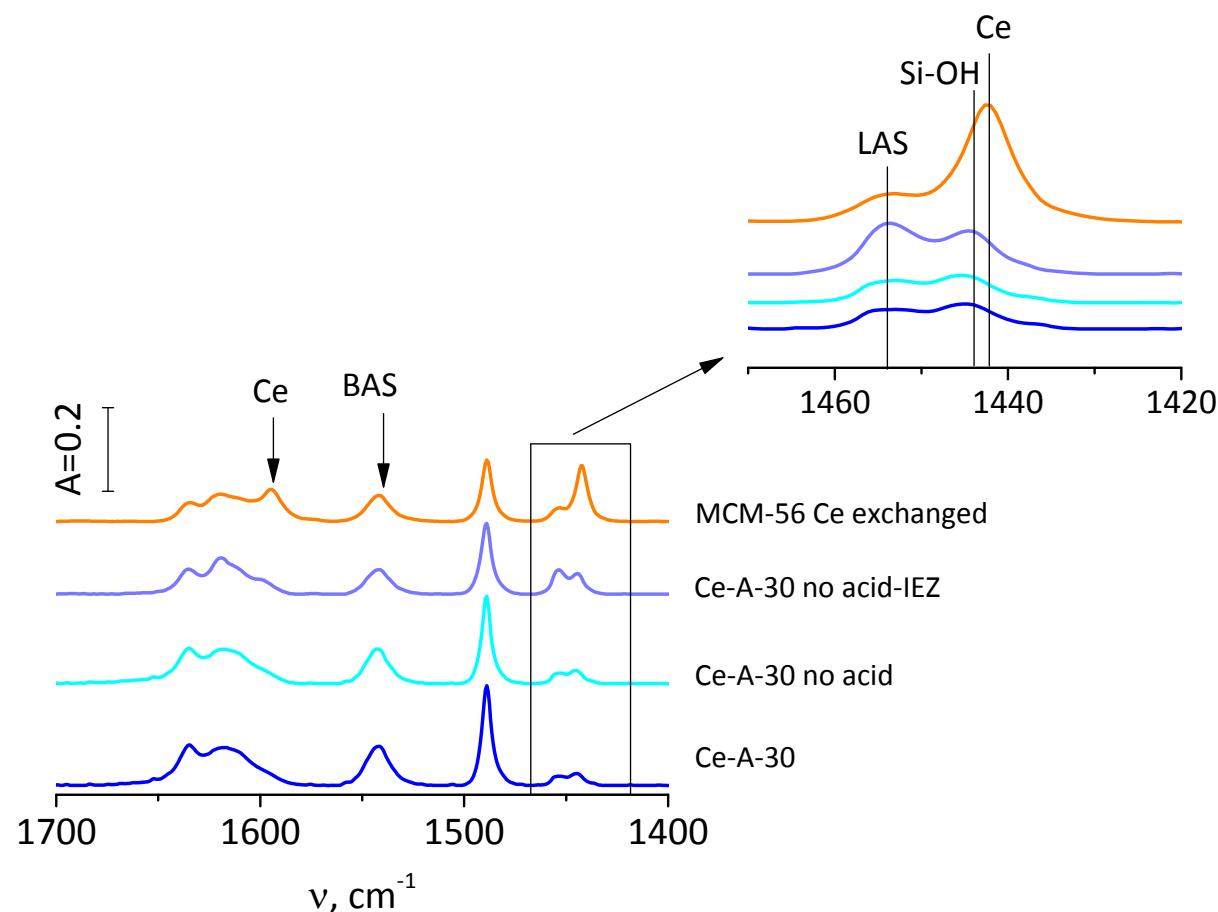


Figure S1 IR spectra of pyridine adsorbed on framework-substituted (Ce-A-30, Ce-A-20 no acid and Ce-A-30 no acid IEZ) and cation-exchanged (MCM-56) MWW zeolites

The spectra recorded after pyridine adsorption (Figure S1) show for all framework-substituted samples only the maxima, characteristic of pyridine adsorbed on BAS (1545 cm^{-1}), LAS (1454 cm^{-1}) and silanol groups (1445 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 cm^{-1} (C-C stretching vibration of pyridine ring) and at 1442 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.

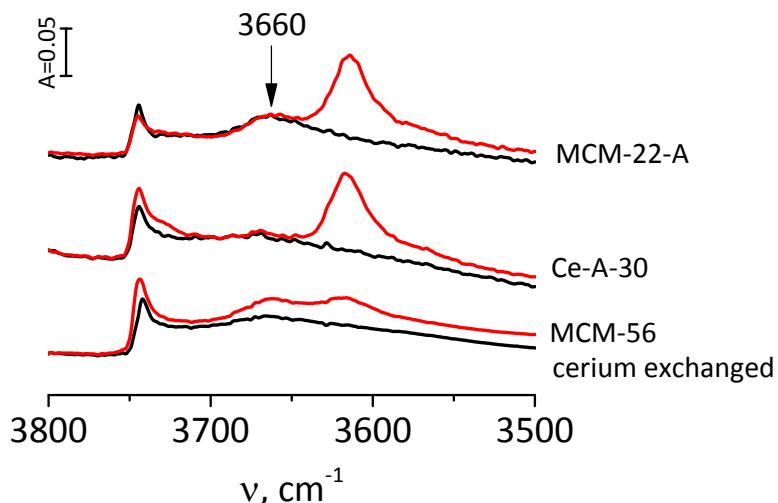


Figure S2 IR spectra of framework-substituted MCM-22 (Ce-A-30), cerium-exchanged MCM-56 and MCM-22-A (no cerium) before (red spectra) and after (black spectra) pyridine adsorption.

Extraframework Ce-OH groups, if present, should give rise to the specific IR maximum in the region 3660–3675 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 cm^{-1} to 3498 cm^{-1} . There are also two other bands, at higher frequency. The first one at 3680 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 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 cm^{-1}) band at 3674 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 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 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 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 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 cm⁻¹.

On the other hand, since the band at 3660 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.