Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Experimental Section Details

The precursor, MCM-22P and high Al-MWW zeolite (MCM-56/49) were prepared according to the published procedures [P. Chlubna, W. J. Roth, A. Zukal, M. Kubu and J. Pavlatova, Catal. Today, 2012, 179, 35–42 and A. S. Fung, S. L. Lawton and W. J. Roth, US Pat., 5,362,697, 1994] using gels comprising Ultrasil (Evonik), sodium aluminate (Riedel-del-Haen), 50% NaOH and hexamethyleneimine (HMI, Sigma Aldrich). The following molar ratios were used: MCM-22P - Si/Al = 25, OH/Si = 0.15, HMI/Si = 0.35 and water/Si = 19.3; MCM-56/49 - Si/Al = 12, OH/Si = 0.19, HMI/Si = 0.35 and water/Si = 19.2. The gels were crystallized at 170°C for 36 hrs and at 143°C for 60 hrs, respectively.

The silylation to produce the IEZ derivative was carried out in a Teflon lined 25 mL Parr reactor according to [P. Wu, J. F. Ruan, L. L. Wang, L. L. Wu, Y. Wang, Y. M. Liu, W. B. Fan, M. Y. He, O. Terasaki and T. Tatsumi, *J. Am. Chem. Soc.*, 2008, 130, 8178-8187]. The reagents were added successively: 10 mL of 1 M HNO_3 (POCh, analytical grade), 0.12mL $CH_3Si(OCH_2CH_3)_2$ (Sigma Aldrich), and 0.5g of the MCM-22P precursor. The mixture was homogenized by stirring, sealed, heated to 170°C and held for 10h. The slurry was filtered and the solid washed several times with distilled water. Subsequent calcination was carried out in air at 540°C for 6 h in a muffle furnace and temperature ramp of 2°C/min. The sample was ion exchanged 3 times with 0.5 M solution of NH_4NO_3 (POCh, analytical grade) for 1 h at RT.

Cerium and lanthanum forms for all samples were prepared by ion-exchange with 0.1 M $Ce(NO_3)_3$/$La(NO_3)_3$ solutions (Sigma Aldrich, analytical grade) at 85°C, filtered, washed with distilled water and dried at room temperature.

Zeolite samples were characterized by X-ray powder diffraction (XRD) using a Philips X'Pert diffractometer APD with CuK a radiation α (λ = 0.154 nm) in the range 5-50° 2θ with steps of 0.02°. Samples for XRD were used in three distinct forms: 1. as-synthesized, 2. calcined, and 3. additionally activated under the same condition as used for IR measurement.

The nitrogen adsorption isotherms were determined at -196°C (liquid nitrogen temperature) using an ASAP 2025 (Micromeritics) static volumetric apparatus. Before adsorption experiments the sample was outgassed at 200°C overnight using turbomolecular pump to remove pre-adsorbed water.

The coordination, oxidation state and aggregation of cerium introduced into MWW zeolites were studied by UV-Vis-DRS method using an Evolution 600 (Thermo) spectrophotometer. The measurements were performed at room temperature in the range 200–900 nm with resolution of 2 nm.

Temperature programmed reduction, using H_2 as the reducing agent was carried out in a modified gas chromatograph with a thermal conductivity detector (TCD). Purified mixture of N_2/H_2 (95/5 vol.%, Air Liquide) served as a combined carrier and reducing gas at a total flow rate 30 $cm^3 min^{-1}$. Before experiment the catalyst sample (100 mg) was preheated in a dry He stream at 250 °C for 60 min, and then cooled to 100 °C. The sample was heated at 10 °C min^{-1} to the final temperature of 650 °C. The H_2 consumption was measured by a thermal conductivity detector.

The materials were investigated by adsorption of CO and pyridine used as probe molecules followed by FTIR spectroscopy. All samples were activated in the form of self-supporting wafers for 1 hour at

450 °C prior to the adsorption of probe molecules. The adsorption temperatures were as follows: 170 °C for pyridine (POCh Gliwice, analytical grade) and -100 °C for CO (Linde Gas Polska, 99.95% used without further purification). IR spectra were recorded with a Bruker Tensor 27 spectrometer equipped with an MCT detector and working with the spectral resolution of 2 cm^{-1}. All spectra presented in this work have been normalized to the standard 10 mg pellet (density 3.2 mg/cm^2).

The reference Ce_2O_3 and CeO_2 spectra were obtained with commercial samples from Merck and Rhodia, respectively.

Additional data on H_2-TPR for Ce-MWW

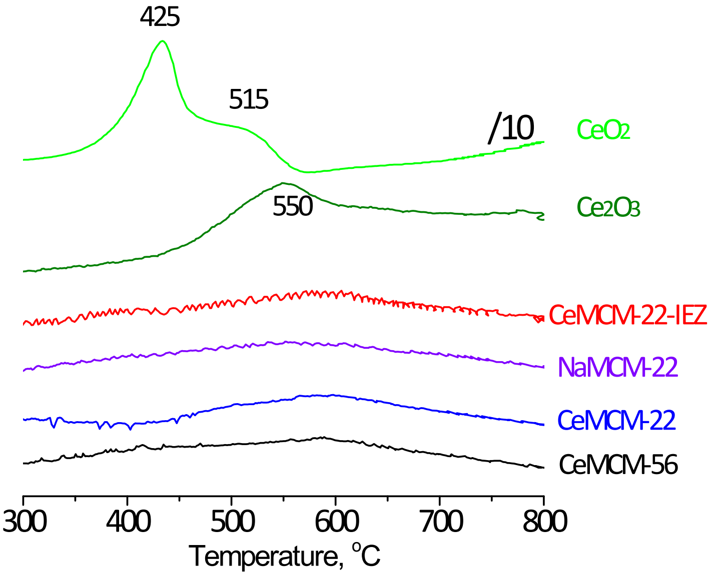

Figure S1. H2-TPR profiles (dependence of TCD signal in arbitrary units on temperature) for cerium-MWW zeolites under study, together with NaMCM-22 and commercial Ce_2O_3 and CeO_2. Profile for Ce_2O_3 is divided by 10.

During thermoprogrammed reduction (H_2-TPR) two peaks appear for commercial CeO_2: at 425 and 515 °C. According to *S. Watanabe, X. Ma, and Ch. Song, J. Phys. Chem. C 2009, 113, 14249–14257* they correspond to the reduction of surface oxygen and bulk oxygen, respectively. A small peak at 550 °C for Ce_2O_3 may result from the reduction of a small amount of surface oxygen defects. The H_2-TPR profiles of cerium-exchanged zeolites show negligible consumption of hydrogen. This is in accordance with the XRD data, showing no presence of detectable cerium oxide particles. Therefore it is possible that oxide-like clusters are either too small to give observable hydrogen consumption or they may be formed by partially binding to framework oxygen atoms, which are not so easily reducible.

Additional data on CO adsorption on La-MWW

The participation and significance of Ce(+) is supported by parallel studies with La-substituted MWW materials, where 3+ to 4+ metal oxidation is not viable. Brønsted acid site concentrations showed similar trends like Ce – slight increase for La-MCM-22 and La-MCM-56/49 with significant drop for La-MCM-22-IEZ. The FTIR spectra for adsorbed CO are shown in Figure S2.

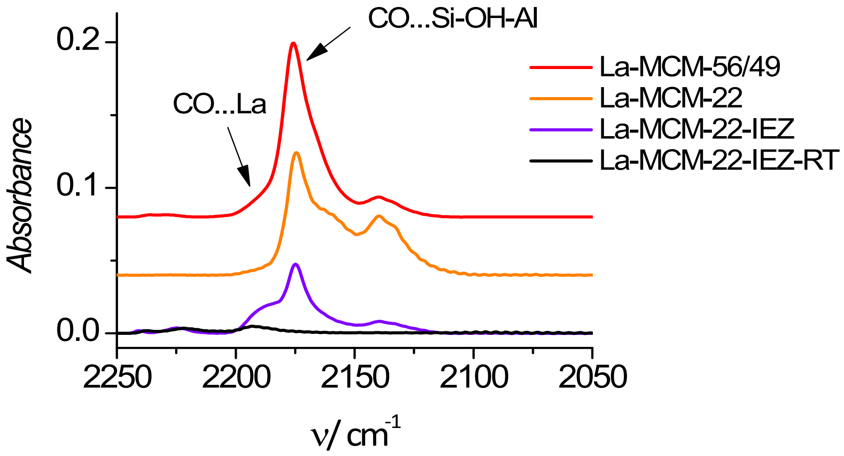

Figure S2. IR spectra of CO adsorbed at -100°C on lanthanum-exchanged zeolites (except La-MCM-IEZ-RT recorded at RT).

Only La-MCM-22-IEZ show significant uptake of CO at low temperature. The adsorption of CO by La-MCM-56/49 is barely noticeable (slight shoulder of CO-OH band) and not detectable with La-MCM-22. There are no bands due to CO adsorbed the zeolite samples at room temperature and no sign of oxidation to CO_2. These results are important in supporting the critical role of redox metal centers exemplified by Ce in contrast to La.

XRD patterns for MWW zeolites together with CeO_2 and Ce_2O_3.

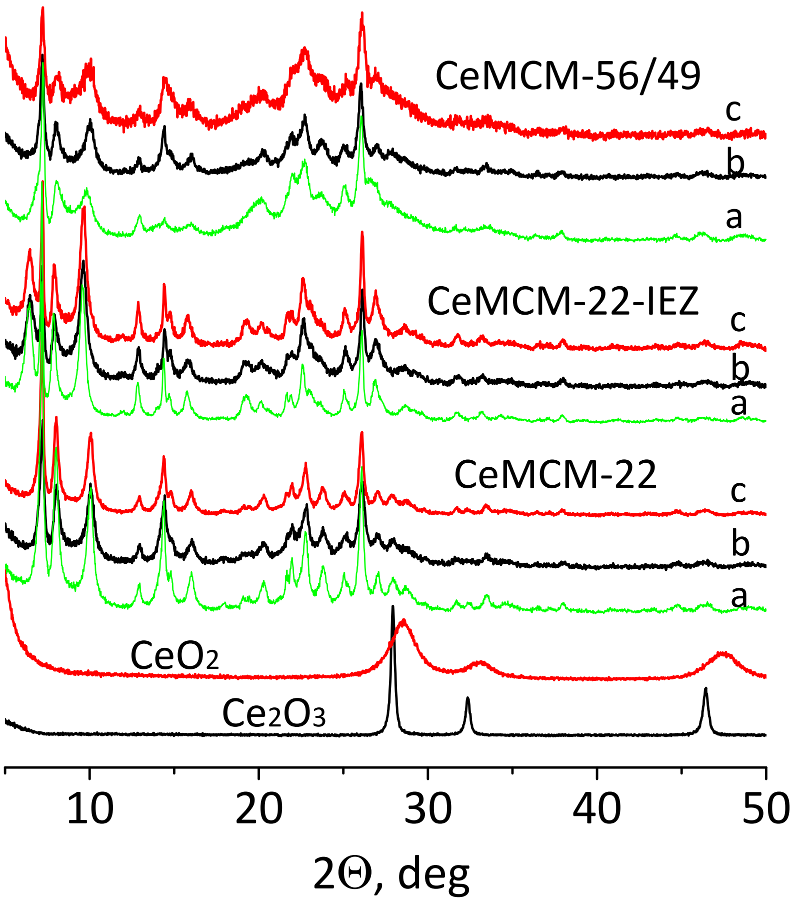

Figure S3 XRD patterns for CeO_2 and Ce_2O_3 (divided by 5) and MCM-22, MCM-22-IEZ and MCM-56/49 zeolites, a – as synthesized and calcined (no ion-exchange), b – calcined and cerium-exchanged, c – calcined, cerium-exchanged and vacuum activated samples.

The XRD patterns show no presence of either CeO_2 or Ce_2O_3 oxides suggesting that the size of formed oxide-like clusters are below detection limit for this method. Region 5-50° 2Θ was used because higher reflections for cerium oxides are even less intensive for commercial samples containing micrometric size crystals and should not be present in smaller crystallites.