Electronic Supplementary Information

Sulfated zirconia foams synthesized by integrative route combining surfactants, air bubbles and sol-gel transition applied to heterogeneous catalysis.

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Pore size distribution, mapping of sulfur content, representative structure of the sulfated zirconia and selectivity of the ceramic foams on reaction of ethanol dehydration.

The pore size distribution was analyzed using the BJH method for the desorption (see Fig. S1). A narrow pore size distribution of 4nm (from gel templating of the sulfated zirconia precursor) and a pore family with wide size distribution was observed for samples prepared with OTAB, IGEPAL and PLURONIC.

**Figure S1.** BJH pore-size distribution of the final ceramic foam.

The mapping of sulfur, zirconium and oxygen content is provided in figure S2. The images reveal that sulfur is homogeneously distributed on the surface of the catalysts and that the amount of sulfur is close to the observed by TGA and XPS.
Figure S2. Mapping of sulfur, zirconium and oxygen distribution in sulfated samples.

An idealized structure of the sulfated zirconia is shown in Figure S3 and the species detected by XPS are indicated as types (1), (2) and (3).

Figure S3. Representative structure and surface chemical composition of the sulfated zirconia foam.
The most active catalysts, OTAB and IGEPAL, were evaluated up to 1 h under ethanol stream as a function of the reaction time at 250 °C (Fig. S5) and presented a quite good stability.

Figure S4. Ethanol conversion as a function of the reaction time at 250 °C for the most active samples: OTAB and IGEPAL.

The figure S4 shows the ethanol conversion on a nonsulfated commercial ZrO$_2$ (Alfa Aesar, 99.7%) reference as a function of the reaction temperature. The conversion was below 5 % at all temperatures.

Figure S5. Ethanol conversion as a function of the reaction temperature for a commercial nonsulfated ZrO$_2$ sample.

Figure S6 presents the rates of product formation (ethene, diethyl ether and acetaldehyde) during the ethanol conversion reaction as a function of the temperature for the ceramic foam prepared with different surfactants. As the ethanol feed rate was 17.1 mmolh$^{-1}$, this value marks the maximum formation rate of products. The temperature dependency of the reaction rate is
similar for foams prepared with OTAB, IGEPAL and PLURONIC. Ethanol is fully converted to ethene at 300 °C by these three foams, a result which has been up to now reported only for higher temperatures and sulfate contents \(^2\). The suppressed formation of acetaldehyde reinforces the existence of strong acid sites, as basic oxygen anions are necessary for the dehydrogenation of ethanol. The SZr-ref and SDS foamed samples presented low product formation rates, an expected result considering their low ethanol conversion.

Figure S6. Reaction selectivity as a function of temperature of the final ceramic foams prepared by aeration and different surfactants: ■ diethyl ether; ○ ethene and ▲ acetaldehyde.
References