Supplementary information for

In situ ATR-IR spectroscopy study of aluminas under aqueous phase reforming conditions

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Calculations of penetration depth of IR radiation for all samples

The penetration depth of evanescent wave during total internal reflection process is determined according to the formula:

$$d_p = \frac{\lambda}{2\pi n_1 \sqrt{(\sin^2 \theta - \left(\frac{n_2}{n_1}\right)^2}}$$

where λ – wavelength, θ – angle of incidence (45°), n_1, n_2 – refractive indices of ZnSe and porous sample, respectively. Since the samples are porous and the pores are filled with water, calculation of refractive index becomes more complex. It is known that enhanced porosity significantly decreases the refractive index of material.[34] Refractive index of a porous material is calculated according to the formula:

$$n_{eff} = \sqrt{(1 - \varphi) n_c^2 + \varphi n_d^2}$$

where φ – porosity, n_c, n_d – refractive indices of solid and water, respectively.

Thickness of the layer was estimated based on sample weight and density of alumina assuming that the layer is uniform along the length of the IRE.

Table S1. Calculated properties of the sample layers.

Sample	Sample loading, mg	Depth of penetration, μm	Estimated layer thickness, μm
γ-Al_2O_3 / H_2O	11.8	0.82	3.0
1.5% wt. Pt/γ-Al_2O_3 / H_2O	10.0	0.82	2.6
γ-Al_2O_3 / EG-H_2O	11.8	0.83	3.0
1.5% wt. Pt/γ-Al_2O_3 / EG-H_2O	10.0	0.84	2.6
AlO(OH) / H_2O	24.1	0.98	6.2
H_2O, no catalyst	-	0.73	-

ATR-IR spectra – complex infrared bands

ATR-IR spectra of Pt/Al_2O_3 and Al_2O_3 samples in water contain not only peaks of water stretching and deformation vibrations (3200-3600 and 1640 cm^{-1}, respectively), and stretching and deformation vibrations of AlO(OH) (3324, 3304, 1064 cm^{-1}) (Fig. 3), but also complex bands derived from IRE. This complex signal increases with temperature and disappears completely when IRE is cooled down to room temperature after experiment.

The origin of this bands is not completely understood yet. Heating and cooling of the bare IRE in water results in similar behavior of these bands.

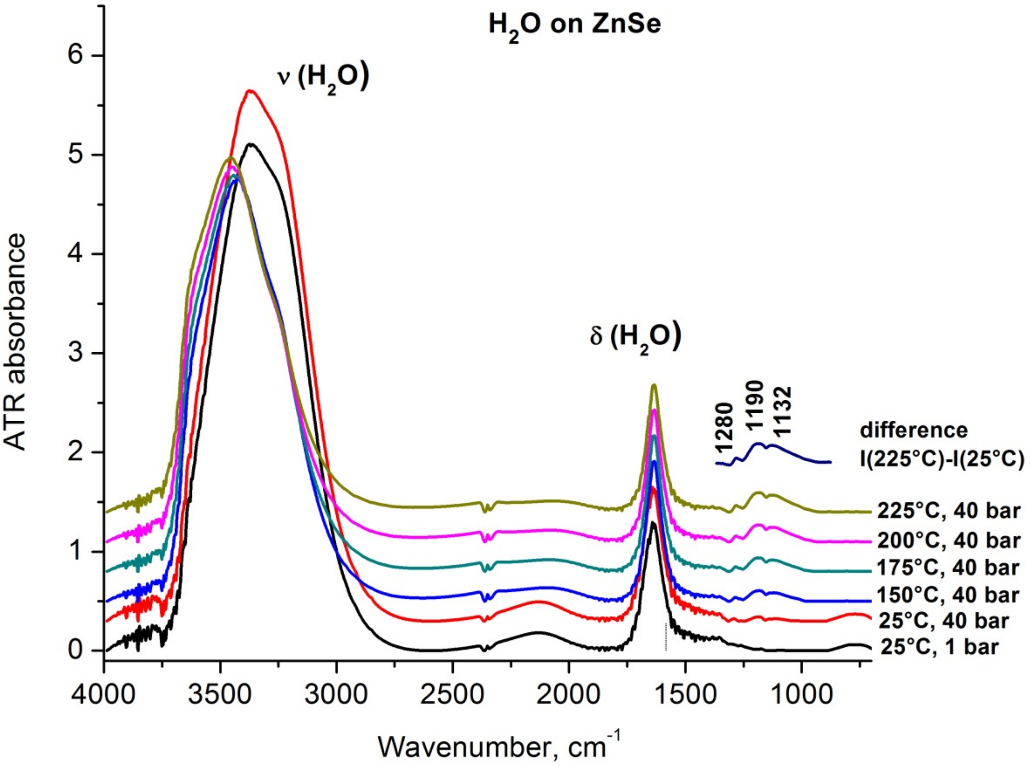

Figure S1. ATR-IR spectra of H_2O on bare ZnSe at 25°C, 40bar and 150-225°C, 40 bar.

Moreover, same phenomenon was observed when IRE was heated in *n*-dodecane (Figure S2). *n*-dodecane is a high boiling point liquid (214°C), thus no pressure is needed to keep it in a liquid state unlike water. Similarity of difference spectra on Fig. S1 and S2 allows to conclude that these complex bands are not related to vibrational bands of liquid or solid material covering IR element.

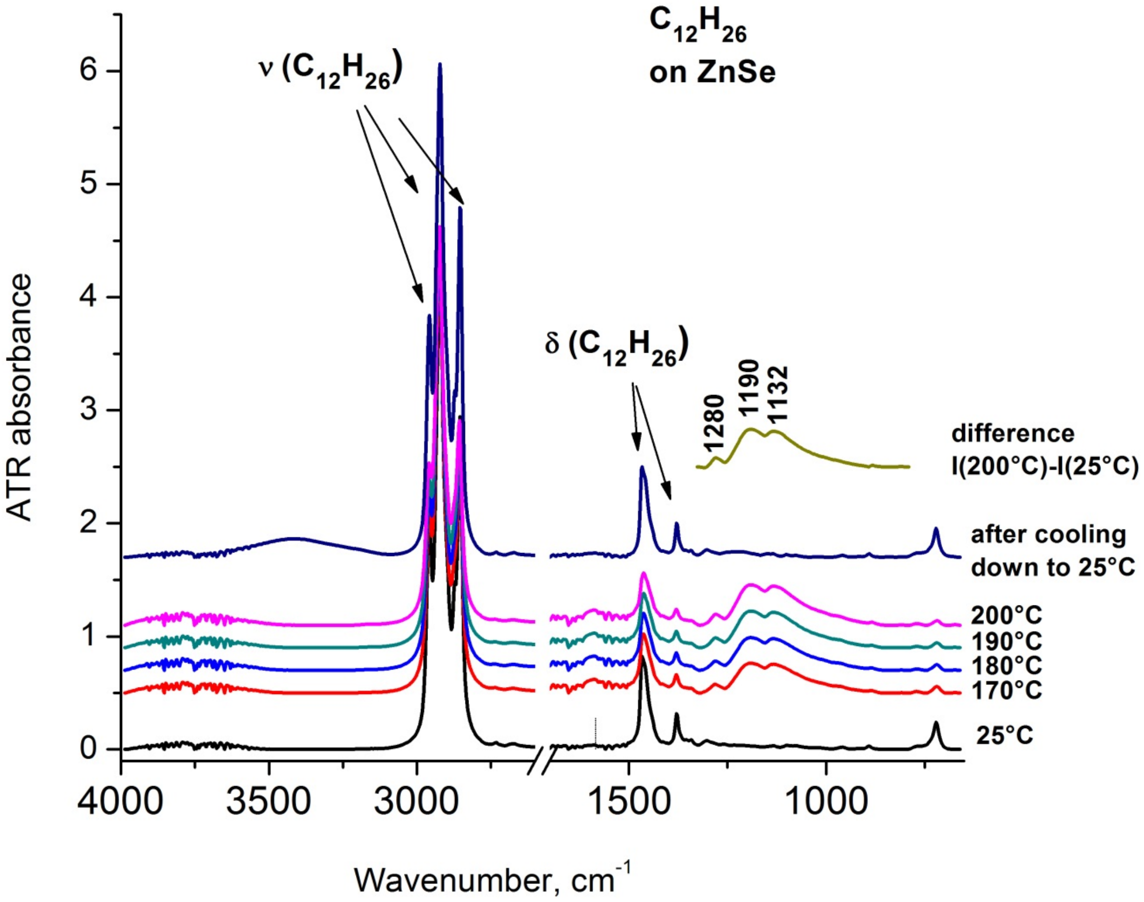

Figure S2. ATR-IR spectra of *n*-dodecane (*n*-$C_{12}H_{26}$) on bare ZnSe at 25°C, 1 bar and 170-200°C, 1 bar.

We attribute these bands to effect of temperature on ZnSe material. Temperature generally effects refractive index of the optical material, which can cause distortions in total reflection phenomenon. Interestingly, phonon vibrations of ZnSe usually appear at frequencies well below 1000 cm^{-1}.[35] This phenomenon is yet to be understood.

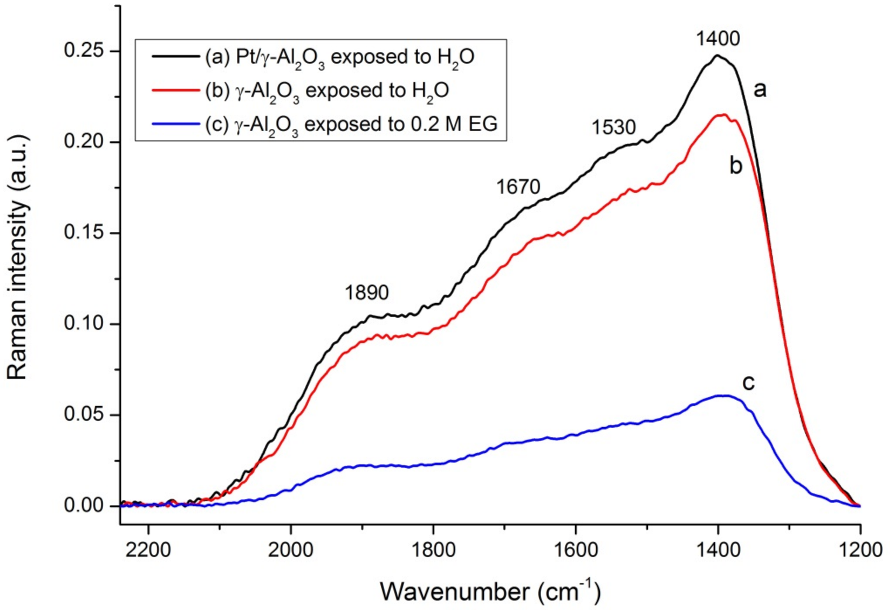

Figure S3. Raman spectra of (a) 1.5% wt. Pt/γ-Al_2O_3 and (b) /γ-Al_2O_3 after exposure to water and (c) γ-Al_2O_3 after exposure to 0.2 M ethylene glycol solution.