Supplementary Materials

Ethanol Coupling Reactions over MgO–Al_2O_3 Mixed Oxide-Based Catalysts for Producing Biofuel Additives

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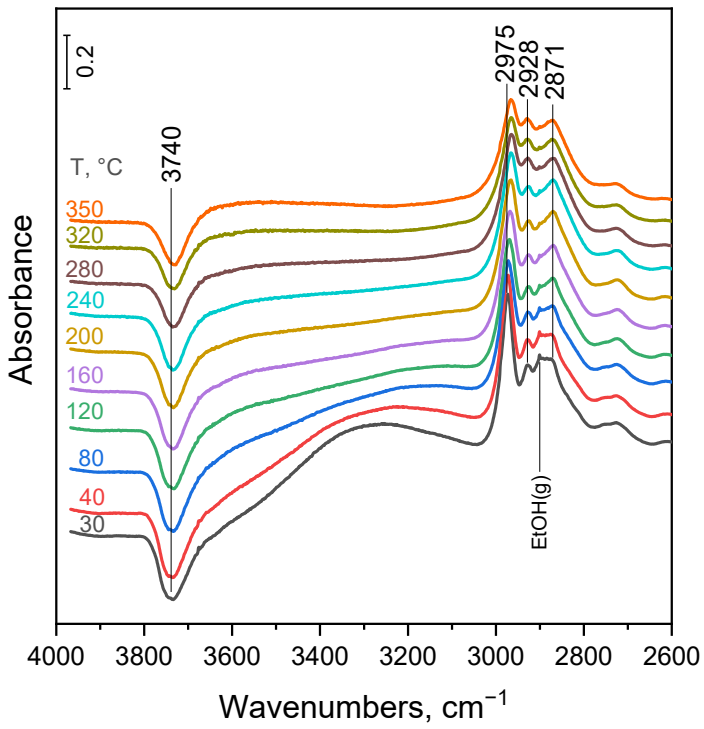

Figure S1. DRIFT spectra of the species obtained from adsorption and reaction of ethanol in He on MgO–Al_2O_3(550) catalyst in the frequency range of O–H and C–H stretching vibrations. The catalyst was contacted with a continuous flow of EtOH/He atmospheric gas mixture, while the temperature was continuously raised at a rate of 2 °C/min from 30 up to 350 °C. The corresponding spectrum of the neat catalyst was subtracted from the spectrum recorded at the indicated temperature.

The results obtained for the MgO–Al_2O_3(550) catalyst in contact with an EtOH/He reactant mixture are presented in Figure S1 (same as Figure 7A in the manuscript, except that the visible spectral range was extended to 4000 cm^{-1}). Adsorption of EtOH on the activated catalyst sample resulted in the appearance of C–H stretching bands due to the formation of surface

species, which was accompanied by the development of a negative absorption band at 3740 cm^{-1} in the range of the ν_{OH} stretching vibrations, suggesting that surface OH-groups are involved in adsorption interaction. The adsorbed species gave main characteristic absorption bands at 2975 and 2928 cm^{-1} in the frequency range of the ν_{CH} stretching vibrations, which can be assigned to the asymmetric stretching vibration of the $–CH_3$ ($\nu_{as}[CH_3]$) and $–CH_2–$ ($\nu_{as}[CH_2]$) groups, respectively. A third band at 2871 cm^{-1} can be attributed to the symmetric stretching vibration of the $–CH_3$ groups ($\nu_s[CH_3]$), probably overlapping with the band of symmetric $–CH_2–$ vibration (a sharp band at 2901 cm^{-1} is also discernible due to the minor contribution of gas-phase ethanol).

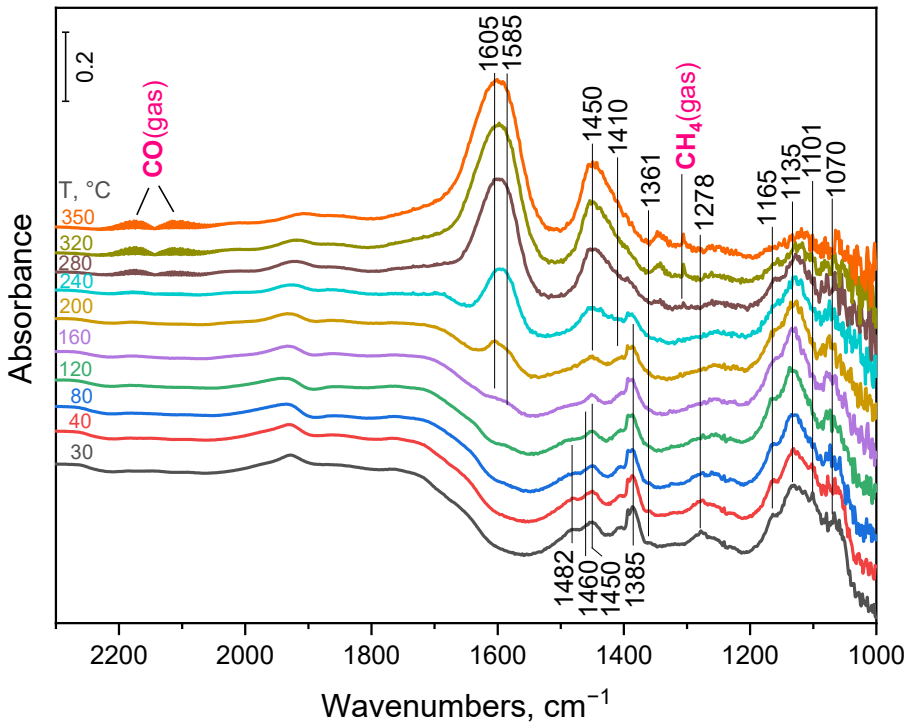

Figure S2. DRIFT spectra of the species obtained from adsorption and reaction of ethanol in H_2 on Pd/$MgO–Al_2O_3$ catalyst in the frequency range of carbonyl stretching and C–H deformation vibrations. The catalyst was contacted with a continuous flow of $EtOH/H_2$ atmospheric gas mixture, while the temperature was continuously raised at a rate of 2 °C/min from 30 up to 350 °C. The corresponding spectrum of the neat catalyst was subtracted from the spectrum recorded at the indicated temperature.

The results obtained for the Pd/$MgO–Al_2O_3$ catalyst in contact with an $EtOH/H_2$ reactant mixture are presented in Figure S2 (same as Figure 10B in the manuscript, except that the visible spectral range was extended to 2300 cm^{-1}). Adsorption of EtOH on the activated catalyst sample resulted in the appearance absorption bands due to C–H deformation vibrations (1500–1000 cm^{-1}) and ν[O-C-O] stretching vibrations of carboxyl species (1700–1400 cm^{-1}) due to the formation of different surface species (for band assignments, see text in the manuscript). Results show that high reaction temperatures (≥280 °C) accelerated the

rate of the hydrodeoxygenation (HDO) reactions, as indicated by the bands of gas-phase CH_4 and CO.