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Electronic Supplementary Information

Figure ESI1: Pore size distributions of the alumina and 20Cu/Al samples obtained by Hg intrusion porosimetry.



Figure ESI2: Raman spectra obtained for unreduced $20Cu/Al_2O_3$ catalyst during the ethanol dehydrogenation reaction between 200 and 400 °C. (a) Raman bands corresponding to the ethanol decomposition (2865 cm⁻¹), and (b) hydrogen formation (585 cm⁻¹).



Figure ESI3: (a) Copper speciation, and (b) distribution of products with ethanol on stream during the ethanol dehydrogenation reaction between 200 and 400 °C for reduced $20Cu/Al_2O_3$ catalyst. Copper speciation and product selectivity were obtained by time-resolved Cu K-edge XANES measurements and mass spectrometry, respectively.



Figure ESI4: (a) Copper speciation, (b) selectivity to H_2 , acetaldehyde and ethyl acetate, and (c) derivative of H_2 and acetaldehyde formation during the ethanol dehydrogenation reaction between 200 and 300 °C. Copper speciation and product selectivity were obtained from time-resolved Cu K-edge XANES measurements and mass spectrometry, respectively.



Mass spectrometry		Raman spectroscopy	
Molecules	m/z	Molecules	Position (cm ⁻¹)
H ₂	2	Ethanol	2865
Acetaldehyde	44 , 43	H_2	575 , 4114
Ethyl acetate	61	Ethene	3004
Diethyl ether	59 , 58	H_2O	3632
Ethene	28, 27		
H ₂ O	18 , 17		

Table ESI1: Mass fragments and Raman band positions of gaseous products analyzed at the reactor outlet.

*Main mass fragments and Raman bands used are in bold.