

Supporting Information

A Study of the Conversion of Ethanol to 1,3-Butadiene: Effects of Chemical and Structural Heterogeneity on the Activity of MgO-SiO₂ Mixed Oxide Catalysts

Blanka Szabó^a, Virág Hutkai^b, Gyula Novodárszki^a, Ferenc Lónyi^a, Zoltán Pászti^a, Zsolt Fogarassy^c, József Valyon^a, Róbert Barthos^{a,*}

^aInstitute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Magyar tudósok körútja 2, Budapest 1117, Hungary

^bErhvervsakademi Aarhus, Sønderhøj 30, 8260 Viby J, Denmark,

^cCentre for Energy Research, Institute for Technical Physics and Materials Science, Konkoly-Thege M. út 29-33, Budapest 1121, Hungary

*Corresponding author. Phone: +36 1 382 6861

E-mail addresses: szabo.blanka@ttk.hu (Blanka Szabó), eaavihu@students.eaaa.dk (Virág Hutkai), novodarszki.gyula@ttk.hu (Gyula Novodárszki), ferenc.lonyi@ttk.hu (Ferenc Lónyi), paszti.zoltan@ttk.hu (Zoltán Pászti), fogarassy.zsolt@energia.mta.hu (Zsolt Fogarassy), valyon.jozsef@ttk.hu (József Valyon) barthos.robort@ttk.hu (Róbert Barthos)

Table S1Integrated peak areas of NH₃- and CO₂-TPD curves.

Sample ID	Acidic properties			Basic properties
	A₁^a	A₂^b	A₁+A₂	A₁^c
SCL	91.2	16.4	107.7	1.8
SCH	126.6	35.3	161.9	7.8
WKL	165.8	137.8	303.7	20.1
WKH	254.4	175.2	429.6	41.3
IHL	36.1	28.2	64.3	26.8
IHH	155.0	56.8	211.8	57.2

^aadsorbed amount of NH₃, μmol g_{cat}⁻¹, amount of sites, having weak acid strength.^b adsorbed amount of NH₃, μmol g_{cat}⁻¹, amount of sites, having medium acid strength.^c adsorbed amount of CO₂, μmol g_{cat}⁻¹.

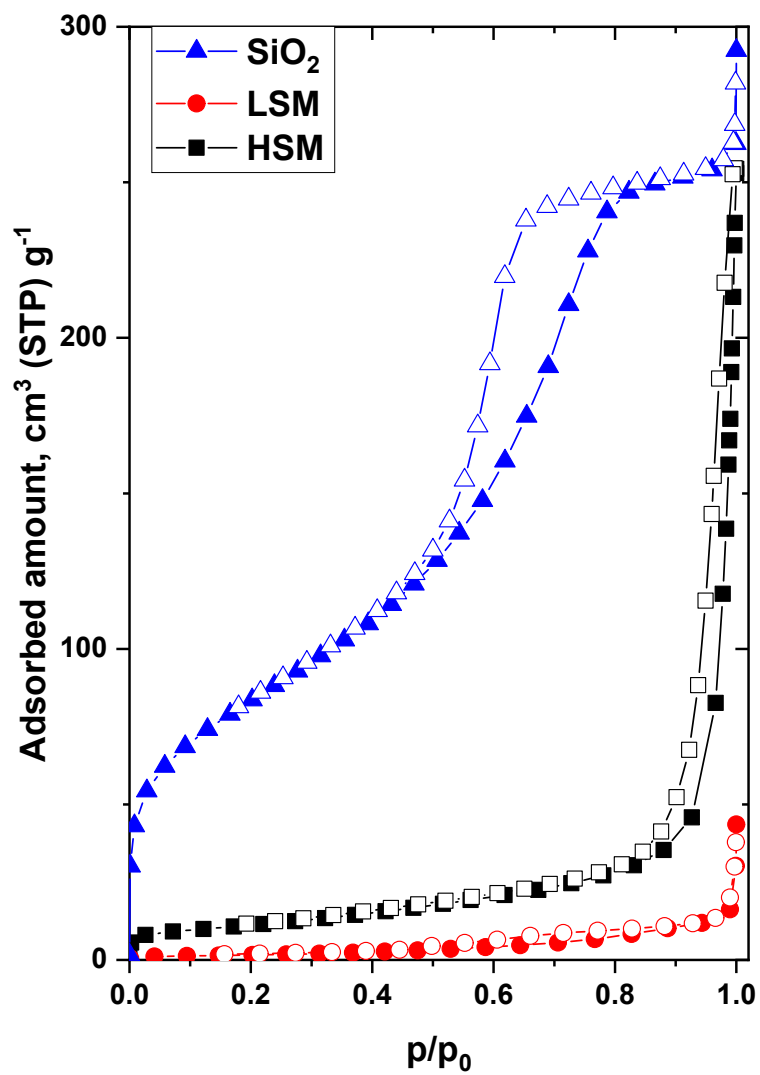


Fig. S1. N₂ physisorption isotherms of the MgO-SiO₂ mixed oxide components: low-SSA MgO (LSM), high-SSA MgO (HSM) and SiO₂. Adsorption: full symbols. Desorption: open symbols.

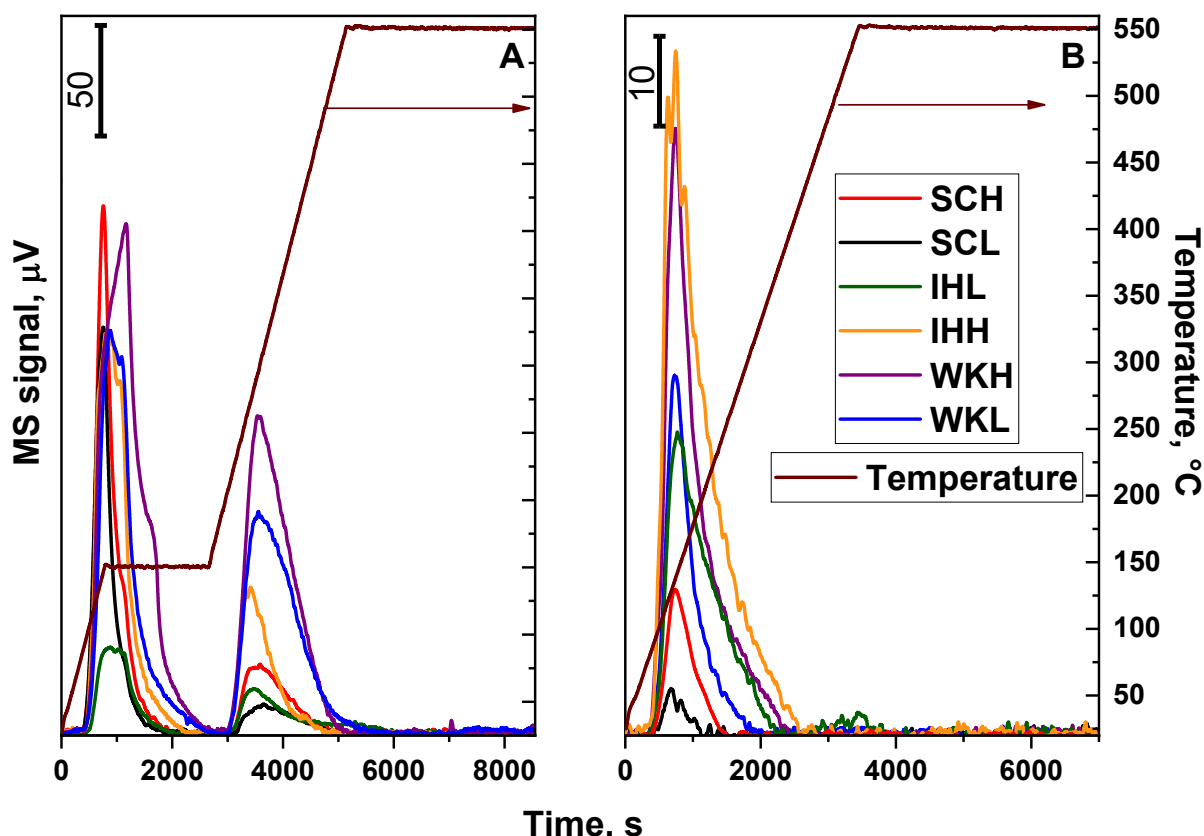


Fig. S2. Results of (A) NH_3 and (B) CO_2 temperature-programmed Desorption (TPD) measurements.

For the NH_3 -TPD measurements the samples were pre-treated in a $30 \text{ cm}^3/\text{min}$ flow of O_2 at $500 \text{ }^\circ\text{C}$ for 1 h, then flushed by N_2 ($30 \text{ cm}^3/\text{min}$) at same temperature for 15 minutes. The pre-treated sample was evacuated at $500 \text{ }^\circ\text{C}$, cooled to room temperature and contacted with about 14 kPa of NH_3 . After 15 minutes the physisorbed molecules were removed by evacuation. Then the reactor temperature was ramped up in He flow ($20 \text{ cm}^3/\text{min}$) at a rate of $10 \text{ }^\circ\text{C min}^{-1}$ to $150 \text{ }^\circ\text{C}$ and held at this temperature for 30 min then heated up to $550 \text{ }^\circ\text{C}$ ($10 \text{ }^\circ\text{C min}^{-1}$) and held at this temperature for 1 h, while the effluent gas was passed through a dry ice-acetone trap and a thermal conductivity detector (TCD).

For CO_2 -TPD measurements the samples were pre-treated in a $30 \text{ cm}^3 \text{ min}^{-1}$ flow of O_2 at $550 \text{ }^\circ\text{C}$ for 1 h, then flushed by N_2 ($30 \text{ cm}^3 \text{ min}^{-1}$) at same temperature for 15 minutes. The pre-treated sample was evacuated at $550 \text{ }^\circ\text{C}$, cooled to room temperature and contacted with about 14 kPa of CO_2 . After 15 minutes the physisorbed molecules were removed by evacuation. Then the reactor temperature was ramped up in He flow ($20 \text{ cm}^3 \text{ min}^{-1}$) at a rate of $10 \text{ }^\circ\text{C min}^{-1}$ to $500 \text{ }^\circ\text{C}$ and held at this temperature for 1 h, while the effluent gas was passed through a dry ice-acetone trap and a TCD detector.

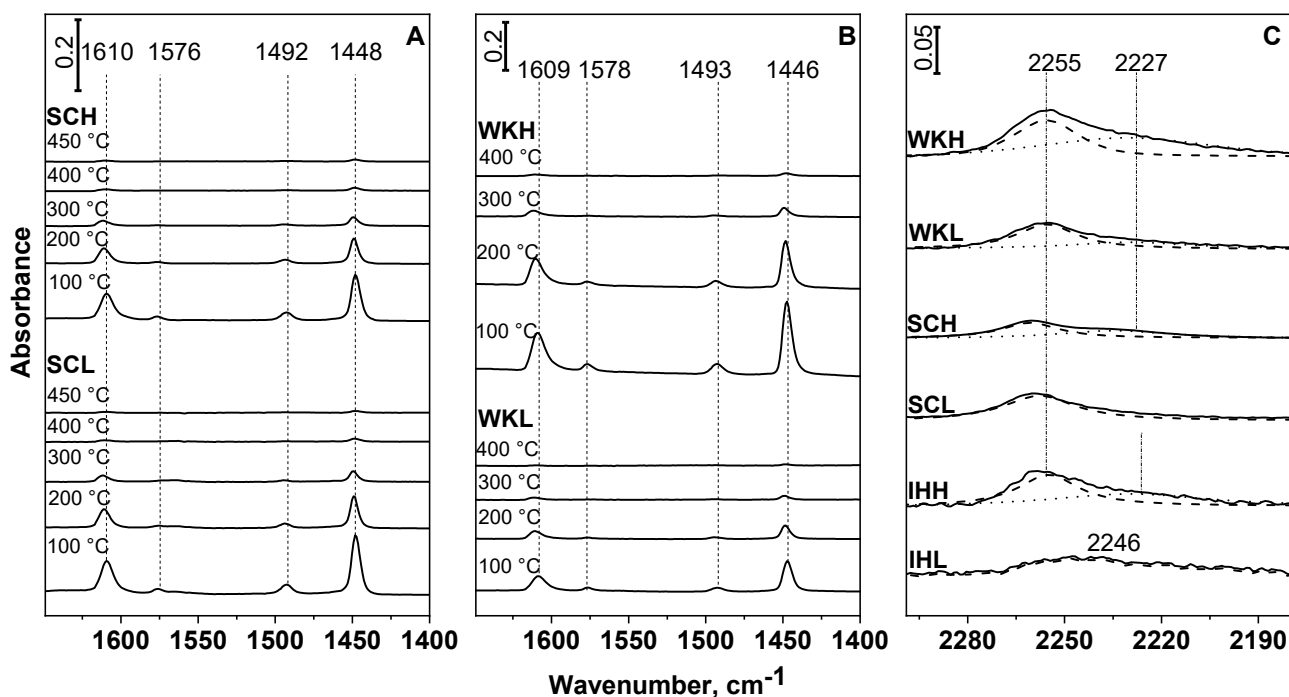


Fig. S3. FT-IR spectra obtained from the adsorption of (A, B) pyridine, and (C) CDCl_3 over MgO-SiO_2 mixed oxide catalysts prepared by the method of silica-coating (SC), and wet-kneading (WK), using LSM (SCL, WKL), and HSM (SCH, WKH) magnesia component. In section (C) also results are shown for the IHL and IHH catalysts. The IHH catalyst was obtained by hydrolyzing TEOS/Mg-methoxide solution within the pores of a mesoporous carbon template (internal hydrolysis, IH), and by burning out then the organic components. The IHL catalyst was prepared applying similar procedure but without using carbon template.

Wafers of $8\text{-}15\text{ mg cm}^{-2}$ thickness were prepared from the samples, pre-treated in vacuum for 1 h at $450\text{ }^\circ\text{C}$. Samples were then cooled to room temperature and background spectrum was recorded.

The wafer was contacted with pyridine at 666 Pa pressure and $200\text{ }^\circ\text{C}$ temperature for 30 min. The wafer temperature was adjusted then to $100\text{ }^\circ\text{C}$ and increased in steps from $100\text{ }^\circ\text{C}$ to 200, 300, 400, and $450\text{ }^\circ\text{C}$ temperature. The samples were evacuated at each temperature for 30 min. After each evacuation treatment a spectrum was recorded at room temperature. Pyridine spectra were generated by subtracting the spectrum of the pre-treated wafer from the spectrum of the wafer loaded by pyridine.

The spectra of CDCl_3 were recorded at room temperature in the presence of CDCl_3 at about 933 Pa pressure.

All spectra were recorded by averaging 64 scans at a resolution of 2 cm^{-1} and normalized to wafer thickness of 5 mg cm^{-2} .

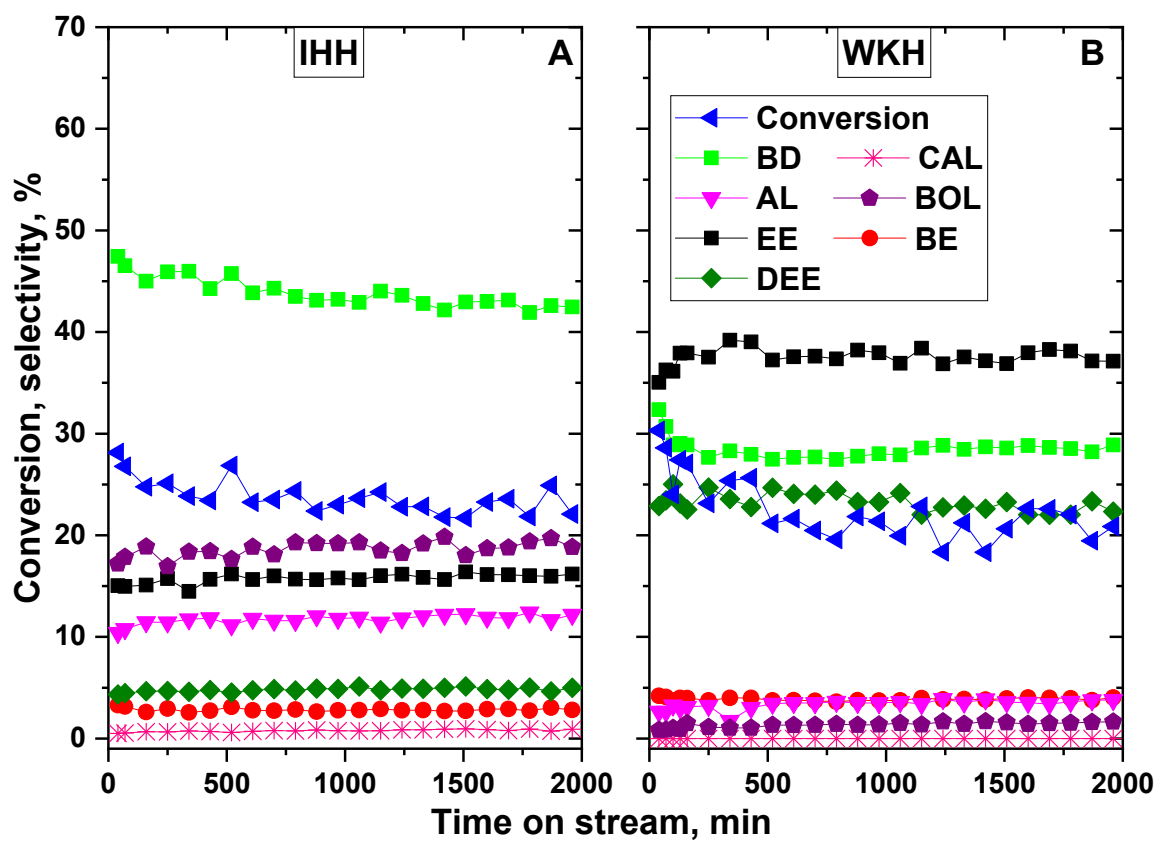


Fig. S4. Effect of time on stream at 400 °C over catalysts (A) IHH and (B) WKH. Reaction conditions: 15 kPa ethanol/He, $0.5 \text{ g}_{\text{ethanol}}\text{g}_{\text{cat}}^{-1}\text{h}^{-1}$, total gas flow rate of 30 ml min^{-1} .

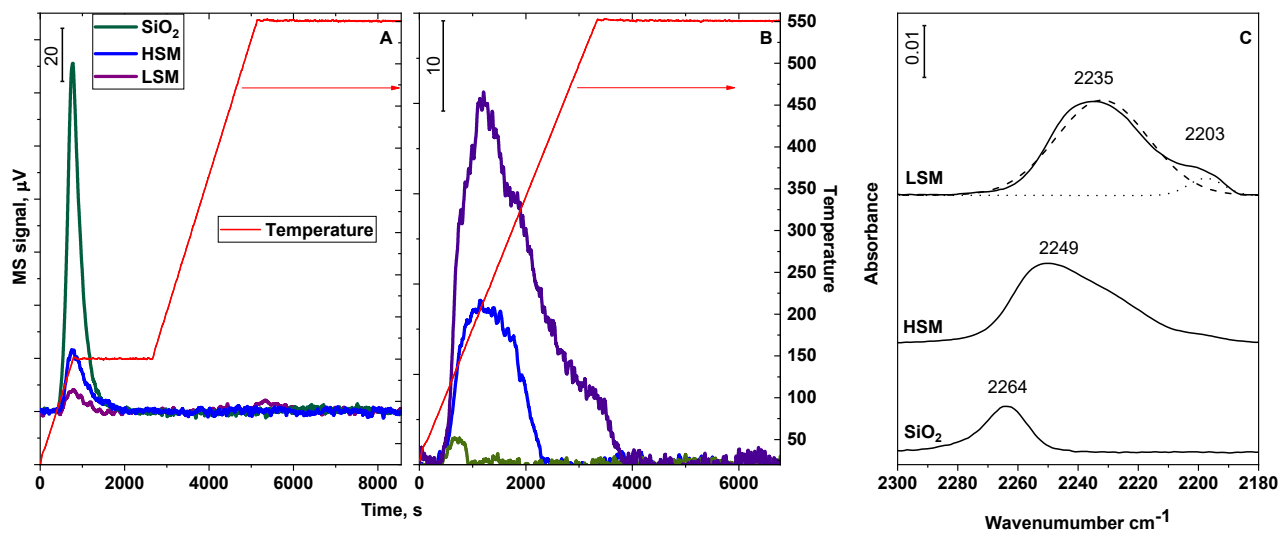


Fig. S5. Temperature-programmed desorption (TPD) curves of (A) NH₃, and (B) CO₂. Section (C) shows the FT-IR spectra obtained from the adsorption of CDCl₃. The characterized materials were the low-SSA MgO (LSM), high-SSA MgO (HSM) and SiO₂. Confer the legends of Figs. S2, and S3 for experimental details.