SUPPLEMENTARY INFORMATION



Microcalorimetry study

Fig. S1 Isotherms of adsorption of SO₂ (left) and NH₃ (right) as a function of equilibrium pressure on magnesium aluminate spinel catalysts at 150 $^{\circ}$ C



Fig. S2 Isotherms of adsorption of methanol as a function of equilibrium pressure on magnesium aluminate spinel catalysts at 30 °C



Fig. S3 Isotherms of adsorption of acetaldehyde (left) and formaldehyde (right) as a function of equilibrium pressure on magnesium aluminate spinel catalysts at 30 °C. The corresponding readsorption curves are in dotted line



Fig. S4 Isotherms and differential heats of adsorption of acetaldehyde, formaldehyde, NH₃ and SO₂ performed at 80 °C on 1Al₂O₃ 1MgO



Fig. S5 Isotherms of adsorption of propionaldehyde as a function of equilibrium pressure on magnesium aluminate spinel catalysts at 30 °C

FTIR study



Fig. S6 Species arising from methanol adsorption on magnesium oxide surface as reported by Tench *et al.*³⁷ and Bensitel *et al.*³⁸



Fig. S7 Species arising from methanol adsorption on alumina surface as reported by Busca et al.²⁶



Fig. S8 FTIR spectra (1000-3900 cm⁻¹) of methanol adsorbed on 1Al₂O₃ 1MgO at RT (a) followed by a desorption at RT (b), 100 °C (c), 200 °C (d), 300 °C(e) and 400 °C(f). The pretreated sample curve is in red (g)



Fig. S9 FTIR spectra (1000-3900 cm⁻¹) of methanol adsorbed on 6Al₂O₃ 1MgO at RT (a) followed by a desorption at RT (b), 100 °C (c), 200 °C (d), 300 °C(e) and 400 °C(f). The pretreated sample curve is in red (g)



Fig. S10 FTIR spectra (1000-3900 cm⁻¹) of methanol adsorbed on 12Al₂O₃ 1MgO at RT (a) followed by a desorption at RT (b), 100 °C (c), 200 °C (d), 300 °C(e) and 400 °C(f). The pretreated sample curve is in red (g)



Fig. S11 FTIR spectra (1000-3900 cm⁻¹) of formaldehyde adsorbed on 1Al₂O₃ 1MgO (a), 3Al₂O₃ 1MgO (b), 6Al₂O₃ 1MgO (c), 12Al₂O₃ 1MgO (d) after formaldehyde adsorption. Curves after pretreatment are represented by dashed lines



Fig. S12 FTIR spectra (1000-1900 cm⁻¹) of formaldehyde adsorbed on $1Al_2O_3 1MgO$ at RT (a) followed by a desorption at RT (b), $100 \degree C$ (c), $200 \degree C$ (d), $300 \degree C$ (e) and $400 \degree C$ (f). The pretreated sample curve is in red (g)



Fig. S13 FTIR spectra (1000-1900 cm⁻¹) of formaldehyde adsorbed on $3Al_2O_3 1MgO$ at RT (a) followed by a desorption at RT (b), $100 \degree C$ (c), $200 \degree C$ (d), $300 \degree C$ (e) and $400 \degree C$ (f). The pretreated sample curve is in red (g)



Fig. S14 FTIR spectra (1000-1900 cm⁻¹) of formaldehyde adsorbed on $6Al_2O_3$ 1MgO at RT (a) followed by a desorption at RT (b), 100 °C (c), 200 °C (d), 300 °C(e) and 400 °C(f). The pretreated sample curve is in red (g)



Fig. S15 FTIR spectra (1000-1900 cm⁻¹) of formaldehyde adsorbed on $12Al_2O_3 1MgO$ at RT (a) followed by a desorption at RT (b), $100 \degree C$ (c), $200 \degree C$ (d), $300 \degree C$ (e) and $400 \degree C$ (f). The pretreated sample curve is in red (g)



Fig. S16 FTIR spectra (1000-3900 cm⁻¹) of acetaldehyde adsorbed on $1Al_2O_3 1MgO$ at RT (a) followed by a desorption at RT (b), $100 \degree C$ (c), $200 \degree C$ (d), $300 \degree C$ (e) and $400 \degree C$ (f). The pretreated sample curve is in red (g)



Fig. S17 FTIR spectra (1000-3900 cm⁻¹) of acetaldehyde adsorbed on $3Al_2O_3 1MgO$ at RT (a) followed by a desorption at RT (b), 100 °C (c), 200 °C (d), 300 °C(e) and 400 °C(f). The pretreated sample curve is in red (g)



Fig. S18 FTIR spectra (1000-3900 cm⁻¹) of acetaldehyde adsorbed on $6Al_2O_3$ 1MgO at RT (a) followed by a desorption at RT (b), 100 °C (c), 200 °C (d), 300 °C(e) and 400 °C(f). The pretreated sample curve is in red (g)



Fig. S19 FTIR spectra (1000-3900 cm⁻¹) of acetaldehyde adsorbed on $12Al_2O_3 1MgO$ at RT (a) followed by a desorption at RT (b), $100 \degree C$ (c), $200 \degree C$ (d), $300 \degree C$ (e) and $400 \degree C$ (f). The pretreated sample curve is in red (g)



Fig. S20 FTIR spectra (1000-3900 cm⁻¹) of acetaldehyde adsorbed on 3Al₂O₃ 1MgO at RT followed by a desorption at RT, 100 °C, 200 °C, 300 °C and 400 °C. The pretreated sample curve is in red



Fig. S21 FTIR spectra (1000-3900 cm⁻¹) of propionaldehyde adsorbed on $1Al_2O_3 1MgO$ at RT (a) followed by a desorption at RT (b), 100 °C (c), 200 °C (d), 300 °C(e) and 400 °C(f). The pretreated sample curve is in red (g)



Fig. S22 FTIR spectra (1000-3900 cm⁻¹) of propionaldehyde adsorbed on 3Al₂O₃ 1MgO at RT (a) followed by a desorption at RT (b), 100 °C (c), 200 °C (d), 300 °C(e) and 400 °C(f). The pretreated sample curve is in red (g)



Fig. S23 FTIR spectra (1000-3900 cm⁻¹) of propionaldehyde adsorbed on $6Al_2O_3$ 1MgO at RT (a) followed by a desorption at RT (b), 100 °C (c), 200 °C (d), 300 °C(e) and 400 °C(f). The pretreated sample curve is in red (g)



Fig. S24 FTIR spectra (1000-3900 cm⁻¹) of propionaldehyde adsorbed on $12Al_2O_3 1MgO$ at RT (a) followed by a desorption at RT (b), 100 °C (c), 200 °C (d), 300 °C(e) and 400 °C(f). The pretreated sample curve is in red (g)



Fig. S25 FTIR spectra (1000-3900 cm⁻¹) of formaldehyde adsorbed on 1Al₂O₃ 1MgO at RT (a) followed by desorption at RT (b) acetaldehyde adsorption at RT (c) and then desorption at RT (d). The pretreated sample curve is in red (e)



Fig. S26 FTIR spectra (1000-3900 cm⁻¹) of formaldehyde adsorbed on 3Al₂O₃ 1MgO at RT (a) followed by desorption at RT (b) acetaldehyde adsorption at RT (c) and then desorption at RT (d). The pretreated sample curve is in red (e)



Fig. S27 FTIR spectra (1000-3900 cm⁻¹) of formaldehyde adsorbed on 6Al₂O₃ 1MgO at RT (a) followed by desorption at RT (b), acetaldehyde adsorption at RT (c) and then desorption at RT (d). The pretreated sample curve is in red (e)



Fig. S28 FTIR spectra (1000-3900 cm⁻¹) of formaldehyde adsorbed on 12Al₂O₃ 1MgO at RT (a) followed by desorption at RT (b), acetaldehyde adsorption at RT (c) and then desorption at RT (d). The pretreated sample curve is in red (e)



Fig. S29 FTIR spectra (1000-3900 cm⁻¹) of acetaldehyde adsorbed on 1Al₂O₃ 1MgO at RT (a) followed by desorption at RT (b), formaldehyde adsorption at RT (c) and then desorption at RT (d). The pretreated sample curve is in red (e)



Fig. S30 FTIR spectra (1000-3900 cm⁻¹) of acetaldehyde adsorbed on 3Al₂O₃ 1MgO at RT (a) followed by desorption at RT (b), formaldehyde adsorption at RT (c) and then desorption at RT (d). The pretreated sample curve is in red (e)



Fig. S31 FTIR spectra (1000-3900 cm⁻¹) of acetaldehyde adsorbed on 6Al₂O₃ 1MgO at RT (a) followed by desorption at RT (b), formaldehyde adsorption at RT (c) and then desorption at RT (d). The pretreated sample curve is in red (e)



Fig. S32 FTIR spectra (1000-3900 cm⁻¹) of acetaldehyde adsorbed on 12Al₂O₃ 1MgO at RT (a) followed by desorption at RT (b), formaldehyde adsorption at RT (cd) and then desorption at RT (d). The pretreated sample curve is in red (e)