catalysts

Supplementary Material

Dehydroisomerisation of α-Pinene and Limonene to P-Cymene Over Silica-Supported ZnO in the Gas Phase

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Abstract: Silica-supported zinc oxide possessing acid and dehydrogenation functions is an efficient, noble-metal-free bifunctional catalyst for the environment-friendly synthesis of p-cymene from renewable monoterpene feedstock by gas-phase dehydroisomerisation of α-pinene and limonene in a fixed-bed reactor. The reaction involves acid-catalysed terpene isomerisation to p-menthadienes followed by dehydrogenation to form p-cymene. Dehydroisomerisation of α-pinene produces p-cymene with 90% yield at 100% conversion at 370 °C and WHSV = 0.01–0.020 h^{-1}. The reaction with limonene gives a 100% p-cymene yield at 325 °C and WHSV = 0.080 h^{-1}. ZnO/SiO_2 catalyst shows stable performance for over 70 h without co-feeding hydrogen.

Keywords: α-pinene; limonene; p-cymene; zinc oxide; bifunctional catalysis

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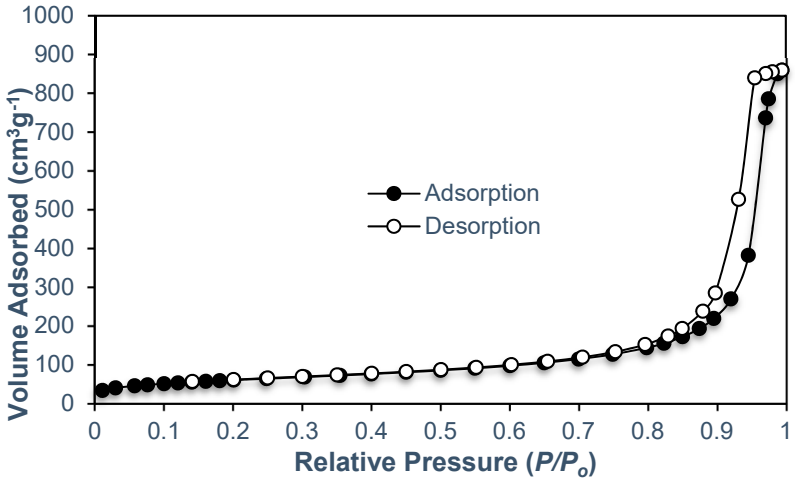

Figure S1. Nitrogen adsorption and desorption isotherms on fresh 10%ZnO/SiO_2(300) with a H1 hysteresis loop typical of amorphous silica.

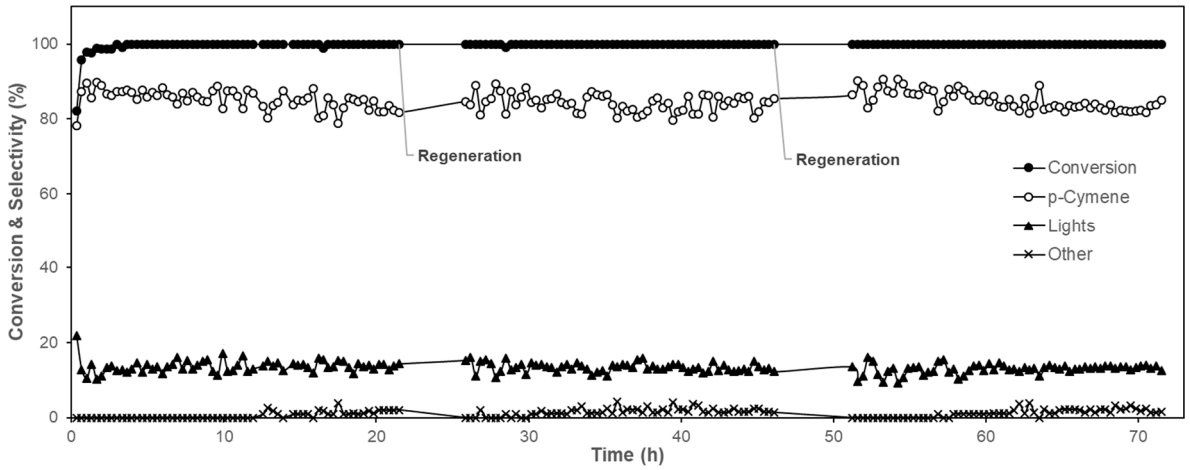

Figure S2. Long-term time course for α-pinene dehydroisomerisation over 10%ZnO/SiO_2(300) with catalyst regeneration: 0.80 g catalyst, 370 °C, 0.48 kPa α-pinene partial pressure, 10 mL min^{-1} flow rate, WHSV = 0.020 h^{-1}; the catalyst regenerated in situ by air flow (10 mL min^{-1}) at 370 °C for 3 h. Average p-cymene selectivity 85% at 100% p-cymene conversion over 70 h TOS.

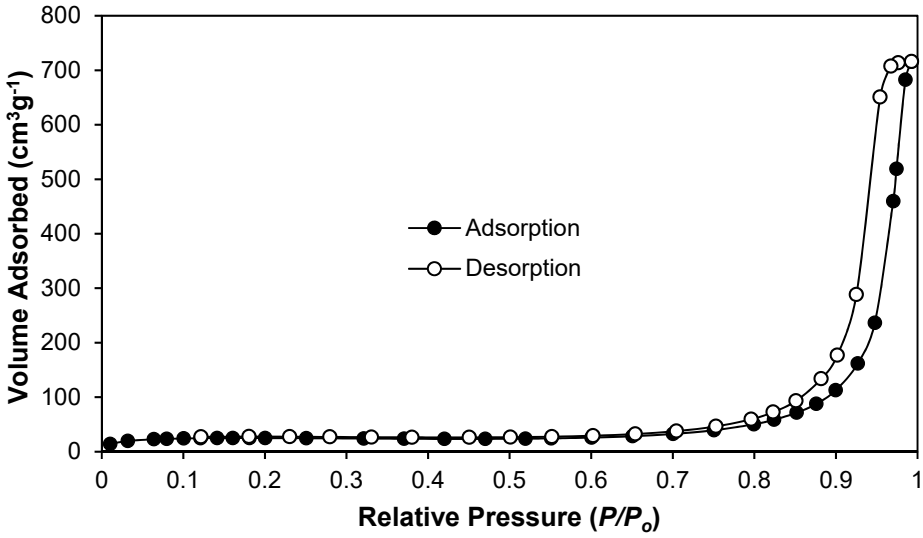

Figure S3. Nitrogen adsorption and desorption isotherms on spent 10%ZnO/SiO_2(300) catalyst after α-pinene dehydroisomerisation at 370 °C, 0.48 kPa α-pinene partial pressure, 10 mL min^{-1} flow rate, WHSV = 0.020 h^{-1}, 24 h TOS. BET surface area, 87 m^2g^{-1}; single point total pore volume, 0.71 cm^3g^{-1}; average pore diameter by BET, 329 Å.

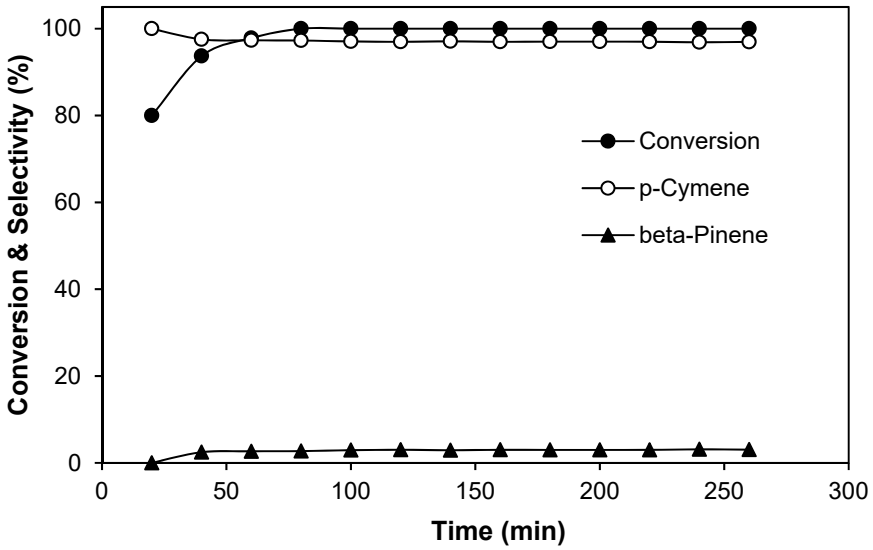

Figure S4. Time course for limonene dehydroisomerisation over 20%ZnO/SiO_2(300):0.20 g catalyst, 300 °C, 0.47 kPa limonene partial pressure, 10 ml min^{-1} flow rate, WHSV = 0.080 h^{-1}.

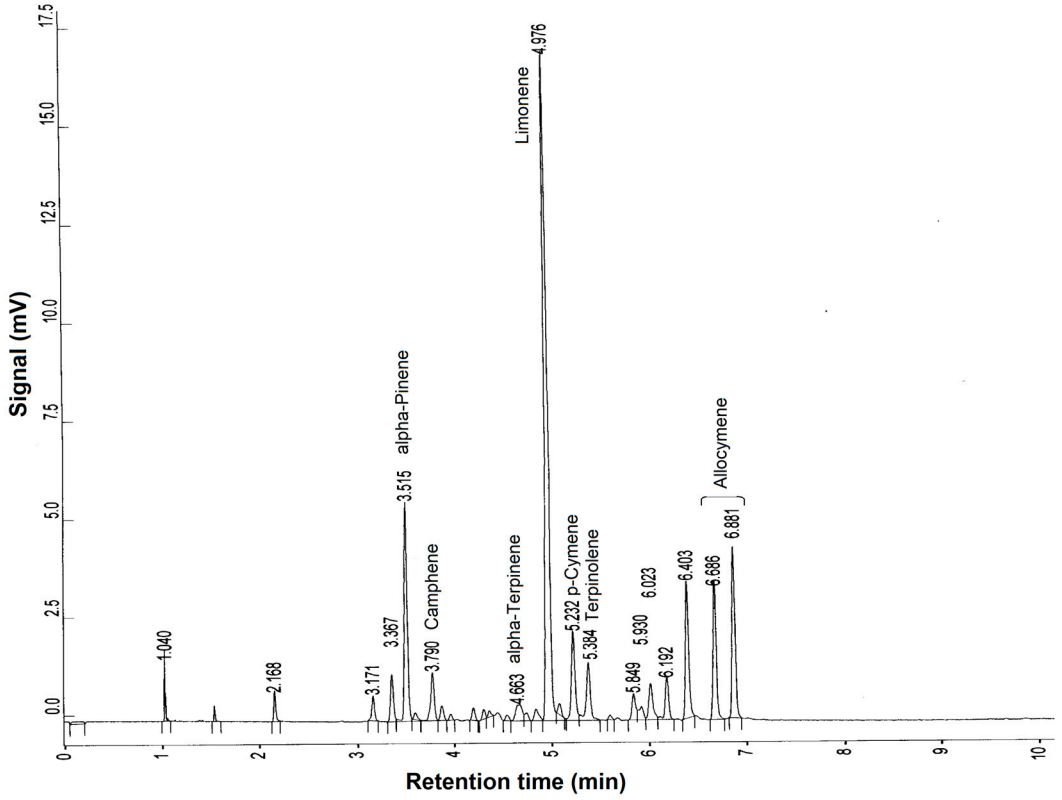

Figure S5. GC trace showing product mixture for α-pinene conversion over bulk Zn–Fe mixed oxide at 350 °C, 0.48 kPa α-pinene partial pressure and 10 mL min^{-1} flow rate to illustrate high resolution of product analysis. The Zn–Fe oxide had much lower activity and selectivity than ZnO/SiO_2, yielding a wide range of by-products. In dehydroisomerisation of α-pinene and limonene on ZnO/SiO_2, much smaller amounts of by-products were formed (Figure S6). From GC traces, α-pinene, limonene, p-cymene, α-terpinene, terpinolene, β-pinene, and camphene were quantified individually. Other p-menthadienes were lumped together as "other" and the cracking products, appearing before α-pinene (retention time 0–3.5 min), as "lights".

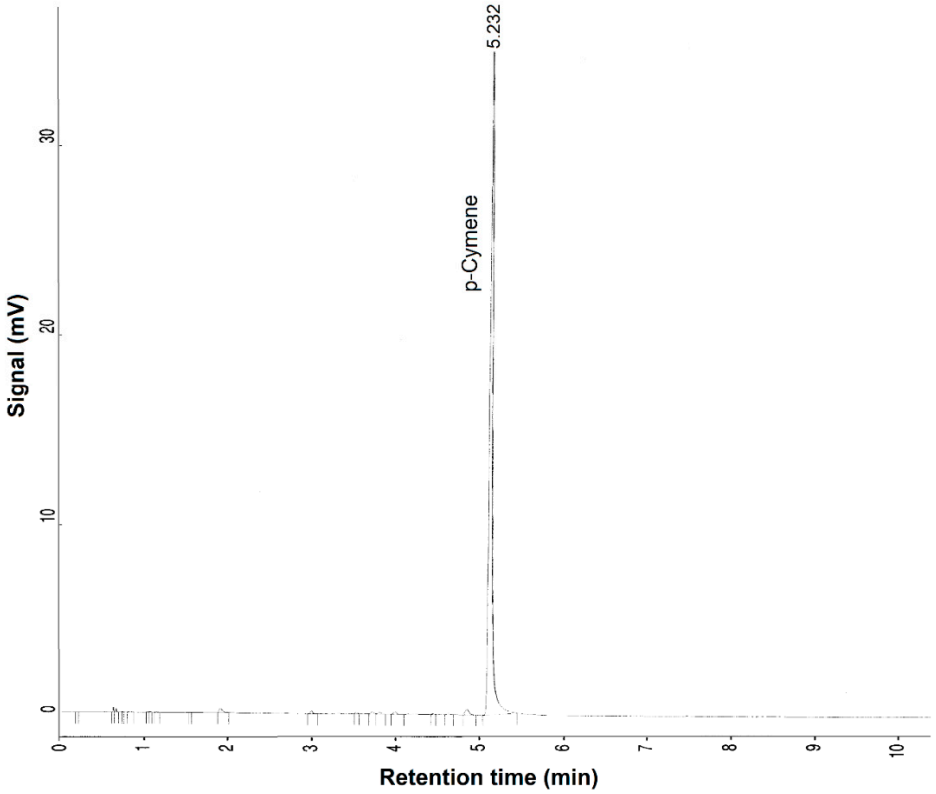

Figure S6. GC trace for limonene conversion over 30%ZnO/SiO_2(300): 0.20 g catalyst, 0.47 kPa limonene partial pressure, 10 mL min^{-1} flow rate, WHSV = 0.080 h^{-1}.