

## Supplementary material

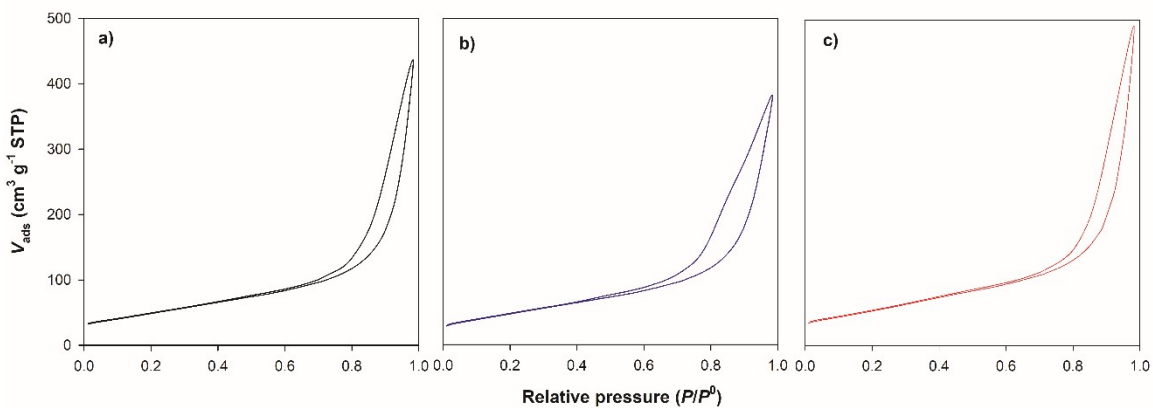


Figure S1. Nitrogen adsorption-desorption isotherms for calcined TiNT (a), reduced Ru/TiNT (b), and reduced Rh/TiNT (c).

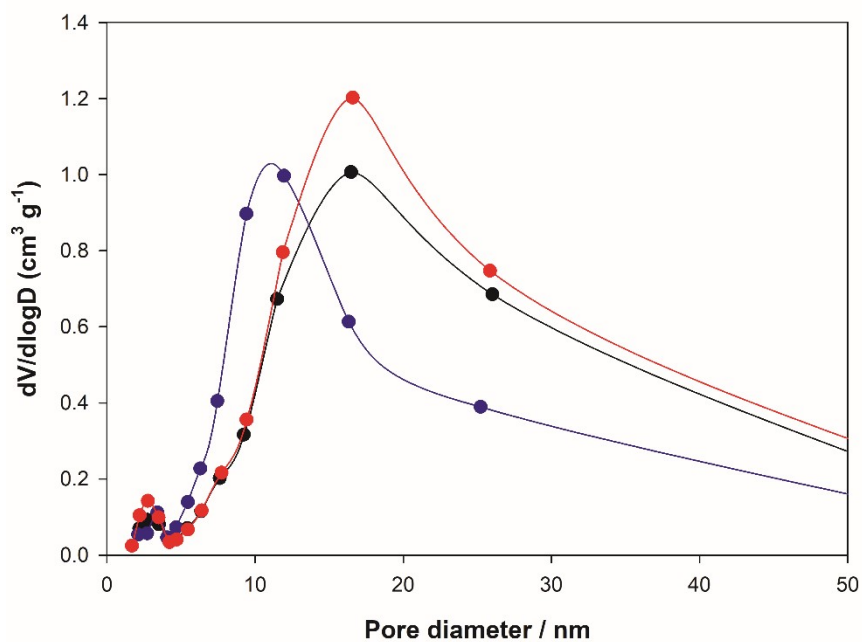


Figure S2. Particle size distribution determined by BJH method for calcined TiNT (black line), reduced Ru/TiNT (blue line), and reduced Rh/TiNT (red line).

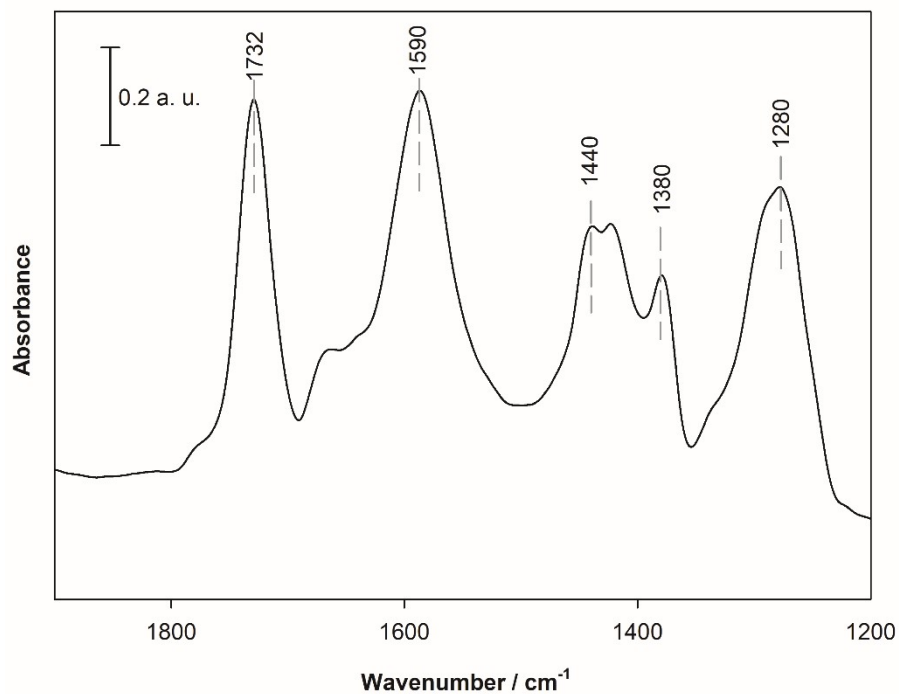


Figure S3. IR spectrum of TiNT at 120 °C in flowing argon after being exposed to a pulse of methyl acetate (c.a. 10  $\mu$ L) and purged in Ar for 15 min.

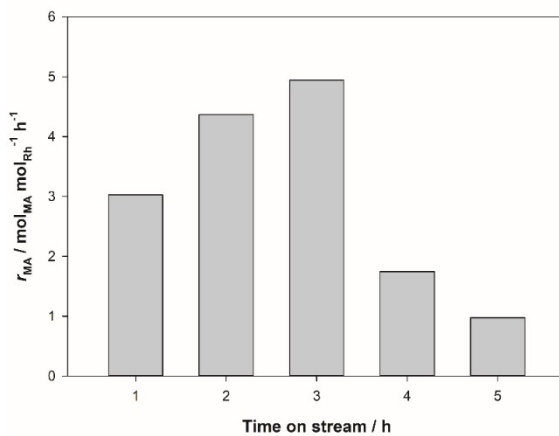


Figure S4. Stability of Rh/TiNT catalyst during the hydrocarboxylation of methanol at 150°C. Mass of catalyst = 0.1 g, pressure = 1 bar, total flow rate = 65 mL  $\text{min}^{-1}$ ,  $p_{CO_2}$  = 70 Torr,  $p_{H_2}$  = 70 Torr,  $p_{MeOH}$  = 21 Torr,  $p_{MeI}$  = 281 Torr, and  $p_{Ar}$  = 318 Torr