Supplementary Material for Chemical Communications

Supplementary Information- Detailed Experimental Section

Instrumentation

Transmission electron micrographs were taken on a Philips CM120 Super Twin 120kV electron microscope with a LaB6 electron source. The spherical nature of the particles was tested by tilting the samples by ±40°. EDS measurements were made using retractable Si(Li)detector with super ultra thin window; the point resolution was 3.0 Å. IR spectra were measured on a Nicolet Protégé 460 FTIR spectrometer prepared as ~5% catalysts in KBr pellets. . Isotope incorporation in substrates and products was measured by GC-MS (HP 5973). Reactions were quantified by GLC (HP 6890) using a 30 m 5% phenylmethyl silicone capillary column with an ID 0.32 mm and 0.25 μm coating (Restek 5MS). The identity of the products was verified by use of reference standards and/or GC-MS (HP 5973) using a 30 m 5% phenylmethyl silicone capillary column with an ID 0.25 mm and 0.25 μm coating (Restek 5MS).

Preparation of metal nanoparticles.

A 10 mM solution of $H_5PV_2Mo_{10}O_{40}\bullet 32H_2O$ (Tsigdinos, G. A.; Hallada, C. J. *Inorg. Chem.* 1968, *7*, 437.) in deionized water was treated with a 100 fold excess of Zn powder under argon. When the color of the solution turned blue after a few minutes, the solution was filtered under argon and diluted to 1 mM reduced $ZnH_5PV_2Mo_{10}O_{40}$.

Ag_n–$ZnH_3PV_2Mo_{10}O_{40}$. 2.5 mL of 1 mM $ZnH_5PV_2Mo_{10}O_{40}$ was treated in a bath sonicator with 0.5 mL 10 mM $AgNO_3$ in acetonitrile. After 10 minutes the color of the solution turned to yellow and remained clear indicating the re-oxidation of the polyoxometalate and the formation of Ag(0) nanoparticles. The solution can be stored under ambient conditions without apparent degradation for days. TEM analysis showed colloids with an average size of 5 nm.

Ru_n–$ZnH_3PV_2Mo_{10}O_{40}$. 2.5 mL of 1 mM $ZnH_5PV_2Mo_{10}O_{40}$was treated in a bath sonicator with 0.25 mL 10 mM $RuCl_2(DMSO)_4$ in 1:1 H_2O/CH_3CN. After 10 minutes the color of the solution turned to dark yellow indicating the re-oxidation of the polyoxometalate and the formation of Ru(0) nanoparticles. The solution can be stored under ambient conditions without apparent degradation for several days. TEM analysis showed colloids with an average size of 5 nm.

Pt_n–$ZnH_3PV_2Mo_{10}O_{40}$. 2.5 mL of 1 mM $ZnH_5PV_2Mo_{10}O_{40}$was treated in a bath sonicator with 0.25 mL 10 mM $K_2[PtCl_4]$ in 1:1 H_2O/CH_3CN. After 10 minutes the color of the solution turned to dark yellow indicating the re-oxidation of the polyoxometalate and the formation of Pt(0) nanoparticles. The solution can be stored under ambient conditions without apparent degradation for several days. TEM analysis showed colloids with an average size of 2.7 nm.

Preparation of metal nanoparticles supported on α-alumina.

α-alumina was pre-treated by stirring 510 mg α-alumina with a solution of 7 mg $NaHCO_3$ in 5 ml H_2O at 50°C. After 2 hours the water was removed under high vacuum. The nanoparticle solutions were mixed α-alumina at a computed 5% w/w ratio at room temperature for two hours. The solvent was then removed under vacuum and the supported catalyst was dried overnight at 80 °C and stored at room temperature in amber vials. The colors of the various M_n–$ZnH_3PV_2Mo_{10}O_{40}/Al_2O_3$ materials ranged from yellow-green for Ag_n–$ZnH_3PV_2Mo_{10}O_{40}/Al_2O_3$, yellow brown for Ru_n–$ZnH_3PV_2Mo_{10}O_{40}/Al_2O_3$ and grayish for Pt_n–$ZnH_3PV_2Mo_{10}O_{40}/Al_2O_3$.

General procedure for the oxidation reactions.

Reactions were carried out in 25 mL glass pressure tubes in a preheated thermostated oil bath (± 2 °C). Thus, typically 0.5 mmol alkene substrate, 15 mg (5% w/w) M_n–$ZnH_3PV_2Mo_{10}O_{40}/\alpha$-$Al_2O_3$, 0.05 mmol anisole (internal standard) and 0.5 mL trifluoromethylbenzene (solvent) were reacted under 2 atm O_2 at the given reaction temperature and time. After cooling the solution, the reaction solutions were quantified by GC after preparation of calibration curves (alkene/internal standard). Products were identified via authentic reference standards and/or GC-MS.