Preparation and characterisation of a highly active bimetallic (Pd–Ru) nanoparticle heterogeneous catalyst†

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The mixed-metal carbonylate cluster $[Pd_6Ru_6(CO)_{24}]^{2-}$ was used as a single-source precursor in the synthesis of a highly active hydrogenation catalyst (stoichiometry PdRu) which has been characterised by electron microscopy and X-ray absorption spectroscopy: PdRu readily hydrogenates alkenes and naphthalene (the latter predominantly to *cis*-decalin) under mild conditions

Bimetallic nanoparticle catalysts occupy a position of high prominence in modern heterogeneous catalysis, especially for reactions of petrochemical significance.[1–3] Published reports[4–9] on such catalysts, typified by Pt–Re, Ir–Sn, Pt–Ru, Ag–Ru and Cu–Ru, reveal that enhanced catalytic performance apparently arises from the synergy between the component elements at the nanoscale which is absent in solid solutions of the two bulk metals.

In this communication we show that a single-source, mixed-metal cluster carbonylate precursor yields (by gentle thermolysis) a uniform distribution of discrete nanoparticles (*ca.* 17 Å diameter) of a Pd–Ru bimetallic catalyst encapsulated within the pores (*ca.* 30 Å diameter) of mesoporous silica. This catalyst is highly active in the hydrogenation of linear alkenes and significantly more so than two other bimetallic catalysts also prepared from single-source carbonylate precursors, Ag_3Ru_{10}[7] and Cu_4Ru_{12}.[9] Moreover, the Pd–Ru catalyst described here is capable of hydrogenating naphthalene under relatively mild conditions.

Fig. 1 (a) Fourier transform of the Pd K-edge EXAFS data (effectively a radial distribution function) for the mixed-metal carbonylate ion $[Pd_6Ru_6(CO)_{24}]^{2-}$ precursor dispersed inside the mesopores of the MCM-41 silica. (b) The corresponding transform for the dispersed precursor after gentle thermolysis (see text). The resulting cluster (see Fig. 2) has an average metal–metal (Pd–Ru and Pd–Pd) distance that peaks at 2.73 Å and the average co-ordination number is 5.3.

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The anionic molecular precursor $[Pd_6Ru_6(CO)_{24}]^{2-}$, **1**, was synthesised as described[10] previously; and isolated as its NEt_4^+ salt. This particular precursor was selected for a variety of reasons including its solubility, stoichiometry, adsorbability at, and dispersion across, the silanol rich[11,12] interior surfaces of the mesoporous silica support (MCM-41), as well as the ease with which it sheds its cloak of carbonyl groups during mild thermal treatment. Of prime importance also was our wish to design a bimetallic catalyst in which a metal (Pd) that readily takes up hydrogen is juxtaposed with one (Ru) that has a strong tendency to bind arenes. A Pd–Ru catalyst should therefore function effectively in the hydrogenation of aromatic molecules.

The methodology for its preparation and encapsulation into the mesopores is essentially that used in our earlier work[7,9] on Ag–Ru and Cu–Ru bimetallic nanocrystals. Retention of the structural integrity of the mixed-metal cluster carbonylate inside the mesoporous silica was deduced from *in situ* spectroscopic analysis, both infra red[9] (Nujol mull) and X-ray absorption using a specially designed cell.[13,14] The respective data sets showed the same structural features as those of the cluster when dispersed in homogeneous solution (tetrahydrofuran as solvent). The characteristic IR absorption peaks were somewhat broadened and slightly shifted (*ca.* 3 cm^{-1}) to lower energy upon encapsulation. Precise structural information (Ru–Ru, Pd–Pd and Ru–Pd distances and associated co-ordination numbers), retrieved from EXAFS analyses for Ru and Pd K-absorption edges, was in good accord with that obtained from the single-crystal X-ray structure[10] of Et_4N^+ salts of the anion **1**.

When the encapsulated carbonylate **1** was heated (10^{-4} Torr) for 1 h, at 180 °C, the sample changed colour from brown to
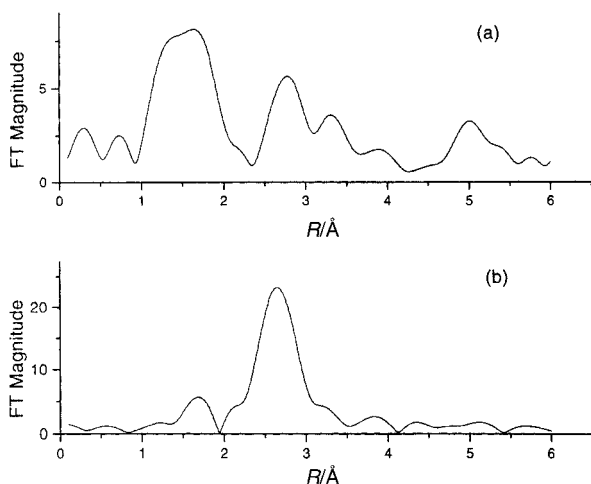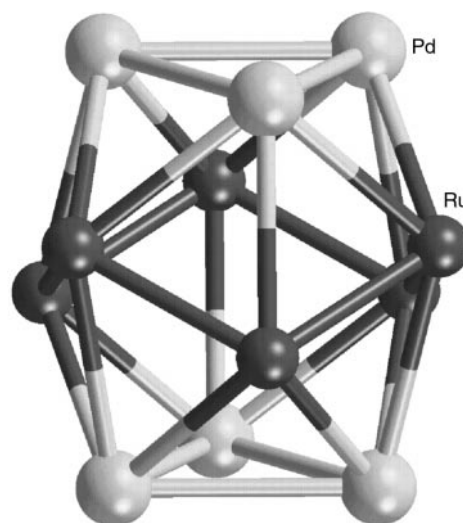

Fig. 2 Schematic diagram of the Pd_6Ru_6 cluster derived from an EXAFS analysis of the Ru and Pd K-edge X-ray absorption spectra (it is difficult to distinguish scattering by Pd atoms from that by Ru atoms).

Table 1 Hydrogenation of olefins—comparison of catalysts

Substrate (mass/g)	Catalyst	Solvent	Reaction time/h	Residual H_2 pressure/bar	Conv. (%)	TOF/ h^{-1}	Product distribution (mol%)		
							n-Hexane	cis-Hex-2-ene	trans-Hex-2-ene
Hex-1-ene (≈ 50 g)	Pd_6Ru_6/MCM-41	—	4	1	99	4954	68	22	9
	Cu_4Ru_{12}/MCM-41	—	4	8	56	2805	51	30	19
	Ru_6/MCM-41	—	4	15	13	325	14	42	45
			24	13	19	277	10	36	53
	Pd/MCM-41	—	4	18	6	250	6	45	48
			24	16	14	196	5	33	63
	No Catalyst	—	24	17	7	—	—	32	67
							n-Dodecane	cis-Dodec-2-ene	trans-Dodec-2-ene
Dodec-1-ene (≈ 50 g)	Pd_6Ru_6/MCM-41	—	4	3	88	2202	63	29	7
	Cu_4Ru_{12}/MCM-41	—	4	7	35	877	54	32	13
							cis-Decalin	trans-Decalin	Others
Naphthalene (≈ 8 g)	Pd_6Ru_6/MCM-41	CH_3CN	8	12	19	50	86	4	9
		Hexadecane	8	10	7	19	50	34	15
		Hexadecane^a	8	20	0		No Reaction		
	Cu_4Ru_{12}/MCM-41	CH_3CN	8	18	0.8	2	—	—	100
		Hexadecane	8	20	0		No Reaction		

Reaction conditions: catalyst = 20 mg; T = 373 K; starting H_2 pressure = 20 bar; solvent ≈ 55 g; ^{a} 200 ppm of sulfur was added in the form of benzothiophene.

black; the IR carbonyl stretching region gradually disappeared; and the atomic structure of the mixed-metal cluster, as seen by details of the XANES and EXAFS, changed dramatically (Fig. 1). High-resolution transmission electron microscopy (HRTEM) revealed[15] that the Pd–Ru bimetallic nanoparticles were of uniform size (ca. 17 Å diameter) and spatially well distributed within the pores of the siliceous support.

The catalytic performance in alkene hydrogenation of the Pd–Ru nanoparticles is compared in Table 1 with those of similarly prepared (and sized) Cu_4Ru_{12} bimetallic nanoparticles. The kinetics of hydrogenation of hex-1-ene and dodec-1-ene reveal that the Pd_6Ru_6 catalysts showed a higher selectivity for n-hexane (or n-dodecane) than Cu_4Ru_{12}. The Pd_6Ru_6 catalyst is more active than Cu_4Ru_{12} for the hydrogenation of hex-1-ene (≈2 times) and dodec-1-ene (≈2.5 times). For comparison, a monometallic Ru_6 cluster was encapsulated in MCM-41 and a Pd/MCM-41 catalyst was prepared following a literature procedure,[16] and both were tested for the hydrogenation of hex-1-ene employing the same reaction conditions. It is very clear from Table 1 that the bimetallic catalysts are far superior in performance (% conversion) than their monometallic analogues and more importantly yield a higher selectivity for hydrogenated products, suggesting a possible synergism between the two bimetallic nanoparticles. The Pd_6Ru_6 catalyst was more effective than Cu_4Ru_{12} in the hydrogenation of naphthalene and higher conversions were obtained when acetonitrile was used as a solvent. Other solvents such as hexadecane showed a lower preference for the production of cis-decalin. The solid catalyst may be recycled without any significant decrease in activity or selectivity. This was done by filtering off the solvent–product mixture and recharging the Parr reactor with fresh material[17] (see Table 1 for reaction conditions). Unsurprisingly,[1–3] the introduction of ≈200 ppm of sulfur in the reaction mixture completely poisons the catalyst.

Surveys by electron-stimulated energy dispersive X-ray emission[17] of the Pd–Ru nanocatalyst particles after their use in four consecutive test runs showed that there was no segregation of the two components of the bimetallic catalyst. Moreover, annular dark field (Z-contrast) high-resolution microscopy showed[15] that there was no evidence of coalescence or sintering of the nanoparticles during catalytic use. Guided by energy-minimisation procedures[18] using density-functional theory computations, we have arrived at the EXAFS model for the structure of the bimetallic cage shown in Fig. 2.

Notes and references

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