SUPPORTING INFORMATION

1. EXAFS SPECTRA

Ru local environment in the structure of the Ru-MNP catalyst was investigated by EXAFS spectroscopy at the Ru K edge (22117 eV). The absorption spectrum of the catalyst was measured in fluorescence mode on a laboratory x-ray absorption spectrometer (Rigaku R-XAS Looper).[1,2] The continuous radiation of a 3 kW x-ray tube with tungsten target was analyzed on a curved Ge(840) single crystal, and monitored by a proportional Ar-filled counter.

The EXAFS analysis was carried out by a standard procedure, using the REX2000 package.[3] After subtraction of pre-edge and post-edge backgrounds from the spectrum, the normalized EXAFS function $\chi(k)$ (k = photoelectron wave vector) was calculated from the absorption post-edge oscillations normalized through the atomic smooth absorption (post-edge background). The k^3-weighted EXAFS was Fourier transformed into the physical r-space, resulting in a radial function with maxima corresponding, up to systematic shifts, to the neighbouring shells of the Ru atoms (Figure 1S). The first maximum of the Fourier transform, corresponding to the nearest neighbours of Ru, was backtransformed into k-space and non-linearly fitted with Cl and/or O neighbours. The fit provided the structural parameters describing the Ru environment: coordination numbers, interatomic distances, and their mean-square fluctuations (σ^2). The electron back-scattering amplitudes, phase shifts, and mean free path for inelastic scatterings were calculated by the FEFF6 code.[4]

The best fit of EXAFS, in the k range 3.0-11.5 Å^{-1}, was achieved for Cl surrounding, consisting of 3.0±0.5 Cl atoms at the Ru-Cl distance of 2.15±0.01 Å, with $\sigma^2 = 0.006 \pm 0.001$ Å^2. Any other attempts to fit the Ru environment with O or (O + Cl) neighbours failed to give reliable results. It is worth noting that this Cl neighbouring is different from that in $RuCl_3$ [5], with 6 Cl atoms at 2.35 Å. The number of Cl neighbours in the catalyst structure is reduced to a half with respect to $RuCl_3$, while the Ru-Cl distance shortens by 0.2 Å.

In order to verify this result, additional EXAFS determinations were performed on RuO_2 and $RuCl_3$ standard compounds (not shown here). The EXAFS analysis of RuO_2 indicated 6 O neighbours at 1.99 Å, in a good agreement with the RuO_2 structure (6 O at 1.97 Å).[6] The analysis of $RuCl_3$ was less reliable, due to the sample hydration during the measurements, which probably changed the Ru environment. However, although the fit of the Cl surrounding was poorer for this sample, the resulted Ru-Cl distance was 2.37 Å, without any shortening with respect to that in $RuCl_3$ structure (2.35 Å).

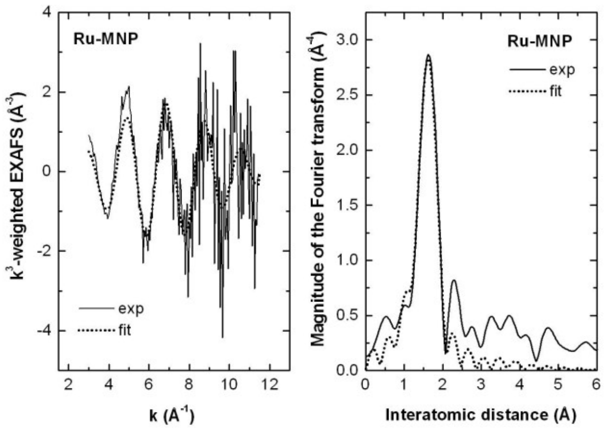

Figure 1S. k^3-weighted Ru K-edge EXAFS of the Ru-MNP catalyst and magnitude of the corresponding Fourier transform. The raw data and their fit with the nearest Cl neighbours of Ru were shown by lines and dots, respectively.

Therefore, the contraction of the Ru-Cl distance in the Ru-MNP catalyst is a real one, and not due to some artifacts of the analysis. This points out that although some Cl ligands were preserved around Ru, their configuration in the catalyst structure is a specific one, rather different from that in the Ru precursor.

2. XPS SPECTRA

The surface composition of the catalyst has been analyzed by X ray photoelectron spectroscopy (XPS).

Peaks belonging to Ru 3d and C 1s are overlapped. However, they can be clearly identified by taking into account the Ru 3d5/2 and Ru 3d3/2 peak distance of 4.2 eV and the expected ratio of intensities $I_{3/2}/I_{5/2} = 0.66$.[7] It is important to mention that peaks belonging to chlorine have also been detected by XPS, a feature that suggests its incomplete removal during the immobilization of the metal precursor on the support. Therefore, as can be seen in Figure 2S, the XPS spectrum for Ru 3d level shows that the ruthenium precursor was not completely decomposed as resulted from the identification of the Ru-Cl component (282.1 eV). Very similar results were collected from the analysis in the Ru3p region (spectra not shown) where the band assigned to Ru-Cl was located at 463.2 eV.

Such a result strongly indicates that the metal is actually coordinated as Ru(III) to the amino-modified silica layer of the core–shell support through hydrochloride -C-$NH_3^+Cl^-$ species, in agree with DRIFT measurements. Most important, these species are preserved after reaction indicating the integrity of the catalysts.

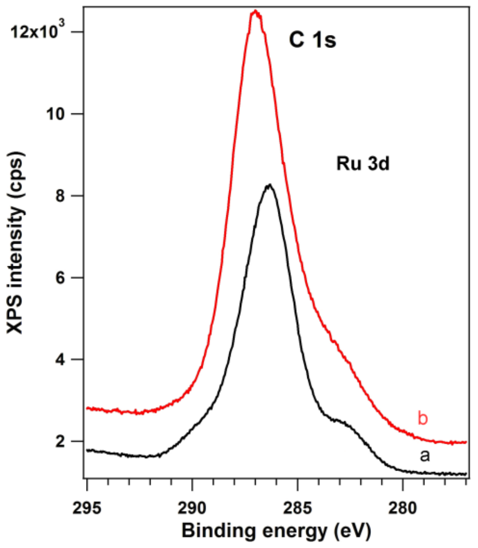

Figure 2S. XPS spectrum of Ru3d for the fresh Ru-MNP (a) and spent Ru-MNP (b) catalytic sample

3. XRD DIFFRACTOGRAM

X-ray diffraction (XRD) patterns were recorded with a Shimadzu XRD 7000 diffractometer using a CuK$_\alpha$ radiation source.

The surface composition of the catalyst before and after reaction has been analyzed by X ray powder diffraction (Figure 3S).

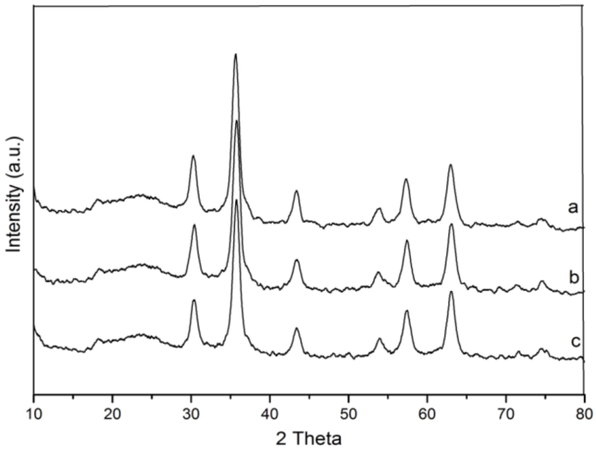

Figure 3S. X-ray powder diffraction patterns of APTES-magnetite nanoparticles (a), fresh Ru-MNP (b) catalyst and Ru-MNP (c) catalyst recovered after reaction (Table 1, entry 4)

The XRD pattern of the catalyst after reaction also proves the integrity of the catalyst, in agree with XPS spectroscopy.

4. GS-MS ANALYSIS

After reaction, the reactor was cooled down and the catalyst was separated with the aid of an external magnet. Products were sylilated, diluted with 1 mL of toluene and analyzed by GC-MS chromatography by using a GC-MS Carlo Erba Instruments QMD 1000 equipped with a Factor Four VF-5HT column. The GS chromatogram and the corresponding MS spectra of the standard succinic acid and the reaction products are given in Figures 4S and 5S.

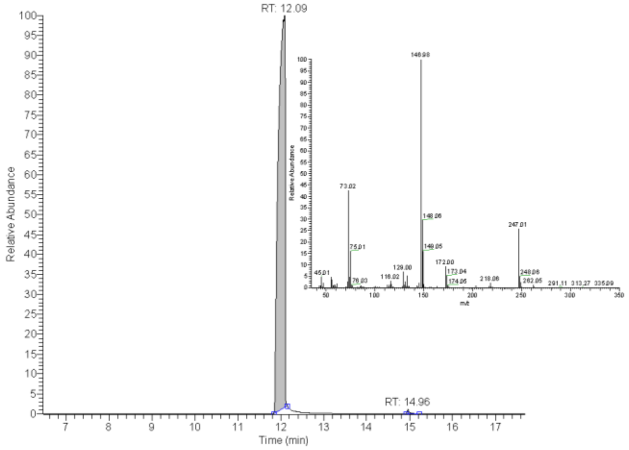

Figure 4S. The GC chromatogram and coresponding MS spectra of standard succinic acid.

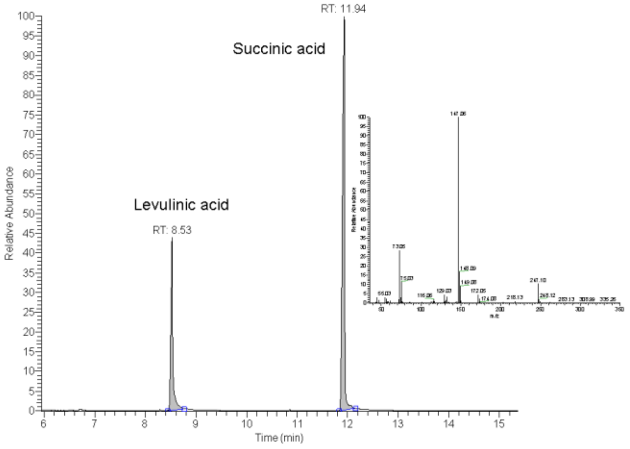

Figure 5S. The GC chromatogram and coresponding MS spectra of the reaction product.

Notes and references

1 T. Taguchi, J. Harada, A. Kiku, K. Tohji and K. Shinoda, *J. Synchrotron Rad.*, 2001, **8**, 363.

2 T. Taguchi, J. Harada, K. Tohji and K. Shinoda, *Adv. X-ray Anal.*, 2002, **45**, 397.

3 T. Taguchi, T. Ozawa and H. Yashiro, *Physica Scripta*, 2005, **T115**, 205.

4 J.J. Rehr, J. Mustre de Leon, S.I. Zabinsky and R.C. Albers, *J. Am. Chem. Soc.,* 1991, **113**, 5135.

5 H. Hillebrecht, T. Ludwig and G. Thiele, *Z. Anorg. Allg. Chem*., 2004, **630**, 2199.

6 J. Haines, J. M. Leger, O. Schulte and S. Hull, *Acta Crystallogr. B***,** 1997, **53**, 880.

7 V. Mazzieri, N. Fıgoli, F.-C. Pascual and P. L'Argentiere, *J. Catal.*, 1997, **172**, 336.