SUPLEMENTARY INFORMATION

A step forward in solvent knitting strategy: ruthenium and gold phosphine complexes polymerization results in effective heterogenized catalysts

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CONTENTS

1. General Considerations 2
2. $^{13}$C and $^{31}$P NMR spectra. 3-5
3. Infrared Spectroscopy spectra 5
4. Scanning electron microscopy (SEM) images 6-7
5. Transmission electron microscopy (TEM) images 8
6. Textural analysis 9
7. X-ray photoelectron spectroscopy (XPS) spectra 10
8. SEM-EDX analysis 11
9. Catalytic and recycling studies 12
10. Chromatograms 13

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1. General Considerations

The solids were characterized by the following techniques:
Elemental analyses were carried out on a Perkin-Elmer CHNS Analyzer 2400 and an Inductively Coupled Plasma Optical Emission Spectroscopy (ICP OES) Perkin Elmer 40 for metal determination.

FTIR spectra were recorded between 4000 and 400 cm$^{-1}$ with a Bruker IFS 66V/S, using the KBr pellets technique (about 1 mg of sample and 300 mg of dry KBr were used in the preparation of pellets).

High resolution $^{13}$C and $^{31}$P MAS NMR spectra of powdered samples were recorded at room temperature under magic angle spinning (MAS) on a Bruker AV-400-WB spectrometer equipped with an FT unit. The $^{13}$C cross-polarization (CP-MAS) spectra were acquired by using a contact time of 3.5 ms and recycle of 4 s. All spectra were recorded with a 4 mm ZrO probe and Kel-F plug and at sample spinning rate of 10 kHz.

The thermogravimetric and differential thermal analyses (TGA-DTA) were performed using Seiko TG/DTA 320U equipment in the temperature range between 25 and 850 ºC in air (100 mL min$^{-1}$ flow) atmosphere and a heating rate of 10 ºC min$^{-1}$.

SEM analysis. Particle morphology and size were studied by a scanning electron microscope (XL30, Philips) operating at 25 k. One droplet (15 – 20 µL) of the corresponding suspension was placed on a glass surface (14 mm diameter) and allowed to dry, after which, the sample was covered with gold or chromium using a sputter coating device (Polaran SC7640, Thermo VG Scientific). Transmission electron microscopy (TEM) micrographs were obtained with a JEOL JEM1010 microscope operating at 25 kV.

The textural properties were analyzed by N$_2$ adsorption/desorption experiments. Isotherms were measured with an AUTOSORB-1 from Quantachrome Instruments at 77K in the relative pressure range of 10-2 to 1. Before adsorption measurements, the samples were activated and outgassed at 473 K overnight. The specific total surface area was calculated using the Brunauer–Emmett–Teller (BET) method$^1$, selecting the adsorption data respective to the P/P$_0$ between 0.05 and 0.2 (adjusting the C value from 50 to 150)$^2$, considering a nitrogen molecule cross-section area value of 0.162 nm$^2$. The external surface area and micropore volume was obtained by means of the t-plot according to De Boer’s method$^4$. The total pore volume(Vp) of the solids was estimated from the amount of nitrogen adsorbed at a relative pressure of 0.99, assuming that the density of the nitrogen condensed in the pores is equal to that of liquid nitrogen at -196 ºC, i.e. 0.81 g/cm$^3$.$^3$ The pore size distributions of microporous and mesoporous regions have been performed by using, respectively, the Horvath–Kawazoe$^6$ and the Barrett–Joyner–Halenda (BJH) methods$^7$. Qualitative and quantitative TXRF analysis were performed with a benchtop S2 PicoFox TXRF spectrometer from Bruker Nano (Germany) equipped with a Mo X-ray source. Conditions: 50 kV, 600 µA, a multilayer monochromator with 80% of reflectivity at 17.5 keV (Mo Kα), a XFlash SDD detector with an effective area of 30 mm$^2$ and an energy resolution better than 150 eV for 5.9 keV (Mn Kα).
2. $^{13}$C and $^{31}$P NMR spectra.

Figure S1. Solid State $^{31}$P-NMR (left) of KPhos(Ru) and $^{31}$P-NMR of KPhos(Ru)-Bi (right).

Figure S2. Solid State $^{31}$P-NMR of KPhos(AuCl) (left) KPhos(AuNTf$_2$) (right).

Figure S3. Solid State $^{13}$C-NMR (left) and $^{31}$P-NMR (right) of KPhosBi.
Figure S4. Solid State $^{13}$C-NMR (left) and $^{31}$P-NMR (right) of KPhosBi(Au).
3. Infrared Spectroscopy spectra

Figure S5. FT-IR of Gold compounds

![Figure S5](image)

Figure S6. FT-IR of KPhos(Ru) after the 7th cycle.

![Figure S6](image)

\[\nu(\text{Ru-H}) = 2055 \text{ cm}^{-1}\]

\[\nu(\text{CO}) = 1982 \text{ cm}^{-1}\]
4. Scanning electron microscopy (SEM) images.

Figure S7. Different regions of KPhos(Ru)

Figure S8. KPhos(Ru)Bi

Figure S9. KPhos(AuNTf$_2$)
Figure S10. KPhos(AuCl)

Figure S11. Post-functionalized KPhosBi(Au).
5. Transmission electron microscopy (TEM) images.

Figure S12. TEM images
6. Textural properties analysis

Figure S13. Pore distribution by N\textsubscript{2}-DFT methods.

Figure S14. N\textsubscript{2} adsorption/desorption isotherms of: A) KPhos(AuNTf\textsubscript{2}), B) KPhos(AuCl)

Figure S15. N\textsubscript{2} adsorption/desorption isotherm of KPhosBi.
7. X-ray photoelectron spectroscopy (XPS) spectra

Figure S16. XPS Survey of polymers
8. SEM-EDX analysis

Figure S17. SEM-EDX analysis.
9. Catalytic studies

Figure S18. a) Kinetic profile of synthesis of imines catalyzed by KPhos(Ru). b) Hot filtration experiment.

Figure S19. Kinetic profile of the hydration of phenylacetylene catalyzed by KPhos(AuCl) in presence of different silver-containing co-catalysts.

Figure S20. Hot filtration experiment for KPhos(AuNTf₂).
Figure S21. XPS spectra of recovered KPhosRu in the region of Ru(3p), P(2p).
10. GC chromatograms. Representative examples

Figure S22. Table 2, entry 1

Figure S23. Table 3, entry 2
Figure S24. Table 3, entry 7.

\[
\text{Ph} = \text{KPhosBi(AuCl)/LiNTf}_2 \rightarrow \text{PhC} = \text{80%}
\]

Figure S25. Table 3, entry 6

\[
\text{Ph} = \text{KPhos(AuCl)/LiNTf}_2 \rightarrow \text{PhC} = \text{100%}
\]

* Biphenyl was added as an external reference.
Figure S26. Table 5, entry 5.

\[ \text{NH}_2 + \text{KPhos(AuCl)/AgNTf}_2 \rightarrow \text{N} \]

5 S. J. Gregg, K. S. W. Sing, Adsorption, Surface Area and Porosity, Academic Press, London, 1982