Mild synthesis of Mesoporous silica supported ruthenium nanoparticles as heterogeneous catalysts in oxidative Wittig coupling reactions

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Materials

Tetraethylorthosilicate (TEOS, 98%) was used as silica precursor. Cetyltrimethylammonium bromide ($C_{16}TAB$, 96%), pluronic (P123) and dodecylamine (DA, 98%) were used as structure-directing agents. Aqueous ammonia solution (NH_4OH, 30%), hydrochloric acid and APTES were also used in the synthetic protocol to obtain the final mesoporous materials. $RuCl_3.xH_2O$ was used as ruthenium source; methyl(triphenylphosphoranylidene) acetate, benzyl alcohol, 1,1'-binaphthyl and the other primary alcohols were purchased from Aldrich and used as received. Anhydrous toluene (spectroscopy grade) was used for the reactions.

Synthesis of mesoporous materials

Synthesis of MCM-41

Synthesis of MCM-41 type silica was performed following published method.[1] Briefly, in a typical procedure, 0.44 g of $C_{16}TAB$ were dissolved in a 35 mM NH_4OH solution (41.92 mL) at 40ºC. Then, 2.33 mL TEOS were added to the solution to achieve a molar composition of the synthesis gel of 1 SiO_2: 0.12 $C_{16}TAB$: 1.41 NH_4OH: 280 H_2O. The gel was then transferred to a 100 mL Teflon-lined stainless steel autoclave and heated at 80ºC under hydrothermal conditions for 24 h. After cooling at room temperature, the solid obtained was washed with water and ethanol, filtered off, and air-dried overnight. Finally, the surfactant was removed by calcination at 550ºC for 8 h (2ºC min^{-1}) under static air atmosphere.

Synthesis of SBA-15

SBA-15 type silica was prepared according to a procedure described elsewhere.[2] In a typical synthesis, 2 g of pluronic (P123) were dispersed in 15 mL of water and 60 mL of 2 M HCl solution. Then, 4.66 mL of TEOS were added to the solution with stirring. This gel mixture was continuously stirred at 40ºC for 24 h and finally precipitated in a Teflon-lined autoclave at 100ºC for 48 h. Then, the solid was filtered, washed with deionized water, dried in air at room temperature and finally calcined at 550ºC under static air conditions for 8 h (2 ºC min^{-1}) in order to remove the surfactant.

Synthesis of hexagonal silica (HMS)

Hexagonal mesoporous silica was synthesized according to the procedure reported by Zhang et al.[3] Thus, 2 mL of TEOS were added dropwise to a stirred mixture containing 10.5 mL of H_2O, 9 mL of absolute ethanol, and 1 g of dodecylamine. The resulting mixture was stirred at room temperature for 18 h. The obtained white solid was filtered, washed several times with water and ethanol, filtered off, and air-dried overnight. Finally, the surfactant was removed by calcination at 550ºC for 8 h (2ºC min^{-1}) under static air atmosphere.

Reusability

To check the reusability of the hybrid materials, they were washed with toluene, filtered out and heated in the oven up to 90 ºC overnight. GC analysis of the last aliquot corroborated the absence of reaction products.

Instrumentation

Nitrogen adsorption-desorption isotherms

The textural properties of the solids were determined from N_2 adsorption at 77 K in an AUTOSORB-6 apparatus. The samples were previously degassed for 4 h at 373 K at 5 $x10^{-5}$ bar. The adsorption branch was used to determine the pore size distribution using the Barret-Joyner-Helender (BJH) method. The surface area was determined using the multipoint BET method in the 0.05-0.30 relative pressure ranges. Mesopore volume was measured at the plateau of the adsorption branch of the nitrogen isotherm, P/Po = 0.8.[1] Gas adsorption at higher P/Po is mainly due to interparticle condensation.

X-ray diffraction studies

Small-angle powder X-ray diffraction (XRD) analysis was carried out with a Rigaku Ultima IV diffractometer using a CuKa radiation (k = 1.541836 Å), operating at 40 kV and 30 mA, at a scanning velocity of 0.03^{o} min^{-1} in the $0.7^{o} < 2\theta < 10^{o}$ range.

TEM analysis

The morphology of the mesoporous materials was characterized by transmission electron microscopy (TEM). TEM analyses were carried out on a JEM-2010 microscope (JEOL, 200 kV, 0.14 nm resolution). For this purpose, samples were prepared from a sonicated suspension of the material in ethanol on a carbon-coated copper grid. The digital analysis of the TEM micrographs was done using DigitalMicrographTM 3.6.1 by Gatan.

X-ray photoelectron spectroscopy (XPS)

The electronic state of ruthenium species was determined by XPS using a SPECS spectrometer with a MCD-9 detector using a monochromatic Al($K\alpha$ = 1486.6 eV) X-ray source. Spectra were recorded using an analyzer pass energy of 50 V, an X-ray power of 200 W, and under an operating pressure of 10^{-9} mbar. Spectra treatment was performed using the CASA software. Binding energies (BE) were referenced to the C1s peak at 283.3 eV.[4]

Inductively coupled plasma optical emission spectroscopy (ICP-AES)

Metal loading was determined by ICP-AES on a Perkin-Elmer Analyst 300 absorption apparatus and plasma ICP Perkin Elmer 40. 25 mg of every sample were digested in

1 mL HF during 12 h prior to analysis by ICP-AES.

References

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