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Selective hydrogenation of phenol to cyclohexanone by SiO_2-supported rhodium nanoparticles under mild conditions

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ABSTRACT

A silica-supported rhodium catalyst for the selective hydrogenation of phenol to cyclohexanone under mild conditions has been developed. As the Rh concentration on the catalyst increased from 0.5 to 15 wt%, the conversion (at phenol/Rh mole ratio 100/1) dropped whereas the initial selectivity to cyclohexanone increased. The direct hydrogenation to cyclohexanol occurred in parallel with partial hydrogenation to cyclohexanone. The negative correlation between selectivity and Rh dispersion suggests that direct hydrogenation occurs at low coordination sites whereas dissociation of phenol to phenoxy followed by hydrogenation to cyclohexanone takes place at higher coordinated terrace sites. DFT calculations revealed that the activation barrier for O–H bond cleavage is lower for phenol adsorbed on a Rh(1 1 1) flat surface than on small particles. By blocking the low coordination edge and step sites through grafting with (3-mercaptopropyl)trimethoxysilane, the cyclohexanone selectivity was improved from 82 to 93% at 100% conversion. The catalyst is active at room temperature and 1 atm H_2 pressure and can be easily activated by *in-situ* reduction.

1. Introduction

Cyclohexanone is an important intermediate in the synthesis of caprolactam for nylon-6 and adipic acid for nylon-6,6 with about 97% of the annual production being devoted for this purpose [1,2]. The balance is used as building block in the synthesis of pharmaceuticals, herbicides, insecticides and as a specialty solvent for resins and lacquers. Commercially, cyclohexanone is prepared by the catalytic oxidation of cyclohexane or via the hydrogenation of phenol in either a one- or two-step process [3]. In the two-step process, phenol is fully hydrogenated to cyclohexanol followed by an endothermic dehydrogenation step to cyclohexanone (Scheme 1). A one-step process where phenol is selectively hydrogenated to cyclohexanone is certainly preferred due to savings in costs and energy.

Phenol hydrogenation can be carried out in the gas or liquid phase [4–10]. Attaining high selectivity at elevated conversions under mild reaction conditions is a challenging catalytic problem as it is difficult to stop the reaction at cyclohexanone. The selectivity for cyclohexanone can be influenced by a number of parameters including the type of metal [5,9–11], its particle size [12–14], and the nature of the support [7,12,14–18]. Various metals such as palladium [6,7,12,14–18], Raney nickel [19], platinum [10,20], rhodium [21–23], as well as bimetallic Pd-Mg, Pd-Ce and Au-Pd [9,24,25] are active for this reaction. In general, palladium catalysts show good selectivity to cyclohexanone although the activity is not high. Therefore, high hydrogen pressure (>5 bar), temperature (>50 °C) and phenol/Pd molar ratios of 5–20 are typically used. Liu et al reported that the activity and cyclohexanone selectivity could be enhanced to >99.9% when Pd/C was used in combination with $AlCl_3$ [7]. The addition of the Lewis acid was suggested to activate the benzene ring for hydrogenation while inhibiting the formed cyclohexanone. However, $AlCl_3$ is hygroscopic and reacts with moisture to form corrosive HCl, posing difficulties in handling and reusability. Hence, recent attention has focused on finding suitable supports that can enhance the activity and selectivity of Pd under moderate temperatures and hydrogen pressure even when water is used as the solvent. Several materials have been reported including high surface area Al_2O_3 [15] and ceria [26], hydroxyapatite [27], TiN [28], hydrophilic carbon [29], metal organic frameworks MIL-101 [14] and ZIF-67 [29], alkali

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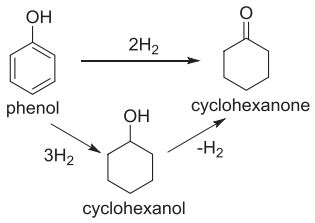

Scheme 1. Hydrogenation of phenol.

metal-promoted TiO_2 [30], poly(N-vinyl-2-pyrrolidone) [30] and polyaniline-functionalized carbon nanotubes [31]. Notably, aqueous phase systems using palladium supported on polymeric mesoporous graphitic carbon nitride (mpg-C_3N_4) [6,32] and TiO_2-C composites [18] gave >99% selectivity to cyclohexanone at 100% conversion. Palladium nanoparticles supported on a specially designed mesostructured silica (MMT-1) was found to exhibit high phenol conversion with 98% selectivity at room temperature and atmospheric H_2 pressure [33]. Besides gaseous hydrogen, potassium formate, sodium formate and formic acid have also been used for phenol hydrogenation [34–36]. However, these alternative hydrogen sources adsorb competitively at the catalyst surface and an optimized ratio must be worked out to avoid inhibition of the reaction.

Rhodium is known for its high activity for hydrogenation of the aromatic ring under very mild conditions [22,37,38]. However, there are only a few studies on its use for phenol hydrogenation due to poor selectivity to cyclohexanone. For example, the use of carbon nanofiber-supported rhodium in supercritical CO_2 resulted in 100% phenol conversion within 0.5 h (at phenol/Rh molar ratio of 436) but the selectivity to cyclohexanone was only 43% [21]. Kempe's group reported that small rhodium nanoclusters of $\sim$1.6 – 2.8 nm stabilized in a polymerderived silicon carbonitride (SiCN) matrix formed highly active catalysts for the selective hydrogenation of phenolic compounds [39]. At 25 °C and 6 bar H_2, 99% phenol conversion was obtained in comparison to 49% and 36% for Al_2O_3- and C-supported Rh, respectively. The selectivity to cyclohexanone for the three catalysts was only 73–78%. In comparison, a high selectivity of 92% at >95% conversion was found for Rh@S-MIL-101 catalyst operating at 50 °C and 5 bar H_2 [40]. The good performance was attributed to host-guest cooperation between the rhodium nanoparticles and sulfonated MIL-101 framework as well as the presence of Cr(III) Lewis acidic sites in the support. Kuklin et al reported 100% yield of cyclohexanone using polyacrylic acid-stabilized rhodium nanoparticles modified with 20-fold excess cyclodextrin at 80 °C and 10 to 40 atm H_2 using n-hexyltriethylammonium bromide as solvent [41].

Although these results showed that selective hydrogenation to cyclohexanone could be obtained over Rh catalysts at higher temperatures and pressures, we were interested in whether the same could be achieved under ambient conditions. This work investigates if metal loading, particle size, support, and selective inhibition of certain active sites can improve the selectivity to cyclohexanone without compromising on the mild reaction conditions. Selective inhibition of the metal sites was carried out by grafting of organic functional groups with amine and thiol moieties onto the catalyst.

2. Experimental

2.1. Catalyst preparation

2.1.1. Synthesis of metal oxide-supported Rh catalysts

Rhodium was supported on the following metal oxides – SiO_2 (Merck), La_2O_3, TiO_2 (Degussa), MgO (Merck) and ZrO_2 (synthesized). For a typical preparation of 5 wt% Rh/SiO_2, 127.9 mg (0.049 mmol) $RhCl_3{\cdot}3H_2O$, 0.95 g (15.8 mmol) SiO_2 and 20 ml deionized water were added into a 100 ml beaker. After stirring at room temperature for 3 h, the orange colored slurry was heated to almost dryness and placed overnight in an oven at 90 °C. The sample was calcined at 400 °C for 4 h in air. Samples with 0.5 to 15 wt Rh% were similarly prepared.

2.1.2. Grafted Rh catalysts

The 5 wt% Rh/SiO_2 sample was grafted with molecules of different chain length and chemical groups as shown in Table 1. The hydroxyl groups of the support react with the methoxysilane moiety to chemically bind the molecules to the surface. In a typical synthesis, 0.1 g of 5 wt% Rh/SiO_2 catalyst, (3-mercaptopropyl)trimethoxysilane (molar ratio to Rh = 2:1) and 20 ml toluene were placed in a two-necked 50 ml round bottom flask equipped with a septum port and a reflux condenser. After stirring at 110 °C for 24 h, the slurry was filtered, washed with acetone three times and dried at room temperature overnight. The samples are named as *molecule*-5 wt% Rh/SiO_2 where *molecule* represents *Amine-n, Glycidyl, Aniline, Thiol* and *Chloro*.

2.2. Catalyst characterization

The surface area and porosity of the catalysts were determined from N_2 adsorption/desorption isotherms (Micromeritics Tristar 3000). Prior to the measurement, the sample was pretreated under a nitrogen flow at 300 °C for 5 h. Powder X-ray diffraction was performed with a Bruker D8 Advance diffractometer equipped with Cu anode, variable slits and a LynxEye XE detector. The 2θ range from 20 to 80° was measured using a step size of 0.02° and a dwell time of 1 s. Transmission electron micrographs (TEM) were obtained using a JEOL 3010 operated at 200 kV. The sample was finely ground and suspended in 2-propanol. A drop of the suspension was placed onto a carbon-coated copper grid and dried at room temperature.

X-ray photoelectron spectroscopy (XPS) was performed using a VG-Scientific ESCALAB Mark 2 spectrometer equipped with a hemispherical electron analyzer and a Mg Kα anode (1253.6 eV) operating at 300 W (15 kV × 20 mA). Wide and detailed spectra were collected in constant analyzer energy mode with a step of 1 and 0.05 eV, respectively. The analyzed area was 3.0 mm in diameter with medium magnification for samples. The binding energy of the elements was referenced to the C 1 s signal of ubiquitous carbon at 285 eV. The spectra were evaluated using a nonlinear (Shirley) background subtraction.

The elemental composition of the samples was measured by inductively coupled plasma optical emission spectroscopy (ICP-OES) using an Optima 5300 DV ICP-OES system. To dissolve the sample, about 5 mg sample was placed in a Teflon liner with 1 ml of hydrofluoric acid (40%) and heated at 98 °C for an hour, followed by the addition of a mixture of concentrated HCl (37%) and HNO_3 (69%) (volume ratio: 20:1). The sample was then placed in a microwave oven and heated at 200 °C for 2 h. The obtained solution was diluted to 10 ml before analysis.

Infrared spectroscopy for CO adsorption was performed using a Perkin Elmer Spectrum Two spectrometer. The sample was pressed into a self-supporting wafer and mounted in an evacuable quartz IR cell with CaF_2 windows. After evacuation, the sample was reduced under H_2 flow at room temperature for 1 h. The cell was evacuated to 10^{-3} mbar and CO was introduced. The sample was equilibrated in 1 atm CO for 1 h. After pumping off the gas, FTIR measurements were performed at different time intervals using a resolution of 2 cm^{-1} and 32 scans. In order to determine the metal dispersion, pulsed CO chemisorption was carried out using a homemade temperature programmed desorption apparatus