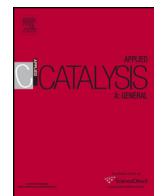




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Liquid phase oxidation of cyclohexane using bimetallic Au–Pd/MgO catalysts

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This paper is dedicated to Professor Jacques Védrine on the event of his 75th birthday.

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ABSTRACT

A detailed study of the selective oxidation of cyclohexane has been performed using bimetallic gold–palladium catalysts supported on magnesium oxide. Mono-metallic supported gold or palladium catalysts show limited activity for cyclohexane oxidation. However, a significantly enhanced catalytic performance is observed when supported gold–palladium alloy catalysts are used for this particular reaction. This synergy is observed for alloys spanning a wide range of gold-to-palladium molar ratios. Mechanistic studies reveal a promotion effect that occurs from alloying palladium with gold on the supported catalyst, which significantly improves the homo-cleavage of the O–O bond in cyclohexyl hydroperoxide, an important intermediate species in cyclohexane oxidation.

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1. Introduction

Aerobic oxidation of cyclohexane is of vital importance due to its use in nylon production [1]. In the present industrial production process, a facile aerobic alkane oxidation method is used, wherein materials such as cobalt naphthenate are utilised as an initiator to promote a radical autoxidation pathway [2,3]. Nevertheless, the autoxidation is not easily controlled, which means that the conversion must typically be kept below 5% in order to achieve > 80% selectivity to the desired alcohol and ketone products [4]. Unfortunately, the development of new efficient and green catalysts is significantly hindered due to kinetic inertness of both the alkane and O₂. Furthermore, a limited understanding of both the autoxidation and the catalytic oxidation routes exists in the literature, as these reactions can be difficult to study. This often causes confusion and misinterpretation concerning the oxidation reaction which is complicated by autoxidation [5]. In order to develop new catalysts

for this reaction that are capable of enhanced selectivity, more effective catalytic approaches and product analysis protocols are needed.

Gold catalysts are promising candidates for cyclohexane oxidation as they can activate molecular oxygen and enable oxidation under mild conditions [6–9]. However, a detailed study of the oxidation of cyclohexane by Hereijgers and Weckhuysen [10] pointed out inconsistencies in the literature concerning critical aspects of product analysis and mechanistic studies. They concluded that supported gold nanoparticles do not operate as a catalyst in the cyclohexane oxidation reaction, but rather as initiators which have a poor performance compared to the standard commercial cobalt naphthenate promoter [10]. On the other hand, we have recently shown that such behaviour can realistically be considered as falling somewhere in between these two extreme situations [11]. In fact, gold was found to be capable of accelerating the reaction, without the need for additional initiators, and so by definition could be considered to be a catalyst for the cyclohexane oxidation. However, the acceleration occurs by virtue of increasing the concentration of the intermediate species, which are chain carriers in the radical pathway of the reaction, and therefore promote catalytic

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autoxidation processes *via* a radical chain mechanism [11]. In addition, the enhancement in conversion caused by monometallic gold is limited when compared to autoxidation. This apparent dual nature of gold in cyclohexane oxidation prompted us to perform further studies in an attempt to achieve more efficient catalysts and gain deeper insights into both gold catalysis and catalytic aerobic oxidation when using gold-based alloy catalysts. In addition, a mechanistic study on promoted autoxidation is warranted due to the importance of this process in industrial nylon production, and could have a direct impact on other radical reactions, such as cobalt-mediated radical polymerisation [12].

Previous studies have shown that the promising properties of Au can be manipulated by the addition of Pd to form Au–Pd bimetallic alloys as green catalysts [13–17]. Herein we report that Au–Pd nanoparticles supported on MgO can improve both conversion and product selectivity in the cyclohexane oxidation reaction as compared to the commercial cobalt naphthenate promoter. Furthermore, the improvements afforded by the MgO-supported Au–Pd particles are effective over a wide range of nominal Au: Pd compositions. Investigation of the reaction mechanism by means of electron paramagnetic resonance (EPR) spin trapping experiments on the catalytic decomposition of cyclohexyl hydroperoxide (CHHP) are used to elucidate the origin of these beneficial effects.

2. Experimental

2.1. Chemicals

HAuCl₄, PdCl₂ and other chemicals were purchased from Aldrich and used without further purification unless otherwise specified.

2.2. Catalyst preparation

1 wt% Au–Pd/MgO catalysts were prepared by using a modified sol-immobilisation method as reported previously [18]. The desired amount of HAuCl₄ and PdCl₂ were added to 800 mL water. After stirring for 15 min, 1.3 mL PVA solution (0.01 g/mL) was added and the solution was stirred for an additional 15 min. Subsequently, 3.3 mL of a freshly prepared NaBH₄ solution (0.1 M) was added to generate the Au–Pd nanoalloy particles. After reduction for 45 min, the MgO support (1.98 g) was added to immobilise the nanoparticles. After filtration and washing, the solid obtained was dried (110 °C, 16 h) before use. The relative amount of gold and palladium salts used was varied in order to obtain a systematic series of supported catalysts with different molar ratios of Au-to-Pd, ranging from 20:1 to 1:20. Mono-metallic Au- or Pd-supported catalysts were also prepared for comparative purposes, using the same total metal loading (*i.e.* 1 wt%).

2.3. Catalyst testing

Catalytic oxidation of cyclohexane (Alfa Aesar, 8.5 g, HPLC grade) was carried out in a glass bench reactor using 6 mg of catalyst. The reaction mixture was magnetically stirred at 140 °C and 3 bar O₂ for 17 h. Samples of the reaction mixture were analysed by gas chromatography (Varian 3200) with a CP-Wax 42 column. Adipic acid was converted to its corresponding ester for quantification purposes, and chlorobenzene was added as an internal standard. Furthermore, CBrCl₃ (150 mg) was used as a carbon centred radical scavenger for studying the mechanisms in these oxidation reactions. CBrCl₃ was added into the reactor prior to the catalytic oxidation under identical reaction conditions. The product distribution as a function of reaction time was monitored by studying a systematic series of reaction batches subjected to different reaction times under the same conditions of temperature and oxygen

partial pressure. Re-usability testing was also performed in an identical glass reactor. Cyclohexane (8.5 g) and an additional amount of 1 wt% Au–Pd/MgO (6 mg) were added into the batch reaction and catalytic oxidation was carried out at 140 °C and 3 bar O₂ for 17 h. After reaction, the ‘used’ catalyst was washed with cyclohexane and dried. Afterwards, the catalytic activity of the used Au–Pd/MgO catalyst was tested under the same reaction conditions (6 mg Au–Pd/MgO, 8.5 g cyclohexane, 140 °C and 3 bar O₂ for 17 h). The obtained reaction mixture was analysed by gas chromatography [19–21]. Subsequent re-usability tests were carried out on the same material by following the same procedure.

2.4. EPR experiments

X-band continuous wave (CW) EPR spectra were recorded at room temperature in deoxygenated cyclohexane using a Bruker EMX spectrometer operating at 100 kHz field modulation in an ER4119HS cavity. The typical instrument acquisition parameters were: centre field 3487 G, sweep width 100 G, sweep time 55 s, time constant 10 ms, power 5 mW, and modulation amplitude of 1 G. Quantitative spectral analyses were carried out using the WinSim software [22,23]. The spin trapping experiments were performed using the following procedure: 5,5-dimethyl-1-pyrroline N-oxide, hereafter labelled DMPO (0.1 mL of 0.1 M solution in cyclohexane), was added to the substrate (0.1 mL of 2.5 molar % solution of CHHP in cyclohexane) in an EPR sample tube. The mixture was deoxygenated by bubbling N₂ for 1 min prior to recording the EPR spectrum in order to enhance the signal (by removing dissolved molecular oxygen which broadens the line-widths) [24]. For the reactions involving the Au/MgO, Pd/MgO and Au–Pd/MgO catalysts, de-oxygenation was carried out at room temperature, 5 min after the mixing of the catalyst with the reaction mixture. Cyclohexyl hydroperoxide was synthesised by a Grignard reagent–oxygen reaction [23,25]. Finally, a solution of 2.5 mol% cyclohexyl hydroperoxide in cyclohexane was obtained.

2.5. Electron microscopy characterisation

Samples of catalysts were prepared for TEM/STEM analysis by dry dispersing the catalyst powder onto a holey carbon TEM grid. Bright field (BF) imaging experiments were carried out on JEOL 2000FX TEM operating at 200 kV. High-angle annular dark field (HAADF) imaging experiments were carried out using a 200 kV JEOL 2200FS scanning transmission electron microscope equipped with a CEOS aberration corrector. This latter microscope was also equipped with a Thermo-Noran X-ray energy dispersive spectroscopy (XEDS) system for compositional analysis.

3. Results and discussion

3.1. Morphologies and catalytic performance of bimetallic catalysts

Our initial studies were centred on 1 wt% Au–Pd/MgO catalysts prepared by sol-immobilisation. A representative bright-field (BF) electron micrograph of the as-prepared 1 wt% Au–Pd/MgO material (with Au: Pd molar ratio of 1:1) is shown in Fig. 1a. The mean size of the Au–Pd nanoparticles was found to be *ca.* 5.0 nm (Fig. 1b). Aberration corrected STEM-HAADF imaging (Fig. 1c) and XEDS analysis of individual particles (Fig. 1d) in the bimetallic materials indicate that the supported particles are in fact homogenous Au–Pd random alloys. For comparison, the BF-TEM images of mono-metallic Au and Pd-catalysts are also shown in Fig. 1e and f, respectively. All three catalysts have rather similar mean diameters of 5.0 nm (Au–Pd), 5.3 nm (Au) and 4.2 nm (Pd), respectively, confirming that

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