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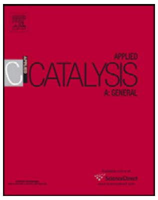

Nanosized gold-catalyzed selective oxidation of alkyl-substituted benzenes and *n*-alkanes

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ABSTRACT

We report the synthesis of nanoporous silica-supported gold nanoparticle catalysts and their selective and efficient catalytic properties toward oxidation reactions of various substituted alkylbenzenes and linear alkanes. The Au nanoparticles were synthesized by reducing Au(III) ions in situ within the nanopores of hemiaminal-functionalized mesoporous silica by using the supported hemiaminal groups as reducing agents. The resulting mesoporous silica-supported gold nanoparticles efficiently catalyzed the oxidation reactions of different alkyl-substituted benzenes and linear alkanes with *t*-butyl hydroperoxide (TBHP) as an oxidant. The catalytic reactions gave up to ~99% reactant conversion and up to ~100% selectivity toward ketone products in some cases. This high selectivity toward ketone products by the catalysts was unprecedented, especially considering the fact that only mild reaction conditions and no additives were employed during the reactions.

1. Introduction

Oxidative catalysis is an important route for the synthesis of many commodity chemicals as well as perfumes, drugs and pharmaceuticals [1]. In particular, alkane oxidation allows the synthesis of a number of value added chemicals from relatively more abundant starting materials. However, alkane oxidation still remains to be one of the most difficult reactions to perform [2] because it requires harsh reaction conditions and corrosive chemical reagents such as potassium permanganate, potassium dichromate or ammonium cerium nitrate [3,4]. Thus, the developmentof catalysts that can efficiently catalyze the oxidation of alkanes through activation of C—H bonds, that can operate under mild reaction conditions and that can generate selectively the desired products currently remain to be among major research efforts in catalysis.

Among the various substrates used in alkane oxidation reactions, linear and phenyl-substituted alkanes such as ethylbenzene stand out because their oxidation products are essential precursors for a broad range of pharmaceuticals and synthetic materials. For instance, the oxidation products of ethylebenzene such as acetophenone and 1-phenylethanol serve as precursors in the synthesis of optically active alcohols [5], benzalacetophenones (chalcones) [6], and hydrazones [7]. Despite its wide range of uses, current industrial practice of ethylbenzene oxidation unfortunately involves high temperature thermal autoxidation in the absence of catalyst. Furthermore, to date only very few catalysts have been explored for oxidation of ethylbenzene, many of which are found to be inefficient catalysts for the reaction [8–12]. For instance, cobalt(II) oxide-immobilized mesoporous silica (Co/SBA-15) was reported to catalyze the oxidation of ethylbenzene; however, the catalytic reaction was shown to work only at relatively high temperatures (120–150 °C) and give only moderate % conversion of ethylbenzene, with the highest reported value being 70.1% in 9 h at 150 °C. Furthermore, the catalyst was reported to form mixed uncontrolled oxidation products such as 1-phenylethyl hydroperoxide, benzoic acid, acetophenone and 1-phenylethanol [8].

The first demonstration on the use of Au (noble metal) nanoparticles as a heterogeneous catalyst for gas phase oxidation reactions was a fascinating research development in the field of oxidation catalysis about two decades ago [9]. Since then, many other papers have also appeared on the use of Au nanoparticles as catalysts for various oxidation reactions [10–24]. For instance, graphite-, SiO_2-, or TiO_2-supported Au nanoparticles syntesized by a method called deposition-precipitation were reported to catalyze the epoxidation reaction of alkenes [18]. The deposition–precipitation method involved a step-wise process of deposition of Au(III) ions onto the graphite, SiO_2, or TiO_2 support materials, followed by the reduction of the Au(III) ions into Au(0) [18]. More recently, a nanoporous Au catalyst prepared by etching away Ag from an AuAg alloy was shown to efficiently catalyze the oxidation of methanol to methyl

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