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Fixed-bed catalytic wet peroxide oxidation of phenol with titania and Au/titania catalysts in dark

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ABSTRACT

It was established that nanostructured TiO_2 with crystal size in range of 4.5–30 nm display stable operation in phenol CWPO in dark [PhOH = 200 ppmw] yielding 52–76% TOC conversion in a fixed-bed reactor at pH = 2.5, $T = 80\,^{\circ}C$ and LHSV = 3.8 h^{-1}. Deposition of ~3 wt.% of Au nanoparticles increases the catalytic activity of TiO_2 in CWPO of phenol defined as pseudo-first-order rate constant of substrate mineralization by a factor of 2.0–2.8 depending on Au crystal size. Small 3–4 nm Au nanoparticles aggregate at reaction conditions with complete deactivation of Au component. Larger 7–8 nm Au nanoparticles are stable against aggregation and deactivation. No leaching of Ti and Au was detected in runs with duration up to 300 h. The CWPO with both Au and TiO_2 catalysts proceeds according to radical mechanism mostly in the part of catalysts layer where H_2O_2 is completely decomposed. At proper operation conditions TiO_2 and Au/TiO_2 catalysts allow reaching >95% mineralization of phenol and stable operation.

1. Introduction

Among the technologies used for treatment of hazardous industrial wastewater the heterogeneous catalytic wet oxidation of dissolved organics with hydrogen peroxide (CWPO) falls in the category of advanced oxidation processes [1,2]. Phenol is known as one of the most important representatives of persistent organic pollutants because of its high toxicity (EC_{50} = 16 mg/l) and well known oxidation chemistry bringing to its complete mineralization, making it a widely used model compound for investigations of CWPO phenomenon [3]. Implementation of "catalytic filters"—tubular reactors filled with solid catalytic material, in principal allows stable long-term operation of wastewater purification processes with highly active and leach-proof catalysts [4]. At present time are known heterogeneous Fenton Fe-based catalysts that yield 70–90% TOC removal in phenol CWPO being tested in fixed-bed reactors at reasonable LHSV [4–6]. But Fe-leaching at acidic conditions required by Fe-Fenton chemistry causes catalysts deactivation after 30–100 h of run. Noble metals supported on titanium oxide are the only known catalytic materials that do not leach at conditions of catalytic wet oxidation of organics in contaminated wastewater [7,8]. But their performance was never tested in a continuous "catalytic filtration" mode in CWPO.

Among the non-leached noble metals the most suitable catalyst for CWPO is nanocrystalline Au. Its ability to decompose hydrogen peroxide yielding •OH radicals according to Haber–Weiss like mechanism (Scheme 1) is well established [9,10]. These radicals with high oxidation potential are the main intermediates in Fenton process chemistry oxidizing the organic molecules in water according to a sequence of chain reactions [11]. The high efficiency of Au nanoparticles supported on hydroxyapatite in CWPO of phenol measured in a batch reactor was first reported by Han and co-workers [12]. A series of followed publications [9,10,13–16] confirmed high efficiency of Au nanoparticles stabilized at various supports (hydroxyapatite, diamond, titanium oxide, activated carbon, Fe_2O_3) in CWPO of phenol in batch reactors. This information was recently reviewed in [17].

In the present work was studied the stability of nanocrystalline Au catalysts deposited on Ti-oxide support. Testing was performed in a fixed-bed reactor. This allows operation at continuous "catalytic filtration" mode without catalysts recycling. The long-time continuous testing is needed for evaluation of possible effects of Au nanoparticles aggregation and accumulation of deposits at the catalysts surface on the catalytic performance. Selection of nanocrystalline titania as supporting material was based on recent findings obtained by DFT calculations that revealed the possibility of selective decomposition of H_2O_2 at hydrated TiO_2 surface in dark yielding •OH radicals as energetically feasible [18]. After

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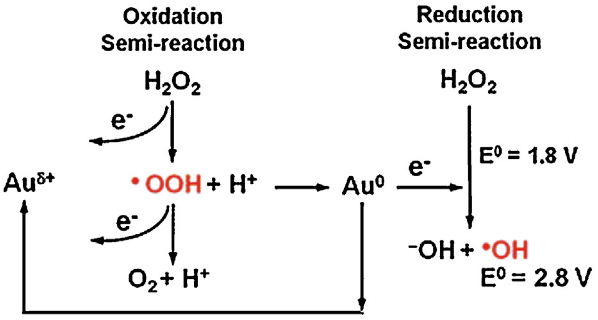


Scheme 1.

hydration of TiO_2 surface where water has undergone dissociative adsorption the adsorption of H_2O_2 and the transition state for its decomposition is mediated by hydrogen bonding with the surface OH-groups followed by O—O cleavage with formation of •OH radicals (Scheme 2). This means that titania support with high enough surface area may serve as a second source of •OH radicals in Au/TiO_2 catalyst significantly enhancing its efficiency. For easier treatment of phenol CWPO kinetics was established the lumped kinetic equation describing the dependence of phenol and TOC conversions on contact time in the fixed-bed reactor. Also experiments were conducted using •OH radicals scavenger for better understanding of the reactions mechanism.

2. Experimental

2.1. Catalysts preparation

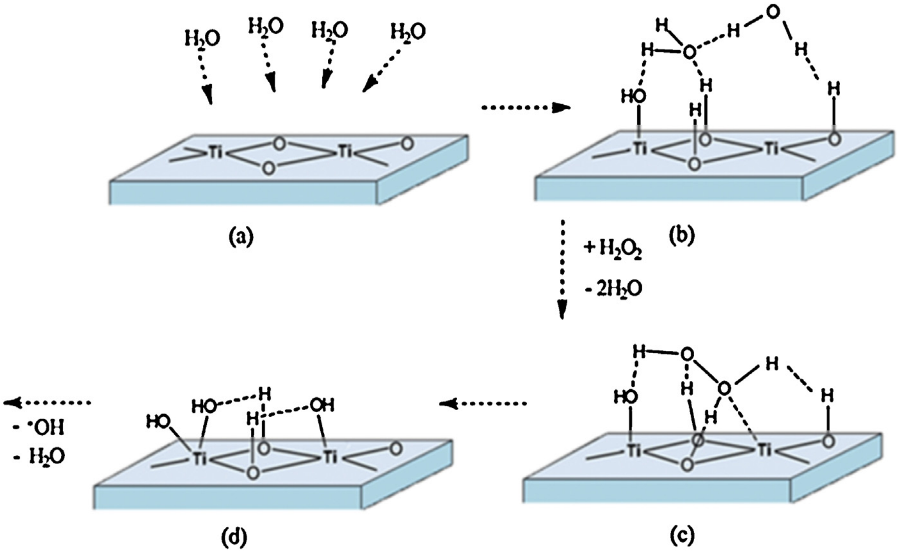
Titanium oxides TiO_2-I and TiO_2-II with anatase structure were purchased from Saint-Gobain NorPro Co. (materials XT25384 and XT25376, respectively). TiO_2-III oxide was prepared by sol–gel method assisted with soft templating according to [19] with molar ratios of Ethanol/HCl/F-127/TTIP/H_2O at 40:0.5:0.005:1:15. The powder after gel evaporation was dried in air at 110 °C for 24 h and twice extracted by acidic ethanol solution (1 ml 32% aqueous HCl in 100 ml EtOH per 1 g solid) for removal of organic template. The slurry was stirred for 12 h at room temperature, separated by filtration, washed with 50 cm^3 of pure ethanol and dried for 6 h at 110 °C. TiO_2-IV oxide was prepared by sol–gel method using urea template according to [20]. Titanium isopropoxide (28.42 g) was mixed with absolute ethanol (198.94 g) and stirred for 10 min at room temperature, then 0.33 cm^3 of 0.3 M HCl aqueous solution was dropped slowly into the above mixture to catalyze the sol–gel reaction for 3 h. After that, an appropriate amount (29.93 g) of urea–alcohol–water (1:5:1 weight ratio) solution was added to the hydrolyzed solution under vigorous stirring in order to obtain a template concentration of 30 wt.% in the final material (TiO_2). The gel was dried in a beaker at room temperature. The solid was extracted by distilled water for three periods of 24 h, in a system with continuous stirring to remove urea. Finally, it was calcined at 250 °C during 24 h.

Gold nanoparticles were deposited on titania powder (0.10–0.25 mm) by two methods–adsorption (Au/TiO_2-AD) and deposition–precipitation (Au/TiO_2-DP). In first case (AD) the pH value of gold aqueous solution (300 ml of 6.65 mM hydrogen tetrachloroaurate(III) dihydrate ($HAuCl_4 \cdot 2H_2O$, 99.9% Alfa Aesar) in three-neck boiling flask at room temperature) was adjusted to 10.0 by adding 1.0 M NaOH (Frutarom Ltd. 97%) under vigorous stirring. The solution was heated to 65 °C, then 5.0 g of TiO_2 powder was added and the mixture was stirred for 2 h with addition of aqueous 0.1 M NaOH solution to keep the pH value at the level of 9.0 during the course of gold adsorption. The as-received precipitate was separated by filtration, washed three times with 100 cm^3 of distilled water, and dried in air overnight at 100 °C, followed by calcination under O_2 flow of 1.8 l/(h g) for 1 h at 300 °C. The temperature was ramped at a rate of 5 °C/min.

In the case of DP 5.0 g TiO_2 was added at room temperature to 250 ml of gold aqueous solution containing 0.35 g hydrogen tetrachloroaurate(III) dihydrate ($HAuCl_4 \cdot 2H_2O$, 99.9% Alfa Aesar) and urea as precipitation agent at gold/urea molar ratio of 1/200. The mixture was then heated to 80 °C under vigorous stirring and kept for 2 h. During this period the pH value gradually increased from 3.0 to 8.0. After completing the DP process the as-received precipitate was separated by filtration, washed three times with 100 cm^3 distilled water, and dried in air overnight at 100 °C, followed by calcination in air for 4 h at 300 °C (2 °C/min). Deposition of gold had no significant effect on the texture of TiO_2 supports.

2.2. Catalysts characterization

Elemental analysis of the synthesized solid catalysts was done by energy dispersive X-ray spectroscopy (EDS) using JEOL JEM 5600 scanning electron microscope (SEM). The TEM micrographs were



Scheme 2.