



# Kinetics of the catalytic oxidation of morin on $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supported gold nanoparticles and determination of gold nanoparticles surface area and sizes by quantitative ligand adsorption



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## ABSTRACT

We report on the kinetic analysis of catalytic activity of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supported gold nanoparticles (AuNPs) on the rate of oxidation of morin by hydrogen peroxide as model reaction. Gold-based catalysts were revealed to be very active in the oxidation of morin under mild conditions, especially when Li<sub>2</sub>O is used as additive, and cationic imidazolium ionic liquids are used as AuNPs stabilizer. All kinetic data could be modeled in terms of the Langmuir–Hinshelwood model; that is both reactants are assumed to be adsorbed on the surface of the nanoparticles. The apparent reaction rate could therefore be related to the surface of the nanoparticles, to the kinetics constant, related to the rate determining steps, and to the adsorption constant of the reactants. The organothiol adsorption-based technique for the determination of specific surface area and particle sizes of AuNPs on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supports is also reported. A fair agreement was found between particle sizes obtained from ligand adsorption and TEM methods. Atomic absorption spectrometry (AAS), X-ray diffraction spectrometry (XRD), N<sub>2</sub>-physisorption (BET), transmission electron microscopy (TEM) and thermogravimetric analysis (TGA) are used for the characterization of the catalysts, while the oxidation reaction and the ligand adsorption was followed by ultraviolet-visible spectrometry (UV-vis).

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## 1. Introduction

One of the features of chemical catalysis is that it regularly undergoes rapid advances. Over the past decades, catalysis of supported transition-metal nanoparticles has been striking, and received more attention for numerous reactions [1–5]. The use of transition-metal nanoparticles in catalysis is crucial as they mimic metal surface activation and catalysis at the nanoscale and thereby bring selectivity and efficiency to heterogeneous catalysis, which benefits from easy removal of catalyst materials [6]. The effective catalytic properties of the transition-metal nanoparticles are mostly based on their inherent high surface area to volume ratio [7–11]. High surface area can provide better dispersion of the active sites and easy diffusion of the reactants and, thus, makes them suitable for catalytic activity [6,10,11].

Due to their unique electromagnetic and chemical properties, gold nanoparticles (AuNPs) have been recognized as active and extraordinary effective green catalysts for various oxidation

reactions [4,12–17]. Well dispersed AuNPs on gamma-alumina ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) support exhibit a high activity in various low-temperature oxidation reactions [4,18,19]. Gamma alumina is of catalytic interest and widely used as a support [3,4,19,20]. It has been conventionally described as a defect spinel (*Fd*-3*m*) with the idealized formula Al<sub>21+1/3□2+2/3</sub>O<sub>32</sub>, where □ denotes a vacancy [21]. Many studies have been reported on oxide-doped alumina supported AuNPs [4,19,22–25]. It was reported that lithium oxide (Li<sub>2</sub>O) has a promoting effect on the activity of the Au/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst in CO oxidation [4,25]. A detailed study by Gluhoi et al. [19,23,24] on the effect of the addition of alkali (earth) metals to Au/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst revealed that the main role of Li<sub>2</sub>O is to stabilize the AuNPs i.e. that of a structural promoter in the investigated reactions.

As mentioned previously, the activity of heterogeneous catalysts benefits strongly from a high surface area. Yet, small nanoparticles are only kinetically stable and will aggregate to thermodynamically more stable larger particles [26], with a concomitant decrease in catalytic activity. This agglomeration is based on the principles of Ostwald ripening [26,27] as a thermodynamically driven spontaneous process because larger particles are energetically favored over smaller ones. There are numerous methods of stabilizing metal nanoparticles including the use of ionic liquids [26], polymers [28],

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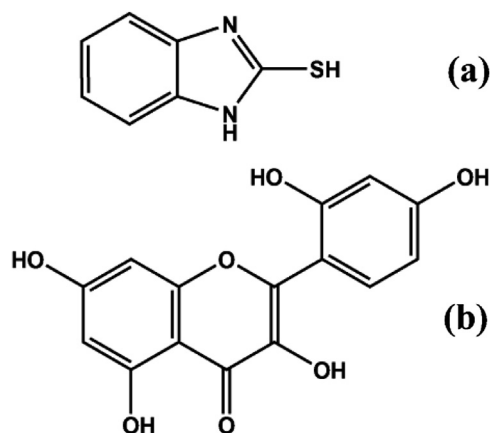


Fig. 1. Structures of (a) 2-mercaptobenzimidazole, and (b) morin dye.

low molecular weight [29] and macromolecular organic ligands [30]. Ionic liquids (ILs) have emerged as one of the most investigated classes of stabilizing agents for the synthesis and stabilization of transition-metal nanoparticles [11,26,31,32]. It may be regarded as a “nanosynthetic template” [26,33] that stabilize metal nanoparticles on the basis of their ionic nature [26,34]. The electrostatic and steric properties of ionic liquids can stabilize metal nanoparticles without the need of protective ligands [26,35–38].

Due to the nanoparticle surface roughness, size distributions, and morphological irregularity, the mechanisms involving the nanoparticle surfaces in catalytic reactions are more difficult to elucidate. As mentioned earlier, true surface area and particle size determination are key aspects of the activity of metal nanoparticle catalysts. Chemisorption methods using organothiols as probe ligands are in principle suitable for the specific surface area determination of the supported AuNPs [39–42]. It was reported that no adsorption is observed, except for CuO and AgO, when organothiols are exposed to oxidic supports [43]. Thus, it can be estimated that organothiols adsorb selectively only on AuNPs and not on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> or Li<sub>2</sub>O/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supports. Obviously, the Au-sulfur bond is sufficiently strong to allow for binding on all gold surface atoms, even at room temperature [40].

This study aims to determine specific surface area of supported AuNPs using 2-mercaptobenzimidazole, C<sub>7</sub>H<sub>6</sub>N<sub>2</sub>S (2-MBI) (Fig. 1(a)) as probe ligand, and to kinetically investigate the catalytic activities of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supported AuNPs on the oxidation of morin, C<sub>15</sub>H<sub>10</sub>O<sub>7</sub> under mild conditions using hydrogen peroxide, H<sub>2</sub>O<sub>2</sub> in aqueous solution as model reaction.

2-MBI was chosen as the probe ligand due to its excellent solubility and stability in water, relative strong UV–vis absorbance at  $\lambda$  299.7 nm, higher binding affinity with AuNPs, and small footprint for AuNPs [44]. A study by Ansar et al. showed that 2-MBI binds bidentately with AuNPs at neutral pH with a binding constant of  $4.44 \pm (1.29) \times 10^6$  M<sup>-1</sup>, and has a saturated packing density of  $0.574 \pm 0.006$  nmol/cm<sup>2</sup> [45]. On the basis of this packing density, the footprint of 2-MBI on AuNPs is 0.289 nm<sup>2</sup> per molecule. It has been reported by Elzey et al. that the ligand packing density of the organothiol 3-mercaptopropionic acid (MPA) on AuNPs is size independent for AuNPs of >5 nm in diameter [46]. This suggests that ligand adsorption can be a reliable method for quantification of the AuNPs surface areas and determination of the AuNPs sizes.

Advanced oxidation processes (AOPs) have emerged as a viable method to degrade dyes in aqueous media [47,48]. The basic concept of these methods is the decomposition of H<sub>2</sub>O<sub>2</sub> with the formation of free radical intermediates, especially the hydroxyl radical. This radical is capable of reacting with a variety of organic compounds leading to either partial or complete degradation. The

oxidation of morin with H<sub>2</sub>O<sub>2</sub> was chosen as a model reaction to kinetically investigate the catalytic activities of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supported AuNPs, prior to their use in other more complex oxidation reactions. Morin (Fig. 1(b)) belongs to a group of flavonoid plant dyes [49]. These compounds are present in tea, fruits and vegetables and can be used as model compounds for studying bleaching processes in laundry detergents [50]. Its two main oxidation products are 2,4-dihydroxybenzoic acid and 2,4,6-trihydroxybenzoic acid [51,52]. The reaction mechanism of the oxidation of morin by AuNPs catalyst is not determined yet.

The catalytic degradation of morin has been carried out in the presence of manganese oxide and dendrimer-encapsulated gold nanoparticles catalysts with H<sub>2</sub>O<sub>2</sub> as the oxidant [53,54]. It was demonstrated that morin dye can be decomposed using manganese oxide and dendrimer-encapsulated gold catalysts and concluded that the reaction occur on the catalyst surface. However, to the best of our knowledge, no reports are available for the use of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supported AuNPs as catalysts for the oxidation of morin by H<sub>2</sub>O<sub>2</sub>.

## 2. Experimental

### 2.1. Materials and reagents

All chemicals were at least analytical grade with high purity and were purchased from suppliers (Merck, Sigma-Aldrich and Pro-mark Chemicals). Organic dye, organothiol, peroxide, metal salts and buffer solutions were freshly prepared in 18 M $\Omega$  cm Millipore water just before the experiment.

### 2.2. Synthesis of catalysts

Lithium oxide on alumina was prepared via pore volume impregnation of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> from the corresponding nitrate [3,4]. Thus, an appropriate amount of LiNO<sub>3</sub> was dissolved in deionized water, and the resultant salt solution was poured onto a suitable amount of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The prepared mixed oxide had an intended Li/Al ratio of 1/15. After calcination at 350 °C for 4 h,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Li<sub>2</sub>O/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were used as supports for the gold particles. The AuNPs were prepared via homogeneous deposition precipitation using urea (CO(NH<sub>2</sub>)<sub>2</sub>) as precipitating agent [3,4], and afterward reduced using sodium borohydride (NaBH<sub>4</sub>). Thus, for catalysts prepared without stabilizing agents, an appropriate amount of HAuCl<sub>4</sub>·3H<sub>2</sub>O was directly added to a suspension of 25 mL of deionized water containing supports, under continuous stirring. However, for catalysts with ionic liquids (ILs), the stable AuNPs were prepared in 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF<sub>4</sub>], BF<sub>4</sub>) and 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF<sub>6</sub>], PF<sub>6</sub>); 0.06348 mmol of BF<sub>4</sub> and PF<sub>6</sub>, were added dropwise under vigorous stirring to 5 mL of aqueous solutions of HAuCl<sub>4</sub>·3H<sub>2</sub>O. After vigorous stirring, the mixture was then added to a suspension of de-ionized water containing supports. The intended M/Al ratio was 1/75 (M=Au). CO(NH<sub>2</sub>)<sub>2</sub> was added to the mixtures and heated for 2 h at 80 °C allowing CO(NH<sub>2</sub>)<sub>2</sub> to decompose. The mixtures were cooled, and an excess of NaBH<sub>4</sub> was added dropwise under vigorous stirring. The colors of the mixtures immediately turned from light yellow to red brown and dark red brown for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Li<sub>2</sub>O/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> mixtures, respectively indicating the formation of AuNPs. After vigorous stirring for 2 h, the slurries were filtered and washed thoroughly with deionized water until no Cl<sup>-</sup> was detected in the solutions. The chlorine concentration was followed by titration with AgNO<sub>3</sub>. The catalyst was dried overnight at 80 °C, and thoroughly ground to ensure that the particle size was in the order of micrometers.

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