

Au/PO₄³⁻-TiO₂ Catalysts for CO Oxidation: Impact of Synthesis Details

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Introduction

Heterogeneous gold catalysis has been extensively studied recently [1,2]. Au/TiO₂ is active for low-temperature CO oxidation, but the high-temperature sintering is the bottleneck that constrains its uses in emission control and organic combustions. The problem can be mitigated to some degree by using TiO₂/SiO₂ [3], Al₂O₃/TiO₂ [4] or nanocrystalline LaPO₄ [5] as support. Here, we attempted to overcome this problem using PO₄³⁻-TiO₂ support. The roles of chloride [6], nitrate [7], and sulfate [8] in gold catalysis were reported, but the effects of phosphate additive were virtually not studied.

Materials and Methods

Au/PO₄³⁻-TiO₂ catalysts were prepared via two routes, according to the sequence of loading phosphate and gold. Au was loaded via deposition-precipitation [9]. CO oxidation was carried out in a plug-flow microreactor: 50 mg catalyst, 1% CO balanced by air, flow rate 37 ml/min. The catalyst was pretreated in 5% O₂ at 200 or 500°C, and cooled down to the reaction temperature. XRD, ICP, and Raman were used to characterize catalysts and supports.

Results and Discussion

In route I, TiO₂ (P25) was treated by diluted H₃PO₄, dried and calcined, and gold loaded. Phosphate additive could not promote the low-temperature CO oxidation, and it only slightly improved the anti-thermal aging ability (Figure 1, left). Control experiments showed that if the phosphate supports were not washed before loading gold, the activity was low.

In route II, Au/TiO₂ was reduced in H₂, followed by post-treatment with diluted H₃PO₄ and washing. The doping of phosphate again slightly reduced the low-temperature activity, but it significantly improved the anti-thermal aging ability: the T₅₀ of 500°C-aged Au/TiO₂ was 126°C, consistent with literature [9], but the T₅₀ of Au/PO₄³⁻-TiO₂ reduced to 17°C (Figure 1, right). Control experiments indicated that the pre-reduction of Au/TiO₂ before soaking H₃PO₄ was beneficial, and the removing of excessive phosphate anions was again crucial.

Our results are surprising, because in literature, Pt/SO₄²⁻-ZrO₂ was commonly made in a way similar to route I: Zr(OH)₄ was soaked into diluted H₃PO₄, followed by drying, calcination, and Pt was loaded via impregnation [10]. However, we found that Au/PO₄³⁻-TiO₂ made via route II was better. Our results are surprising, also because it was not necessary to wash the sulfated supports in literature, but we found that the washing of phosphated supports was useful.

Nevertheless, our data are endorsed by several key observations: (1) although Pt/SO₄²⁻-ZrO₂ was more active than Pt/ZrO₂ for organic combustion, it was poorer in CO oxidation [11]; (2) trace SO₂ could be oxidized to sulfate on Au/TiO₂, thus blocking the active sites for CO

oxidation [12,13]; (3) extra immersing of Au/SO₄²⁻-TiO₂-ZrO₂ into 16% H₂SO₄ reduced its activity in CO oxidation [8]; (4) while trace NaNO₃ promoted Au/TiO₂ for CO oxidation, excessive NaNO₃ damaged it [7]. In acid-catalyzed reactions, high sulfur content is welcome, so washing was not applied [10]. However, in CO oxidation, the metal's oxidation function should be guaranteed, thus excessive sulfate or phosphate reduced the activity [8,11-13].

In addition, in route I, if the phosphated support was not washed, adsorbed phosphate anions were partially leached during the deposition-precipitation of gold, which perturbed the pH environment. This is different from preparation of Pt/SO₄²⁻-ZrO₂ via impregnation [10]. Lai et al. also found the leaching of sulfate from Au/SO₄²⁻-TiO₂-ZrO₂ during deposition-precipitation [8]. However, via route II, the deposition-precipitation process was not perturbed. The creation of surface defects may be responsible for the stabilization of gold nano particles.

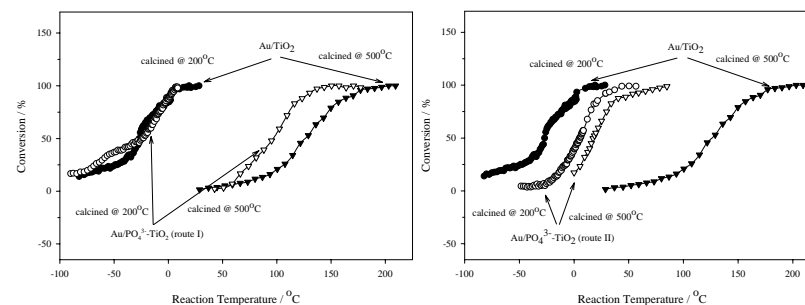


Figure 1. The conversion curves of Au/TiO₂ and Au/PO₄³⁻-TiO₂ catalysts for CO oxidation.

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