



TiO₂ Nanotubes for Hydroformylation of Vinyl Acetate from Syngas

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Abstract

TiO₂ nanotubes (TNTs) have emerged as promising supports for heterogeneous catalysts due to their unique physicochemical properties, including high surface area, ion-exchange capacity, and structural stability. This review focuses on the work of Chuai et al., who systematically explored TNTs as supports for Rh-based catalysts in the hydroformylation of functionalized olefins, particularly vinyl acetate, using syngas (CO/H₂). Their studies demonstrated that modifying TNTs with transition metal (Ru), alkali/alkaline earth cations (Li⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺, Sr²⁺), and rare-earth metal (La³⁺) significantly enhances catalytic activity, selectivity, and turnover frequency (TOF). Key findings include the synergistic effects of Rh-Ru systems, the promotional role of alkali cations in CO adsorption, and the exceptional performance of La-decorated Rh/TNTs (TOF = 5796 h⁻¹). Beyond hydroformylation, the potential applications of TNTs in other catalytic processes, such as Fischer-Tropsch synthesis, hydrogenation, and environmental catalysis, are discussed. This review highlights the versatility of TNTs as catalyst supports and provides insights into future research directions.

Keywords: Hydroformylation; TiO₂ Nanotubes; Vinyl Acetate; Syngas

Introduction

Hydroformylation, the addition of syngas (CO/H₂) to olefins to form aldehydes, is a cornerstone of industrial chemistry, with annual production exceeding 22 million tons [1]. Rhodium-based catalysts dominate this field due to their high activity and selectivity under mild conditions [2]. However, challenges persist, including the high cost of Rh, its deactivation by functionalized olefins (e.g., vinyl acetate), and the requirement for efficient heterogeneous catalytic systems.

TiO₂ nanotubes (TNTs), synthesized via hydrothermal methods, offer a compelling solution as catalyst supports. Their high surface area (up to 300 m²/g), nanotubular morphology, and tunable surface acidity make them ideal for stabilizing metal nanoparticles and facilitating reactant adsorption [3]. Chuai et al. explored the use of TNTs in hydroformylation, demonstrating their efficacy in enhancing Rh catalyst performance through strategic modifications.

This review synthesizes Chuai et al.'s contributions, covering:

1. **Rh/TNTs and bimetallic systems** (Rh-Ru) for vinyl acetate hydroformylation.
2. **Alkali/alkaline earth cation-modified TNTs** to improve CO adsorption and Lewis acid-base interactions.

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3. **Rare-earth metal promotion** (La^{3+}) for creating LaO_x –Rh active sites.

4. **Prospects for TNTs** in other catalytic applications.

Rh/TNTs and Bimetallic Systems for Vinyl Acetate Hydroformylation

Rh/TNTs: Baseline Performance

Chuai et al. prepared Rh/TNTs via impregnation-photoreduction, achieving Rh nanoparticles uniformly dispersed on TNTs [4]. In vinyl acetate hydroformylation, $\text{Rh}_{0.25}$ /TNTs showed 60% conversion and 60% aldehyde selectivity ($\text{TOF} = 3168 \text{ h}^{-1}$). The regioselectivity for 2-acetoxypromanal (branched aldehyde) was 100%, attributed to the stability of a five-membered ring intermediate [5].

Key limitations:

- Functional groups (e.g., acetate in vinyl acetate) coordinate with Rh, reducing activity.
- Low H_2 adsorption capacity limits aldehyde yield.

Rh-Ru/TNTs: Synergistic Effects

To mitigate chelation effects, Chuai et al. developed Rh-Ru/TNTs, where Ru acts as a Lewis acid to attract vinyl acetate's carboxyl group, freeing Rh for hydroformylation [4].

Key results:

- **Vinyl acetate:** Conversion increased from 39% (Rh/TNTs, 1 h) to 45% (Rh-Ru/TNTs, 1 h), but aldehyde selectivity dropped from 82% to 57% due to Ru's hydrogenation activity.
- **Cyclohexene:** Ru had no promotional effect, confirming its role is specific to functionalized olefins.

Mechanism: Ru enhances CO adsorption (FT-IR peaks at 2066 cm^{-1} and 1997 cm^{-1}) and weakens substrate-catalyst chelation [4].

Alkali/Alkaline Earth Cation-Modified TNTs

Design and Characterization

Chuai et al. decorated TNTs with Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , and Sr^{2+} via impregnation [6]. These cations:

- Increased CO adsorption (FT-IR peak intensity at 2068 cm^{-1}).
- Acted as Lewis acids to attract vinyl acetate (Lewis base).

Notable catalysts:

- **$\text{Rh}_{0.25}$ /Li-TNTs-P5:** 100% conversion, 67% selectivity ($\text{TOF} = 3581 \text{ h}^{-1}$).
- **$\text{Rh}_{0.25}$ /Mg-TNTs-P5:** 99% conversion, 76% selectivity ($\text{TOF} = 2826 \text{ h}^{-1}$) [6].

Promotion Mechanism

1. **Electronic effects:** Cations (e.g., Mg^{2+}) donate electrons to Rh, facilitating CO insertion (XPS shifts in Rh 3d) [6].
2. **Concentration effect:** Cations pre-concentrate substrates near active sites.

Trend: Smaller cations ($\text{Li}^+ > \text{Na}^+ > \text{K}^+$) showed higher polarizing power and better performance [6].

Rare-Earth Metal Promotion: La-Decorated Rh/TNTs

La's Unique Role

Chuai et al. introduced La^{3+} to Rh/TNTs, achieving:

- **$\text{Rh}_{0.25}$ -La/TNTs:** 89% conversion, 66% selectivity, $\text{TOF} = 5796 \text{ h}^{-1}$ [7].
- **H_2 -TPD:** Enhanced H_2 adsorption (peak at 307°C) due to LaO_x –Rh sites [7].

Mechanism

La forms highly dispersed La_2O_3 (XPS BE = 835.3 eV) that interacts with Rh^{2+} , creating LaO_x –Rh interfaces to boost H_2 activation and CO insertion [7].

Prospects for TNTs in Other Catalytic Applications

Fischer-Tropsch Synthesis (FTS)

TNTs' high surface area and metal-support interactions could stabilize Co or Fe nanoparticles. La-promoted TNTs may mimic Co-La/ SiO_2 systems, enhancing C_5^+ selectivity [8].

Hydrogenation Reactions

Ru/TNTs' hydrogenation activity (observed in hydroformylation) could be leveraged for nitroarene reduction or bio-oil upgrading.

Environmental Catalysis

TNTs' photocatalytic properties (e.g., for CO oxidation [9]) may be combined with metal sites for VOC degradation.

Conclusion

Chuai et al.'s work establishes TNTs as versatile supports for hydroformylation catalysts. Key advances include:

- **Bimetallic systems:** Rh-Ru for enhanced activity in the hydroformylation of vinyl acetate.
- **Cation promotion:** Alkali/alkaline earth metals optimize CO adsorption and Lewis acid-base interactions.
- **La decoration:** Creates LaO_x –Rh sites for higher TOFs.

Future research should explore:

1. **TNTs in tandem reactions** (e.g., hydroformylation-hydrogenation).

2. Multifunctional TNTs for coupled redox processes.

3. Scalable synthesis for industrial adoption.

TNTs' adaptability positions them as a platform for next-generation catalysts beyond hydroformylation.

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