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Selective Oxidation of Alkyl Aromatics using Molecular Oxygen by Supported Silver Nanoparticles with Visible Light

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PURPOSE OF THE ABSTRACT

Introduction: Selective oxidation of primary carbon-hydrogen bond in aromatics is a big challenge in organic synthesis, which was normally achieved in harsh reaction conditions. To date, only a very few examples are known for the direct formation of carbon-oxygen bond from primary carbon-hydrogen bond in aromatic compounds. Of these studies, activated oxygen donor is always in require, which will lead to the low activity and selectivity to alcohol and aldehyde. From the view of green chemistry, it would be a promising process to drive the reaction under mild reaction conditions through irradiation with visible light-the major component of abundant solar spectrum. In this study, we reported a visible light driven, one-pot process for direct oxidation of primary C-H bond to C-O bond in aromatic compounds, which using molecular oxygen as oxidant. In the mild condition, silver nanoparticles (NPs) supported on zirconium oxide (ZrO₂) was utilized as recycled photocatalyst for oxidation of primary C-H bond under visible light irradiation under mild condition.

Experimental: 3 wt% Ag NPs on ZrO₂ (Ag@ZrO₂) was prepared by the impregnation/reduction method. AgNO₃ (82.3 mg) and ZrO₂ nanopowder (2.0 g) were dissolved in 60 mL deionized water, to the abovementioned solution 20 mL lysine aqueous (0.01 M) solution was added. To this suspension, 10 mL of freshly prepared aqueous NaBH₄ (0.35 M) solution was added dropwise. The mixture was aged for 24 h. The precipitate was then separated by centrifugation, washed and dried at 60 °C in vacuum for 24 h. The collected powder was used directly as a catalyst.

Result and discussion: The Ag@ZrO₂ photocatalyst exhibits excellent activity for oxidation primary C-H bond using molecular oxygen as the oxidant under visible light irradiation at 90 oC. It is worth noting that the control reaction in the dark gives zero conversion even the temperatures rises to the boiling point of toluene at 110 oC. Thus, the Ag NPs mediated toluene oxidation can only be triggered by light irradiation.

Furthermore, other metal NPs (Pd, Ni, Au, Cu) were prepared by the same process as catalyst for this reaction, only Ag NPs showed the best photocatalytic activity. It is reported that Au, Ag, Cu NPs can strongly absorb visible light through the localized surface plasmon resonance (LSPR) effect. The LSPR effect is the collective oscillation of conduction electrons in the metal NPs induced by the electromagnetic field of incident light. Through this process, the light excited electrons of NPs can gain energy from light and activate reactant molecules adsorbed on the metal surface and trigger chemical reactions. This can explain how the light can convert this reaction in the presence of Ag NPs as catalyst.

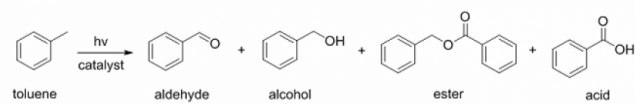
To further confirm the reaction pathway, the oxidation of toluene was conducted at different atmosphere (oxygen, air, hydrogen and argon). The reducing atmosphere (H₂ and Ar) cannot promote this reaction, which confirms that molecular oxygen is the oxidant for this reaction. Then to analysis how the oxygen was activated in this reaction, scavengers for different oxygen activation was added into the reaction system respectively. It is clear that with the addition of 1,4-Diazabicyclo [2,2,2]octane (DABCO), which can capture singlet oxygen, the reaction was ceased. It means molecular oxygen was activated as singlet oxygen in the light irradiation by Ag NPs.

In conclusion, a green photocatalytic process for the selective oxidation of primary C-H bond driven by light irradiation can be achieved using Ag NPs as catalyst. The photocatalysts are efficient and readily recyclable. This study is the first example to utilize molecular oxygen as oxidants and light energy to drive the organic synthesis in

mild condition.

FIGURES

Table 1. Activity test and catalyst screening for the oxidation of toluene.



Entry	Catalyst	Atmosphere	TON	Rate (mmol·g ⁻¹ ·h ⁻¹)	Select. (%)			
					aldehyde	alcohol	ester	acid
1	3%Ag@ZrO ₂	O ₂	67.6	7.82	58.8	39.3	0	1.9
2	3%Ag@ZrO ₂	Air	54.0	20.9	58	42	0	0
3	3%Ag@ZrO ₂	Argon	1.5	0.6	33	67	0	0
4	3%Ag@ZrO ₂	H ₂	0.4	0.2	93	7	0	0
5	3% Au@ZrO ₂	O ₂	37.8	4.3	89	11	0	0
6	3% Cu@ZrO ₂	O ₂	52.6	6.1	68	32	0	0
7	3% Pd@ZrO ₂	O ₂	39.1	4.5	58	11	31	0
8	3% Ni@ZrO ₂	O ₂	48.6	5.6	32	68	0	0
9	ZrO ₂	O ₂	8	3.1	91	9	0	0
10	5% Ag@ZrO ₂	O ₂	38.5	4.5	58	42	0	0
11	8% Ag@ZrO ₂	O ₂	28.4	3.3	52.4	47.6	0	0

Reaction conditions: 20 mg photocatalyst, 2 mL substrate as reactant and solvent. Selected gas was bubbled for 3 min and then reaction tube was sealed. The reaction mixture was stirred under visible light irradiation (0.7 W/cm²) at 90°C for 24 h.

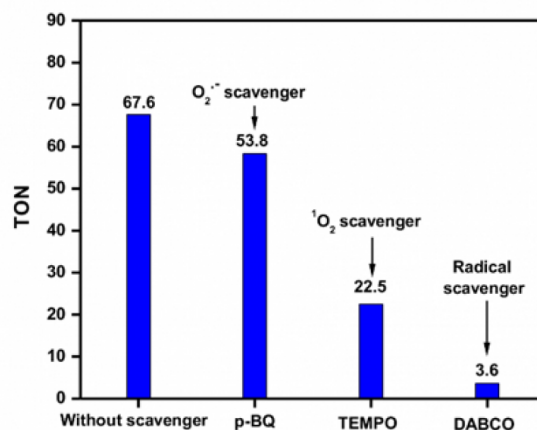


FIGURE 1

Figure 1

Activity test and catalyst screening for the oxidation of toluene.

FIGURE 2

Figure 2

The photocatalytic oxidation of toluene in the presence of specific scavengers.

KEYWORDS

photocatalysis | silve nanoparticle | LSPR | singlet oxygen

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