Assembling Ni^{2+} complexes and silver nanoparticles on γ-Al_2O_3 as visible light photocatalysts for hydrogenolysis of lignin model compounds

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Abstract: Visible light photocatalysis for organic reactions is a long sought after and rarely achieved aim in modern catalyst chemistry. New mechanisms for achieving visible light photocatalysis of chemical are limited. Here, we propose a new strategy that can utilize the localized surface plasmon resonance effect of plasmonic metal nanoparticles (NPs) to promote the catalytic performance of transition metal complexes under mild reaction conditions. By immobilizing Ni^{2+} complexes on γ-Al_2O_3 nanofibers and loading silver NPs on the fibers, a new photocatalyst was synthesized and utilized in cleaving of aryl ether C-O bonds in lignin model compounds at 80-90°C under visible-light irradiation.

Keywords: photocatalysis, visible light, lignin model compounds.

1. Introduction

Lignin is a main constituent (15-30% by weight, 40% by energy) of lignocellulosic biomass,[1] which refers to the most abundantly available raw material on the earth for the production of bio-fuels. Besides, a large volume of lignin waste is produced annually by the paper industry. However, the aryl ether bonds of lignin are relatively unreactive, depolymerisation of lignin into small molecules is challenging, so more than 98% of lignin is currently simply burned to provide heat for other industrial processes.

The major repeating units of lignin are orthomethoxy-substituted C_9 phenolic moieties, which are cross-linked by relatively unreactive C-O bonds, contributed by β-O-4 (45-62%), α-O-4 (3-12%), and 4-O-5 (4-9%) linkages.[2] The conversion of lignin into high-volume and low-molecular weight aromatic molecules has become the center of interest for scientists worldwide.

Nickel has been found as an effective element in catalyzing C-O bond cleavage of lignin models by hydrogenolysis,[3-6] but the operating temperature (>150 °C) is still high that over-reduction could easily happen and by-products like saturated cycloalkanols would be obtained inevitably.[4]

Herein, the photocatalytic performance of the Ag-Ni^{2+} system for the cleavage of benzyl phenyl ether and 2-phenyl phenyl ether that have α-O-4 and β-O-4 linkages, respectively, is investigated. The catalytic activity of Ni complexes can be enhanced by the localized surface plasmon resonance (LSPR) effect of nearby Ag nanoparticles under visible light irradiation, thus making the reactions happened at mild temperatures (80-90°C).

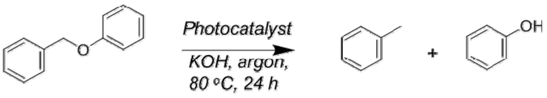
2. Experimental

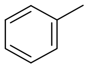
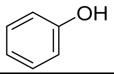
The photocatalytic reaction was conducted in a light reaction chamber. A 10 mL Pyrex glass tube was used as the reaction container. After adding the reactants and catalyst, the tube was filled with argon and sealed with a rubber septum cap. Then the tube was placed on a magnetic stirrer with stirring, and illuminated under a halogen lamp (Philips Industries: 500W, wavelength in the range 400-750 nm). An air conditioner was set to the light reaction chamber to control the reaction temperature. The reaction temperature in the dark was maintained the same as the reaction under irradiation. All the reactions in the dark were conducted using an oil bath placed on a magnetic stirrer. The tube was wrapped with aluminum foil to avoid exposure of the reaction to light.

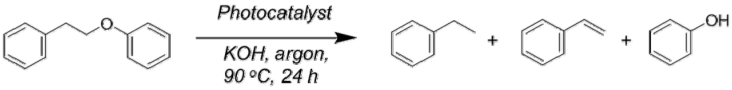
3. Results and discussion

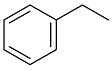
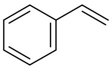
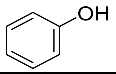
As shown in the Table below, 4.3Ag@Al_2O_3-silane-NH_2-Ni^{2+} catalyst exhibited excellent conversions (96%) under visible light irradiation while no reaction was observed in the dark at 80°C (Entry 1). The catalytic activities of the sample with Ni^{2+} complexes but no Ag NPs (Entry 3), the sample with Ag NPs but no Ni^{2+} ions (Entry 2) are very low (conversion of 5%) It should be noted that the product selectivity of phenol is around 50%, indicating a homolytic route of the α-O-4 model compound cleavage in the system. Similar situation was observed for the cleavage of β-O-4 compound under visible light irradiation at 90°C (Entries 4-6). It reveals the significant synergistic effect of the immobilized Ni (II) complexes and Ag NPs, which results in the superior photocatalytic activities of the composite photocatalyst to the photocatalysts without Ni^{2+} or Ag NPs.

Table 1. Catalytic performances of the photocatalysts for C-O bond cleavage of lignin model compounds



Entry	Catalysts	Irradiation	Conversion (%)	Product Selectivity (%) 	
1	$4.3Ag@Al_2O_3$-silane-NH_2-Ni^{2+}	Light	96	49	51
		Dark	0	/	/
2	$4.3Ag@Al_2O_3$-silane-NH_2	Light	5	39	61
		Dark	0	/	/
3	Al_2O_3-silane-NH_2-Ni^{2+}	Light	5	46	54
		Dark	0	/	/



Entry	Catalysts	Irradiation	Conversion (%)	Product Selectivity (%) 		
4*	$4.3Ag@Al_2O_3$-silane-NH_2-Ni^{2+}	Light	>99	56	/	44
		Dark	7	52	/	48
5*	$4.3Ag@Al_2O_3$-silane-NH_2	Light	48	2	48	50
		Dark	0	/	/	/
6*	Al_2O_3-silane-NH_2-Ni^{2+}	Light	11	0	47	53
		Dark	0	/	/	/

Reaction conditions: α-O-4 model (0.05 mmol), KOH (0.15 mmol), 2 mL of IPA solvent, mixed with 20 mg of catalysts in argon atmosphere. Light source was a halogen light of 0.96 W cm^{-2}, and the reaction was conducted at 80°C for 24 h. *β-O-4 model (0.05 mmol), halogen light intensity: 1.11 W cm^{-2}, at 90°C.

4. Conclusions

The Ag-Ni^{2+} catalytic system could be applied to cleavage of aromatic ether C-O bonds of model α-O-4 and β-O-4 lignin compounds under visible light irradiation at 80-90°C. The photocatalytic system showed an obvious higher catalytic performance compared with monometallic catalysts (supported Ag NPs and immobilized Ni^{2+} complexes). The synergistic effect between the supported plasmonic metal NPs and the immobilized Ni^{2+} complexes was studied. We propose that the aromatic ring in the reactant molecules could serve as a "molecular bridge" for the transfer of the hot electrons from the Ag NPs to Ni^{2+} complexes yielding Ni^0 species that can activate the hydrogenolysis of the reactants, because the reduction potential of Ni^{2+} to Ni (0) is more negative than that of the two lignin model compounds. Our findings demonstrate a new photocatalystic system design that combines plasmonic metal NPs and transition metal complexes for chemical transformations driven by sunlight.

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