

## Photocatalytic Hydroxylation of Phenol with Fe-Al-silicate Photocatalyst: A Clean and Highly Selective Synthesis of Dihydroxybenzenes

TiO<sub>2</sub> photocatalytic reactions for organic synthesis have recently been the subject of many reports. The choice and reaction conditions of catalysts are very important in the phenol hydroxylation using H<sub>2</sub>O<sub>2</sub> as oxidant. In this study, a new type of photocatalyst based on silicate (Fe-Al-silicate) was prepared and characterized with a goal to effectively utilize in photocatalytic organic synthesis of dihydroxybenzenes from phenol. Fe-Al-silicate, which was readily obtained by ions adsorption process, can catalyze the phenol to catechol and hydroquinone in the presence of H<sub>2</sub>O<sub>2</sub> with the assistance of UV irradiation at the wavelength 365nm. From the FT-IR spectra (Fig.1), we preliminarily infer that the metal elements are incorporated into the silicate.

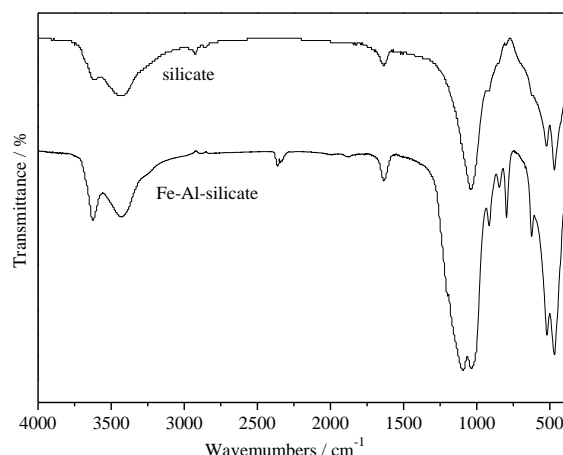


Fig. 1 FT-IR spectra of Fe-Al-silicate and silicate calcined at 500 °C for 5h.

But the main structure of the catalyst was not changed compared with the silicate. The band gap of Fe-Al-silicate is 3.1eV (Fig.2), so the absorption edge wavelength ( $\lambda_g$ ) of catalyst is 400nm matched with the lamp emission (365nm). It is beneficial for the photocatalytic reaction.

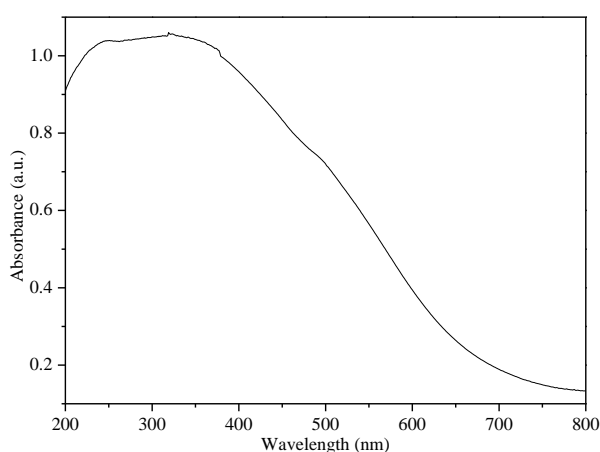


Fig.2 UV-vis diffuse reflectance spectrum of Fe-Al-silicate calcined at 500°C for 5h

This oxidation relies on the generation of the powerful oxidant •OH radicals as H<sub>2</sub>O<sub>2</sub> reacts with a conduction band electron and the redox process in presence of iron ions, then phenol can be directly converted into catechol and hydroquinone by reacting with •OH.

The catalyst showed high activity and selectivity on photocatalytic phenol hydroxylation, which was then pursued under various parameters in attempts to find the optimal reaction conditions. The effects of various parameters, such as types and amount of co-solvent, amount of catalyst, reaction time and amount of H<sub>2</sub>O<sub>2</sub>, on photocatalytic hydroxylation of phenol were studied to explore the better reaction conditions. The addition of appropriate amount acetonitrile can increase the yield. Longer reaction time directly increased the phenol conversion, during the first 4h of reaction, accumulation of catechol and hydroquinone was concomitant with the removal of phenol. The yield of catechol and hydroquinone can reach 39.3% and 22.3%, respectively. Meanwhile, the selectivity can reach 95% (Table 1).

**Table 1:** Hydroxylation of phenol under different condition <sup>a</sup>

Entry	Catalyst /g	UV light	Phenol conversion (%)	Yield (%)		Selectivity (%)
				Catechol	Hydroquinone	
1	No	Yes	31.7	3.4	no detected	10.7
2	0.1	No	8.0	no detected	no detected	-
3	0.1	Yes	64.9	39.3	22.3	95.0

<sup>a</sup> phenol, 0.5g; water, 15.0mL; acetonitrile, 4.0mL; H<sub>2</sub>O<sub>2</sub>, 1.0mL; reaction time, 4.0h

H<sub>2</sub>O<sub>2</sub> is so reactive and non-selective that oxidative degradation and mineralization are prevalent, the phenol conversion was increased by a high concentration of H<sub>2</sub>O<sub>2</sub>, but it decreased the selectivity. The conversion of phenol increased when continuously increasing the amount of catalyst, but the yield and selectivity decreased when the catalyst loading was increased to 0.15g. The active catalytic sites may be considered to have responsibility for these phenomena. Above all, the selectivity of photocatalytic hydroxylation decreased while by-products are increased at extended reaction times or large amounts of catalyst and H<sub>2</sub>O<sub>2</sub>. Acetonitrile was found to be an effective co-solvent to facilitate the photocatalytic hydroxylation process. Through an improvement of photocatalyst with a convenient and cost-effective preparation, environmentally-friendly industrial production of dihydroxybenzenes utilizing photocatalytic techniques could be realized.



*Photo: The Hiden Analytical HPR-20 QIC in the School of Chemical Engineering and Technology, Tianjin University, China*

**Hidden Reference: AP0172**  
**Hidden Product: HPR-20 QIC Real time Gas Analyser**



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**Hidden Product:**

HPR-20 QIC Real time gas analyser for multiple species gas and vapour analysis

**Follow the link to the product catalogue on our website for further information:**

<http://www.hidenanalytical.com/index.php/en/product-catalog/181-gas-analysers-qic-series/439-hpr-20-qic-atmospheric-gas-analysis-system->