A Sustainable Process for Phenol Production
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Overview

Phenol is an important industrial commodity used as a precursor to many useful compounds. It is being utilized in huge amounts in a wide range of industry sectors including pharmaceuticals, plastic-related-products production, paints & coatings, electrical equipment, foams and fuel additives. The current most prevalent method for phenol production is the three-step cumene hydroperoxide process that while established, has serious drawbacks related to safety, low selectivity in the formation of cumene hydroperoxide, low per pass yield and the formation of acetone as a byproduct. A new phenol production method developed at the Weizmann Institute of Science based on electrocatalytic oxidation of benzene, allows for simple, efficient, cost-effective and selective production of phenol. This new method can result in a drastic cost reduction that will further be emphasized in the future with the ongoing reduced need of the current process, byproduct, acetone. The method suggested here can also be applied in the future in other processes for conversion of arenes to the corresponding phenols.

The Need

The cumene hydroperoxide process, which is the most commonly used phenol production process nowadays, is both complicated, with low per pass cumene conversion and is producing acetone as a byproduct. This method also involves a highly explosive intermediate, making this unspecific process potentially hazardous. These drawbacks require a solution that will show higher selectivity, sustainability and efficiency. The electrochemical phenol production method from benzene described here is a simple process that does not involve as many intermediates as the cumene hydroperoxide process, does not require high temperatures and most importantly has a ~100% selectivity, eliminating the dependence on acetone sales to ensure high profit.

The Solution

An electrocatalytic transformation using formic acid to oxidize benzene and its halogenated derivatives to selectively yield aryl formates that are easily hydrolyzed by water yielding the corresponding phenols. The formylation reaction occurs on a Pt anode in the presence of [Co(III)W12O40]5 - and similar anions as a catalyst and Li formate as electrolyte via the formation of a formyloxyl radical as the reactive species, which was trapped by a BMPO spin trap and identified by EPR. Hydrogen was formed at the Pt cathode. The sum transformation is ArH + H2O Â® ArOH + H2. Non-optimized reaction conditions showed a Faradaic efficiency of 75-80 % and selective formation of the mono-oxidized phenol product in a 35 % yield. The decomposition of formic acid to CO2 and H2 is the side reaction.

Applications and Advantages

Advantages


- A simple, fast and cost-effective process:
- Direct and Highly selective (no acetone as a co-product)
- Low temperature process
- High safety

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Applications

Main process:

- Production of phenol from benzene

The technology can potentially be applied for additional chemical processes:

- Production of acetaldehyde from ethylene
- Production of malonic and/or pyruvic acids from acrylic acid
- Production of various alcohols from aliphatic and aromatic hydrocarbons

Development Status

The researchers have demonstrated the first example that explicitly indicates the in-situ formation of a formyloxy radical from formic acid in an oxidative electrochemical transformation and further its reactivity - in this case the C-H bond activation of arenes to yield a formate ester. The new electrochemical transformation described may provide new opportunities for the sustainable preparation of phenol and some of its derivatives on our way to diverge from the complicated cumene hydroperoxide process (with low per pass conversion of cumene and acetone as co-product). For now this was demonstrated for benzene and is expected to be established for other hydrocarbons as well. (Published in: Angew. Chem. Int. Ed. 2018, 57, No. 19, 5403-5407 [1]).

Market Opportunity

According to recent reports, the global phenol market is predicted to witness a robust CAGR of 6.8% during the period of 2018-2022 reaching a volume of 14 Million Tons by the end of the forecasted period, which will account for $17 bn in value. The global phenol market is driven in large part by the demand for bisphenol-A (which currently accounts for roughly half the revenue of the phenol market). Other markets of phenol-related products are expecting an increasing demand, including the Nylon - KA oil phenol segment and the phenol-formaldehyde resin market, which is expected to witness a robust CAGR of a little under 8% during the same period. Along with APAC, North America and Europe are poised to cross a billion dollars in terms of value in the phenol-formaldehyde resin segment of the phenol market at the end of 2022.

The acetone market is expected to witness a CAGR of approximately 3.6% during the period of 2018-2023. A significantly lower increase than that of the phenol market, suggesting that the currently prevalent cumene hydroperoxide phenol production process, resulting in acetone as a byproduct is expected to dramatically lower this process's profitability in the near future. Considering this expected gap, a new efficient and selective production method is required.

The new phenol production method developed at the Weizmann Institute of Science can have a huge impact on the increasing phenol markets, answering the need for a more simple, efficient, sustainable, and most importantly, selective production process of phenol from benzene.
Patent Status

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