



Simple and effective synthesis of methoxy-dimethylbenzene from electrochemical oxidation of *p*-xylene in methanol solvent catalyzed by $\text{SO}_4^{2-}/\text{ZrO}_2\text{-M}_x\text{O}_y$

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ARTICLE INFO

Article history:

Received 8 November 2007

Received in revised form 20 April 2008

Accepted 19 May 2008

Available online 23 May 2008

Keywords:

Electrochemical catalytic oxidation

P-Xylene

Methanol

Solid superacid

ABSTRACT

A series of composite solid superacid catalysts $\text{SO}_4^{2-}/\text{ZrO}_2\text{-M}_x\text{O}_y$ ($M = \text{Ti, Ni, Si}$) were prepared and investigated by means of Fourier transform infrared (FT-IR) and X-ray photoelectron spectroscopy (XPS). All catalysts exhibit good catalytic activity in the electrochemical reaction of *p*-xylene with methanol assisted with a pair of porous graphite plane electrodes and the selectivity of main products higher than 90% were observed. In particular, $\text{SO}_4^{2-}/\text{ZrO}_2\text{-SiO}_2$ catalyst exhibited excellent catalytic activity. According to the experimental results, a possible free radical reaction mechanism confirmed by XPS and ultraviolet–visible (UV–vis) spectra was proposed. It may be concluded that a simple and feasible electrochemical catalytic oxidation reaction at room temperature and standard atmosphere may be possible.

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1. Introduction

Sulphated zirconia ($\text{SO}_4^{2-}/\text{ZrO}_2$) is well known as a super solid acid, which has strong acidity. Many researchers have applied this type of catalyst in the various organic synthesis reactions [1–3]. Especially, $\text{SO}_4^{2-}/\text{ZrO}_2$ catalyst shows the high catalytic activity in the isomerization reaction of low molecular weight paraffins such as *n*-pentane and *n*-hexane. Metal modified sulphated zirconia has been shown to be highly active even at room temperature, such promotion in activity of catalyst has been confirmed by several other research groups [4,5].

Oxidation of organic compounds in the liquid phase was the basis of several industrial processes developed in the past 50 years [6]. As a clean and convenient method for the generation on a preparative scale of many reactive intermediates (radical ions, radicals, carbanions, carbocations, quinodimethanes), electrochemical synthesis in microreactors, avoiding toxic, expensive organic solvents, and often providing unique pathways to control the reactant and product distribution [7,8]. So electrochemical synthesis provides an attractive approach to organic synthesis and electrochemical technology, and becomes one of the highlights in the organic synthesis and industrial chemistry [9–11].

p-Xylene is an important chemical primary material and mostly used in synthesis of terephthalic acid and *p*-methylbenzaldehyde. Its derivatives can be obtained usually from chemical synthesis process. The relatively higher temperature (100–250 °C) and catalyst (acid and metal) were all necessary in this process [6,12–14]. Little attention has been paid on the electrochemical catalytic oxidation, acylations or esterification researches at room temperature and standard atmosphere.

Here, we report the synthesis of a series of solid superacid catalysts and a simply and effectively method of high selective oxidation reaction of *p*-xylene with methanol on a pair of porous graphite plate electrodes assisted with clean catalytic catalysts $\text{SO}_4^{2-}/\text{ZrO}_2\text{-M}_x\text{O}_y$ ($M = \text{Ti, Ni, Si}$) to methoxy-dimethylbenzene at room temperature and atmospheric pressure. The catalysts were detected by Fourier transform infrared (FT-IR) and X-ray photoelectron spectroscopy (XPS), the electrochemical catalytic process was inspected by ultraviolet–visible (UV–vis) spectrum and the products were analyzed by gas chromatography/mass spectrometry (GC/MS), the effect of the different medium was also discussed.

2. Experimental

2.1. Materials and general methods

All chemicals reagent in the experiment were analytical grade and used without any further purification.

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The effect of different catalysts on the reaction extent was inspected by UV–vis (UV–vis 7504, Shanghai Xinmao Co.). The component and its distribution of the products distillation were analyzed by GC/MS (QP2010, Japan). The catalyst was detected by FT-IR (Eouinx55, Germany) and XPS (PerkinElmer PHI-5400).

2.2. Preparation of $\text{SO}_4^{2-}/\text{ZrO}_2\text{-M}_x\text{O}_y$ catalysts

$\text{SO}_4^{2-}/\text{ZrO}_2\text{-M}_x\text{O}_y$ (M = Ti, Ni, Si) catalyst were prepared by two steps. In the first stage, $\text{Zr}(\text{OH})_4$ and $\text{M}(\text{OH})_{2y/x}$ were obtained by adding aqueous ammonia slowly into an aqueous solution of mixture of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and $\text{MCl}_{2y/x} \cdot z\text{H}_2\text{O}$, then the final pH of the solution was adjusted to 9. The precipitates were filtered, washed and then dried at 373 K for 12 h. Secondly, the prepared oxide powder was sulphated by percolating 200 ml 1.0 mol/l H_2SO_4 solution through it for 24 h, filtered by suction, dried at 383 K for 2 h, and finally calcined in air at 823 K for 3 h for obtaining $\text{SO}_4^{2-}/\text{ZrO}_2\text{-M}_x\text{O}_y$ (M = Ti, Ni, Si) [15].

2.3. Experimental set-up

Fig. 1 shows the schematic diagram of the electrochemical reaction. The experiments were conducted in a single cell of 0.25 l capacity at 30.0 V voltage and 2.0 A current intensity. The reaction cell was cooled by the cooling water in a trough to form the room temperature condition. The reaction cell was airproofed to prevent the volatilization of the methanol. The anode and cathode were positioned vertically and paralleled to each other with a constant inter gap of 1.0 cm. The anode and cathode were both the porous graphite plate (Supplied by Spring Chemical Industrial Company Limited, Shaanxi, China, 50 mm × 50 mm × 6 mm). 3.0 g catalyst of the solid superacid and 3.0 g assisted catalyst of KF were packed around the working electrode, forming a multi-phase electrochemical oxidation packed bed. The solution was constantly stirred at 300 rpm using a magnetic stirrer in order to maintain uniform concentration of the electrolyte solution. The electric power was supplied with regulated dc power supply, WYK302b, Xi'an, China. The current and voltage were adjustable in the range of 0–2.5 A and 0–35 V respectively.

2.4. Electrolysis procedures

The electrolysis was carried out in cells without compartments. The anode and cathode (graphite plate) were activated by methanol solution before using. The solvent-supporting electrolyte system was formed as follows: 3.0 g KF and 50 ml *p*-xylene were added in 50 ml anhydrous methanol with 3.0 g $\text{SO}_4^{2-}/\text{ZrO}_2\text{-M}_x\text{O}_y$ (M = Ti, Ni, Si, respectively). The resulting solutions were placed in the cells and electrolyzed at a current intensity of 2.0 A (with the time prolong, the current intensity decrease to 0.8 A gradually) with stirring at room temperature. The conversion of starting material was investigated by UV–vis spectrometry. The electronic spectra of the reaction system were detected during each electrolysis and the conversion of starting material was investigated by UV–vis spectrum every 30 min as follows: transferring 0.01 ml solution by transfer-pipette accurately and diluting it to 20 ml in a volumetric flask, then the electronic spectra were observed at the range of 200–400 nm using methanol as blank. The methanol used for the research of UV–vis spectrum was reclaimed for the next experiment without pollutions and waste.

2.5. Characterization of the products and the catalyst

After the reaction finished, the solution was distilled under the air pressure. The distillates were analyzed by GC/MS system using capillary column (0.25 cm × 30 m). The catalyst was washed with water for several times, dried in vacuo, then detected by XPS.

3. Results and discussion

3.1. Characterization of the catalysts

3.1.1. Infrared spectroscopy

The different catalyst samples, which were dried in vacuo at 373 K for 1 h first, were diluted in KBr. They showed the infrared absorption spectra, at room temperature, displayed in Fig. 2. In all case the strong absorption peak at 3432.47 cm^{-1} and mild peak at 1631 cm^{-1} corresponding to the flexion vibration band of H_2O molecule which was ascribed to the physisorbed water in the catalyst. The peaks between 800 and 1400 cm^{-1} assigned to the S=O bond or S–O bond were the characteristic peaks, the structure of the

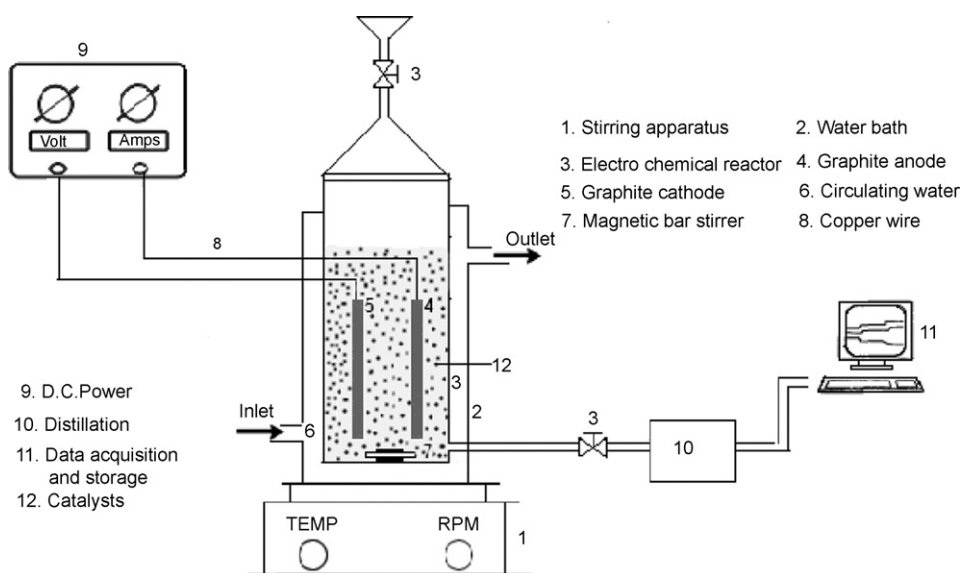


Fig. 1. Experimental set-up for the electrochemical catalytic oxidation.

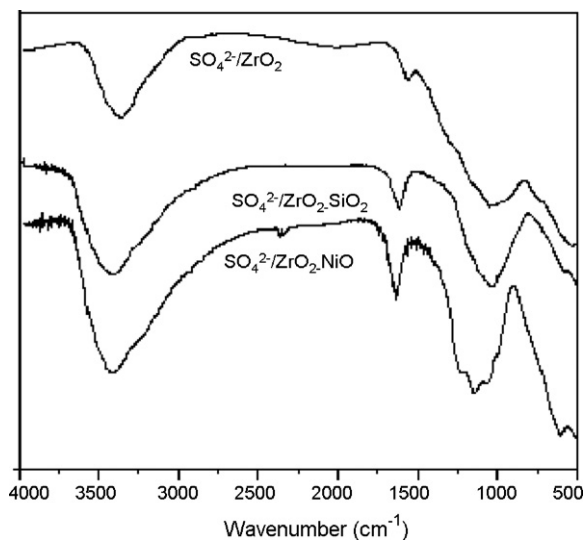


Fig. 2. Representative infrared spectrum of solid superacid.

solid catalysts remained stable even when many other components existed [14,16,17].

As Fig. 2 shows, the bonds at 980, 1097 and 1388 cm^{-1} can be attributed to the symmetric and asymmetric stretching vibration of S=O bond, respectively. It was noted that a chelate bidentate SO_4^{2-} coordinated to metal oxides such as Zr^{4+} because the highest stretching vibration of the SO_4^{2-} in the samples was above 1200 cm^{-1} . It should be pointed out that the bands of 1240–1310 and 1352–1390 cm^{-1} belonged to the inorganic chelate in which the S=O was mainly in the shape of ionic bond and organic sulphate structure in which it was covalent double bond. According to Fig. 2, the S=O of the solid catalysts was covalent double bond, so it could induce the acid and improve the catalysis and the $\text{SO}_4^{2-}/\text{ZrO}_2$ solid superacid have been formed.

3.1.2. XPS

After the coupling reaction, the solid superacid catalyst was dried in vacuo and tested by XPS. The binding energy and its composition of the catalyst were shown in Fig. 3. XPS Zr 3d3/2 peak of $\text{SO}_4^{2-}/\text{ZrO}_2\text{-SiO}_2$ solid superacid catalyst after the reaction was shown in Fig. 4. Because of the adsorbability of the catalyst, XPS signals of C, O and F have been detected, which can help us to analyze

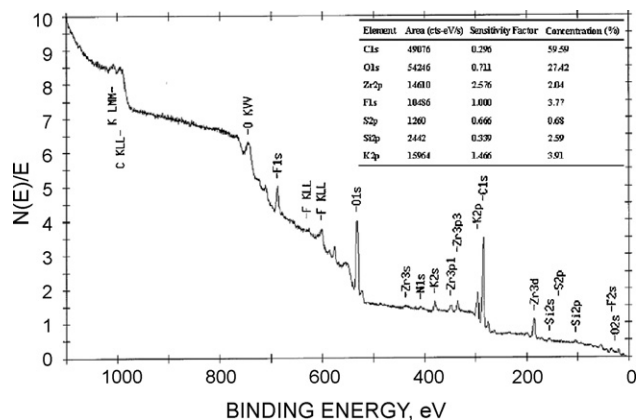


Fig. 3. XPS of $\text{SO}_4^{2-}/\text{ZrO}_2\text{-SiO}_2$ catalyst after the reaction.

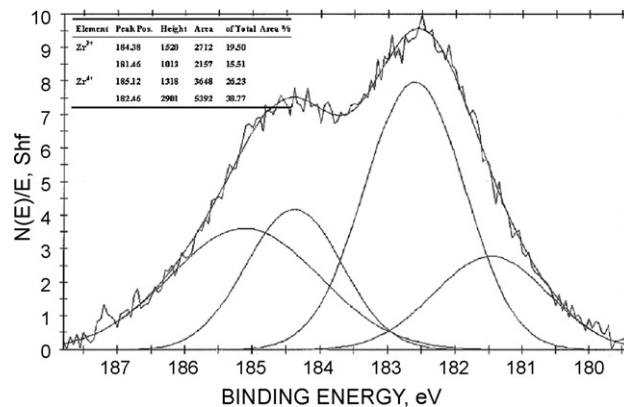


Fig. 4. Zr 3d3/2 binding energy of $\text{SO}_4^{2-}/\text{ZrO}_2\text{-SiO}_2$ catalyst after the reaction.

the mechanism of reaction. A new modality (C–O) was produced after the reaction, implying the formation of the methoxy group (Fig. 5).

The XPS Zr 3d3/2 peak has been deconvoluted to two different valent components (Zr^{4+} and Zr^{2+}) and the ratio of two atoms is 65.00:35.01 (molar ratio), inferred that the zirconium was the mixture of Zr^{4+} and Zr^{2+} in the catalyst after the reaction. Compared to that Zr^{4+} occupied 100% of the total zirconium element before reaction, it illuminated that Zr^{4+} was reduced to Zr^{2+} during this process.

XPS of the other solid superacid catalysts were also studied. The results indicated that the metal ion in the catalyst was involved with the coupling reaction.

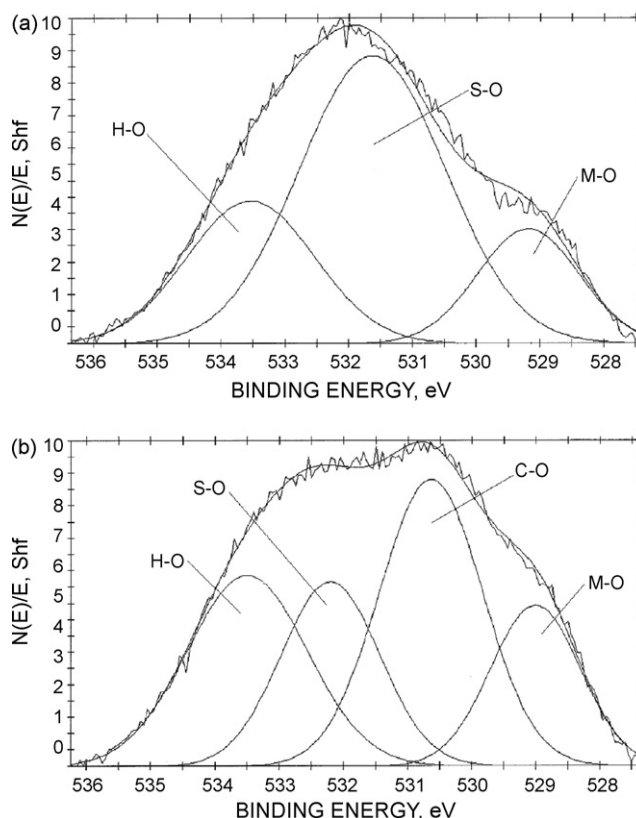


Fig. 5. O 2p binding energy of $\text{SO}_4^{2-}/\text{ZrO}_2\text{-SiO}_2$ (a) before and (b) after the reaction.

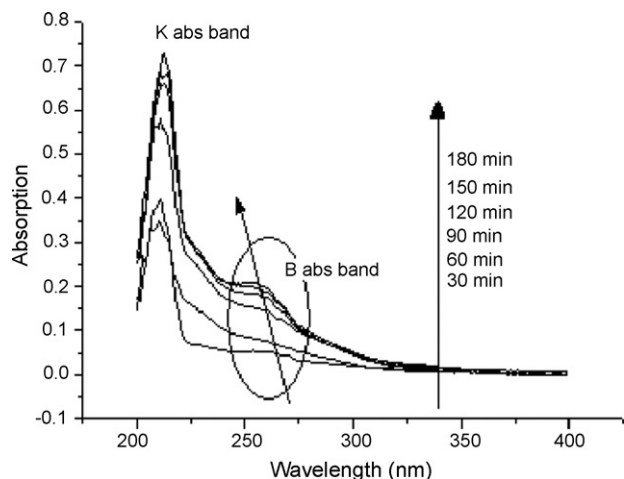


Fig. 6. The effect of time on the coupling reaction with $\text{SO}_4^{2-}/\text{ZrO}_2\text{-TiO}_2$ as the catalyst.

3.2. Liquid products

3.2.1. UV spectroscopy analysis

Fig. 6 shows the effect of time on the coupling reaction detected by UV–vis adsorption spectroscopy in the presence of the solid superacid catalyst. With the time prolong, the K adsorption band of the benzene ring shifted but changed unconspicuously, and the B adsorption band of the benzene ring hypsochromic shifted from 267 to 255 nm (arrowhead area), owing to the interaction between the methyl of *p*-xylene and hydroxyl group enlarged the energy band of $\pi \rightarrow \pi^*$ contrast to that of the benzene ring while hydrogen atom in *p*-xylene was substituted by a methoxy group or a hydroxyl group, the conjugation between the methyl group in *p*-xylene and the benzene ring was weakened, the energy needed by $\pi \rightarrow \pi^*$ transition increased. The increased absorption band indicated that the reaction extent was proportioned directly to the reaction time and the content of the oxygenous aromatic products. The electronic spectra of the reaction system in the different mediums at the same reaction time (180 min) and the identical current intensity (0.8 A) were also investigated. It can be found that the peak height of B adsorption band was decreased as follows: $\text{SO}_4^{2-}/\text{ZrO}_2\text{-SiO}_2$ catalyst > $\text{SO}_4^{2-}/\text{ZrO}_2\text{-NiO}$ catalyst > $\text{SO}_4^{2-}/\text{ZrO}_2\text{-TiO}_2$ catalyst > $\text{SO}_4^{2-}/\text{ZrO}_2$ catalyst. This suggested that the electrochemical catalytic oxidation extent increased with the enhancement of catalytic activity of the different solid superacid catalysts.

3.2.2. GC/MS spectrum

The GC of the products was shown in Fig. 7 (the peak of the solvent was taken off). Alternatively, gas chromatography in conjunction with mass spectrometry (GC–MS) has been known for its superior separation of complex organic compounds, greater sensitivity, and shorter measuring time, hence is better suited for the detection and identification of volatile organic compounds [18]. Table 1 compares the product selectivity in different mediums at the same reaction time of 180 min and the identical current intensity of 0.8 A. It can be found that the highest yield and selectivity of methoxy-dimethylbenzene was obtained simultaneously when $\text{SO}_4^{2-}/\text{ZrO}_2\text{-SiO}_2$ was applied as the catalyst, indicated that methoxy-dimethylbenzene can be simply synthesized by electrochemical coupling of *p*-xylene under mild conditions, which may simplify the synthetic technology of aromatic ether and methanol utilizing in an economic way.

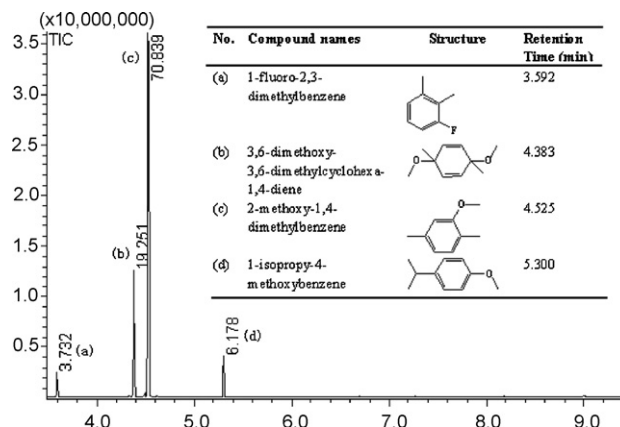


Fig. 7. The gas chromatography of the products ($\text{SO}_4^{2-}/\text{ZrO}_2\text{-SiO}_2$ as catalyst).

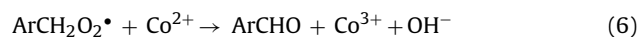
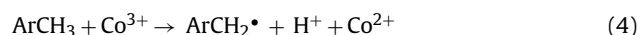
3.3. Possible mechanism

Oxidation conducted in the liquid phase provides good yield and selectivity due to the mild conditions afforded by the use of transition metals as catalysts. The mechanism of the oxidation was generally accepted as three kinds: (i) reaction with free radicals; (ii) reaction with metal ions; (iii) reaction with free radical cation.

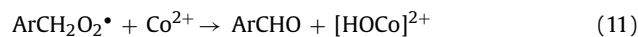
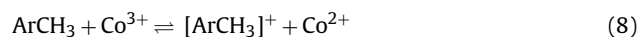
- (i) Generally, oxidation of hydrocarbons took place according to a radical chain process in which an initiator extracted a hydrogen atom from the hydrocarbon to form a radical that reacted with dioxygen [19–21]:



- (ii) Chemical processes involving activated reactions by metals between alkyl aromatics and molecular oxygen were of great industrial importance and extensive studies had been performed in this area. Oxidation proceeds via a free radical chain mechanism, which was initiated by a change in the oxidation state of the metal. The benzyl radical reacted rapidly with triplet dioxygen. In the presence of a catalyst the process was ended by acid formation [14,22]:



- (iii) As a general rule oxidation of alkyl aromatics by oxygen was realized in acetic acid in the presence of a catalytic redox couple such as $\text{Co}^{3+}/\text{Co}^{2+}$ [23]:



The Co^{III} regenerated by reaction (11) pursues the catalytic cycle of reactions (8)–(11).

The assumed mechanism of this electrochemical reaction was also proposed. A part of the hydroxyl anions were adsorbed near

Table 1
The electrolysis of *p*-xylene in methanol solvent by the different catalysts

Catalyst	Conversion of <i>p</i> -xylene	Methoxymethyl selectivity	Product selectivity (%)			
			(a)	(b)	(c)	(d)
SO ₄ ²⁻ /ZrO ₂	51.3	76.466	9.737	34.531	41.935	6.924
SO ₄ ²⁻ /ZrO ₂ -TiO ₂	55.6	85.049	6.169	34.266	50.783	8.781
SO ₄ ²⁻ /ZrO ₂ -NiO	61.6	89.999	5.114	26.910	63.089	4.887
SO ₄ ²⁻ /ZrO ₂ -SiO ₂	70.5	90.090	3.732	19.251	70.839	6.178

Reaction conditions: Current intensity (0.8 A); reaction temperature (298 K); reaction time (180 min). GC/MS spectrum, 70 eV, *M/e* (relative intensity):

1-Fluoro-2,3-dimethylbenzene (a): 124 M⁺ (65), 109 (100), 96 (5), 77 (10), 57 (5), 51 (10), 39 (6), 27 (4);

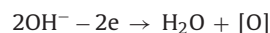
3,6-Dimethoxy-3,6-dimethylcyclohexa-1,4-diene (b): 168 M (2), 153 (100), 137 (85), 122 (80), 105 (18), 91 (47), 77 (41), 65 (18), 43 (35) 39 (28) 31 (10);

2-Methoxy-1,4-dimethylbenzene (c): 136 M (100), 121 (92), 105 (20), 91 (50), 77 (33), 65 (12), 51 (10), 27 (5);

1-Isopropyl-4-methoxybenzene (d): 150 M⁺ (38), 135 (100), 120 (5), 105 (18), 91 (10), 77 (8), 65 (6), 51 (4), 39 (4), 27 (2).

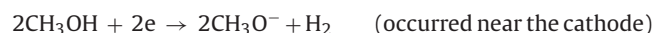
the anode, forming a thin layer between the solvent and the anode; the other part of the hydroxyl anions were adsorbed on the surface of the catalyst.

The anode reaction:



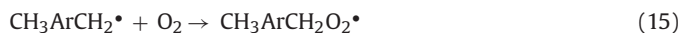
(occurred at the thin hydroxyl anions layer near the anode)

The cathode reaction:

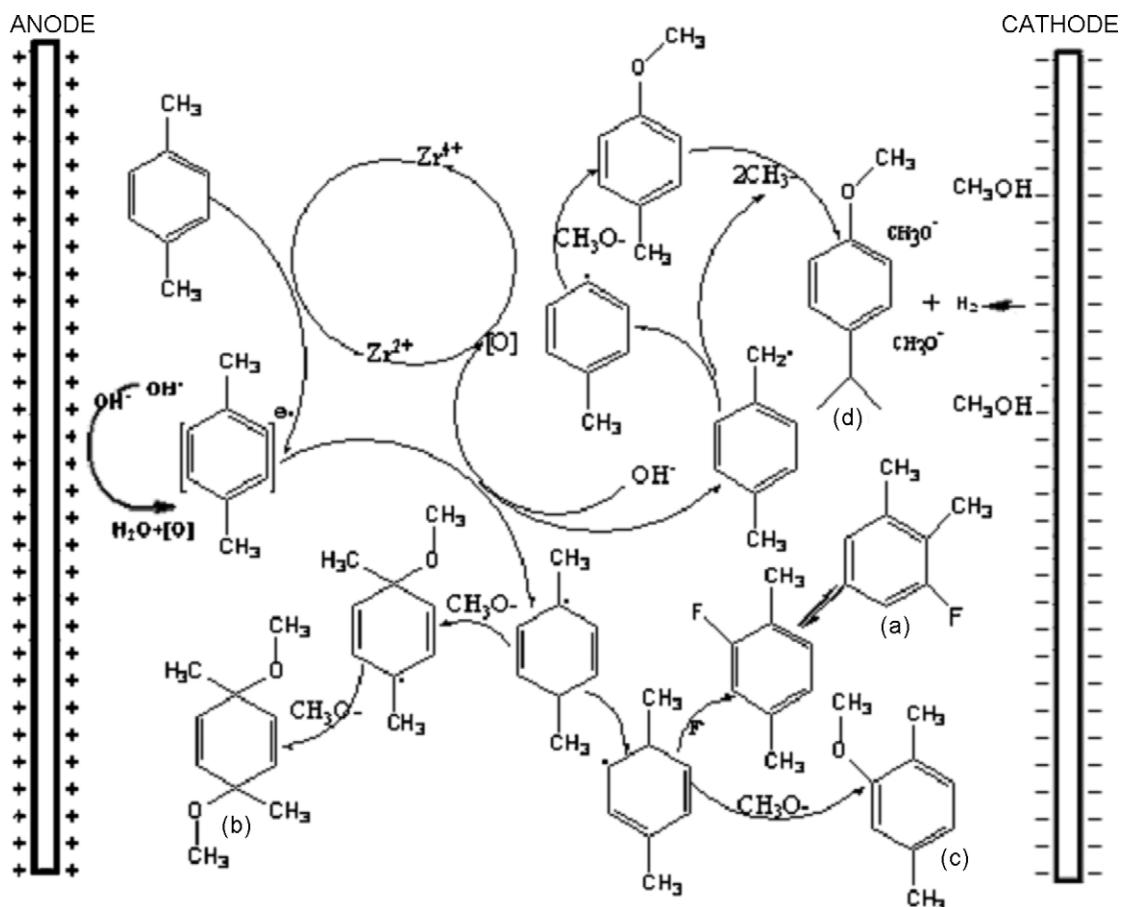


A *p*-xylene free radical cation formed in the oxidation of side-chain of toluene assisted by SO₄²⁻/ZrO₂-M_xO_y (M=Ti, Ni, Si) catalysts then produce a free radical. All products were obtained by the reaction of the free radical with toluene or methanol.

Oxidation proceeds via a free radical chain mechanism, which was initiated by a change in the oxidation state of the metal, which was confirmed by XPS spectra. The benzyl radical reacted rapidly with the triplet dioxygen. In the presence of a catalyst the process was ended by aromatic aldehyde formation.



The catalytic cycle of reactions (13)–(16): A *p*-xylene free radical cation formed in the oxidation of side-chain of *p*-xylene, then combined with a hydroxyl anion to produce a free radical. All products



Scheme 1. The possible mechanism for the main reactions.

were produced by the reaction of the free radical and the anion. It can be assumed that all the useful reactions were accomplished at the surface of the catalyst and the thin hydroxyl anions layer near the anode. The possible mechanism was proposed and shown in Scheme 1. The formation of *p*-xylene free radical cation was the rate-determining step in the coupling reaction. Hereby, the spectra of the different medium and reaction time were various.

4. Conclusion

A simple method for synthesis of methoxy-dimethylbenzene with high selectivity from the electrochemical oxidation of *p*-xylene with methanol at room temperature and atmospheric pressure, catalyzed by $\text{SO}_4^{2-}/\text{ZrO}_2\text{-M}_x\text{O}_y$ ($\text{M} = \text{Ti, Ni, Si}$) catalysts was studied. It can be concluded that $\text{SO}_4^{2-}/\text{ZrO}_2\text{-SiO}_2$ solid superacid show high catalytic activity in the electrochemical reaction of *p*-xylene.

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