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Short communication

One-step production of methoxymethyl benzene by selective oxidation of toluene in a electrochemical system assisted by $SO_4^{2-}/Fe_2O_3–MoO_3$

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ABSTRACT

Methoxymethyl benzene was synthesized through direct oxidation of toluene in methanol at room temperature and standard atmosphere using an electrochemical catalytic reactor assisted by $SO_4^{2-}/Fe_2O_3–MoO_3$ catalyst has been studied by UV–vis spectrum and gas chromatography/mass spectrometry (GC/MS). This new system showed a high selectivity to methoxymethyl benzene, minimizing its over-oxidation and other by-products production. $SO_4^{2-}/Fe_2O_3–MoO_3$ catalysts were prepared and characterized by Fourier transform infrared (FT-IR) and X-ray photoelectron spectroscopy (XPS). The effect of various dosage of MoO_3 in the catalyst was also investigated. The results showed that 5.0 g $SO_4^{2-}/Fe_2O_3–20\%$ MoO_3 as the catalyst, 3.0 g KF as the assisted catalyst, current intensity at 0.8 A for 120 min at room temperature (298 K), gave the better system performance in terms of produced methoxymethyl benzene with high selectivity (51.341%).

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1. Introduction

Electrochemical synthesis, an interdisciplinary science of organic chemistry and electrochemical technology, have received considerable attention in recent years, because of its potential applications in the synthesis of pharmaceutical drugs, amino acids, dyestuffs, pesticides, spicery and organic reagents [1,2]. In industrialized production about 100 organic compounds were synthesized by electrochemical synthesis methods because of its efficiency and lower environmental contamination.

Toluene is one of the most important aromatic hydrocarbons, its selective oxidation with air to methoxymethyl benzene, which is versatile intermediates in the chemical industry, has been an attractive field as well as an important chemical challenge [3]. However, no much attention has been paid on the electrochemical catalytic oxidation, acylations or esterification researches at room temperature and air pressure.

Solid acid catalysts have numerous applications in many areas of the chemical industry. It can be said that solid acids are the most important heterogeneous catalysts used today, considering in terms of both the total amounts used and the final economical impact. According to recent review of industrial acid–base catalysis of the 127 processes identified, over 115 are solid acid-catalyzed [4]. It clearly indicates the significance of these materials and the scope of their commercial exploitation. These are extremely useful in many large volume applications, especially in the petroleum industry for alkylation and isomerization reactions [5–8]. As useful acid catalysts in the field such as selective hydrocarbon isomerizations, acylations and esterification reactions due to their strong Lewis acidity, a large number of solid superacid (SO_4^{2-}/M_xO_y) researches have been reported [9–12].

Here, we report the preparation of molybdenum-modified SO_4^{2-}/Fe_2O_3 catalyst, and a novel synthesis method for 1-(methoxymethyl) benzene simply and effectively with high selectivity (51.341%) from electrochemical oxidation of toluene in methanol solvent catalyzed by $SO_4^{2-}/Fe_2O_3–xMoO_3$ ($x = 0\%$, 5%, 10%, 20%) catalysts at room temperature and atmospheric pressure may be possible. In addition, the results of the research showed the increasing of 1-(methoxymethyl) benzene yield with the dosage of MoO_3 in the catalyst adding, indicating the catalyst activity was affected by the molybdenum content increasing. The catalysts were detected by Fourier transform infrared (FT-IR) and X-ray photoelectron spectroscopy (XPS), the electrochemical catalytic process was inspected by UV–vis spectra and the products were analyzed by gas chromatography/mass spectrometry (GC/MS).

2. Experimental

2.1. Materials and general methods

All chemicals reagent used in the experiment were analytical grade and without any further purification. $Fe(OH)_3$ was provided by Tianjin Dengfeng Reagent Co., H_2SO_4 (Xi'An Reagent Co.) and

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MoO_3 (Shanghai Colloid Reagent Co.), China. CH_3OH, KF and $ArCH_3$ were obtained from Xi'An Reagent Co.

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 molybdenum-modified solid acid catalyst ($SO_4^{2-}/Fe_2O_3–MoO_3$)

Mixing 20 g $Fe(OH)_3$ and a certain amount of MoO_3 (0 g, 1 g, 2 g and 4 g, respectively) and sulphated this mixture with 200 ml 0.5 mol/l H_2SO_4 solution for 12 h, finally calcined at 823 K for 3 h to obtain $SO_4^{2-}/Fe_2O_3–xMoO_3$ (x = 0%, 5%, 10%, 20%, wt%) catalyst.

2.3. Electrolysis procedures

The electrolysis was carried out in 250 ml cells without compartments. The anode and cathode both were the porous graphite plate (supplied by Spring Chemical Industrial Company Limited, Shaanxi, China, 50 mm × 50 mm × 6 mm) and were positioned vertically and paralleled to each other with a constant intergap of 1.0 cm. The anode and cathode (graphite plate) were activated by methanol solution with metal anion before using. The solvent-supporting electrolyte system was formed as follows: 3.0 g KF and 50 ml toluene were added in 60 ml anhydrous methanol with 5.0 g $SO_4^{2-}/Fe_2O_3–xMoO_3$ (x = 0%, 5%, 10%, 20%). 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) at room temperature with stirring and detecting by UV–vis spectrometry. The electronic spectra of the reaction system were detected during electrolysis process 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 detected by UV–vis spectrometry at the range of 200–400 nm using methanol as blank. The current was interrupted in the moment of higher yield of the products. The methanol used for the research of UV–vis spectrum was reclaimed for the next experiment without pollutions and waste.

2.4. Characterization of the products and the catalyst

When the reaction finished, the solution was distilled under 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, and then analyzed by XPS.

3. Results and discussion

3.1. UV spectroscopy

Fig. 1 showed the effect of time on the coupling reaction catalyzed by $SO_4^{2-}/Fe_2O_3–5.0\%\ MoO_3$ catalyst detected by UV–vis adsorption spectrophotometer. It can be found that with the time prolong (0–120 min), the K absorption band (219 nm) of the benzene ring shifted but changed unconspicuously, the B adsorption band of the benzene ring hypsochromic shifted from 262 nm to 251 nm (arrowhead area) and the shoulder peak appeared from 90 min in the region of 228–258 nm, indicating the interaction between the methyl of the toluene and methanol. The increased absorption band indicated that the reaction extent and the content of the oxygenous aromatic products were proportional directly to the reaction time.

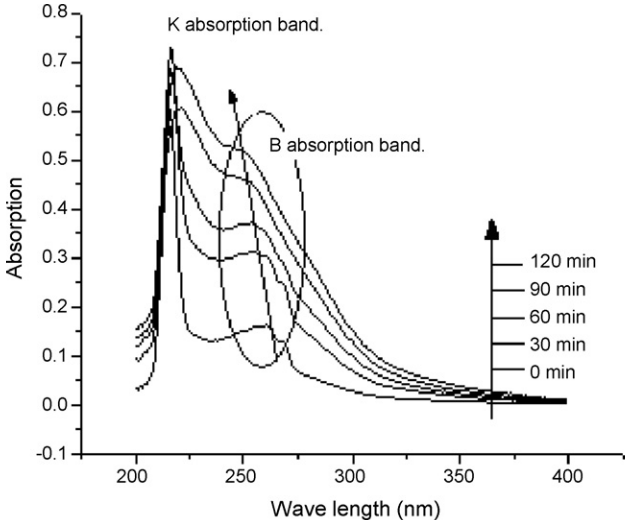


Fig. 1. Effect of time on the coupling reaction with $SO_4^{2-}/Fe_2O_3–5.0\%\ MoO_3$ catalyst.

The electronic spectra of the reaction system with the different dosage of MoO_3 in the catalyst at the same reaction time of 90 min and the identical current intensity of 2.0 A were shown in Fig. 2. It can be found that the K absorption band shifted unconspicuously; the B absorption band hypsochromic shifted and increased with the increasing of MoO_3 dosage in the catalyst, suggesting that

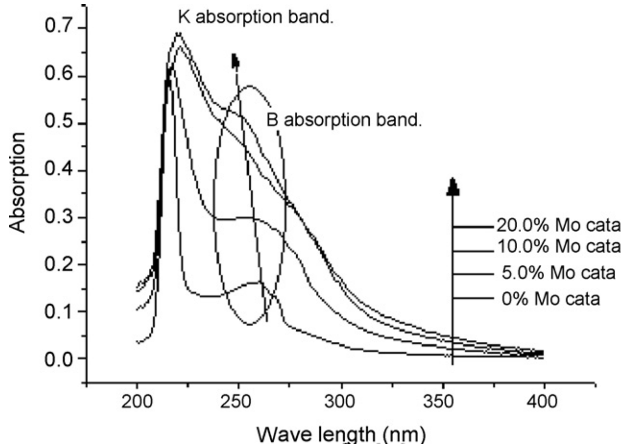


Fig. 2. Effect of various dosage of MoO_3 in the catalysts on the reaction (90 min).

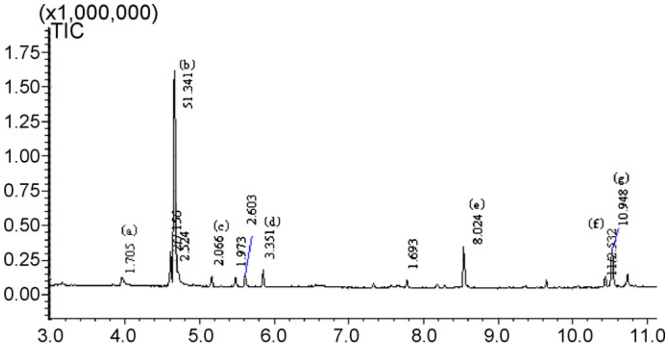


Fig. 3. GC of the products ($SO_4^{2-}/Fe_2O_3–20\%\ MoO_3$ catalyst) (a)1-(fluoromethyl) benzene; (b)1-(methoxymethyl) benzene;(c)4-methylbenzenesulfinic acid; (d)1-(dimethoxymethyl) benzene; (e)methyl4-methoxybenzoate; (f)2-*tert*-butyl-4-(2-phenyl propan-2yl) phenol; (g)7-methoxy-2,3-diphenyl-4H-chromen-4-one.

Table 1
The electrolysis of toluene in methanol solvent by $SO_4^{2-}/Fe_2O_3–xMoO_3$ catalysts[a]

Catalyst	Products concentration (mass%)							Total (mass%)
	(a)	(b)	(c)	(d)	(e)	(f)	(g)	
0% MoO_3	Little	17.455	10.877	Little	5.931	46.418	9.903	90.584
5.0% MoO_3	4.801	38.405	9.495	4.924	8.272	23.175	5.612	94.684
10.0% MoO_3	9.435	41.057	Little	11.277	2.641	16.730	7.396	88.536
20.0% MoO_3	Little	51.341	2.066	2.603	8.024	2.532	10.948	77.541

GC/MS spectrum, 70 eV, *M/e* (relative intensity): 1-(fluoromethyl) benzene (a): 109 M^+ (100), 91 (10), 83 (14), 63 (8), 51 (10), 39 (12), 27 (1); 1-(methoxymethyl) benzene (b): 122 M^+ (50), 105 (8), 91 (100), 77 (32), 65 (24), 51 (22), 39 (22), 15 (15), 12 (2); 4-methylbenzenesulfinic acid (c): 155 M^+ (2), 126 (6), 123 (80), 107 (22), 91 (100), 79 (28), 65 (28), 45 (25), 39 (20), 27 (2); 1-(dimethoxymethyl) benzene (d): 151 M^+ (1), 121 (100), 105 (10), 91 (10), 77 (22), 59 (2), 51 (8), 29 (2), 15 (2); methyl 3-methoxybenzoate (e): 166 M^+ (32), 135 (100), 123 (2), 107 (11), 92 (18), 77 (26), 64 (13), 50 (7), 38 (5), 31 (1); 2-*tert*-butyl-4-(2-phenylpropan-2-yl) phenol (f): 268 M^+ (28), 253 (100), 223 (2), 191 (6), 178 (1), 165 (2), 152 (1), 128 (1), 119 (11), 105 (14), 91 (11), 77 (4), 57 (17), 55 (1), 41 (10); 7-methoxy-2,3-diphenyl-4H-chromen-4-one (g): 327 M^+ (100), 312 (2), 296 (1), 284 (6), 271 (1), 255 (1), 239 (1), 226 (1), 207 (1), 178 (13), 164 (6), 151 (4), 126 (1), 113 (1), 101 (1), 77 (1), 63 (1), 51 (1).

[a] Reaction conditions: current intensity, 2.0 A; reaction temperature, 298 K; reaction time, 120 min.

reaction extent of the electrochemical catalytic oxidation enhanced with the increasing of molybdenum element content in the catalysts.

3.2. GC/MS spectrum

The GC of the products was shown in Fig. 3 (the peak of the solvent was taken off). The concentration of the products with the various dosage of MoO_3 at the same reaction time of 120 min and the identical current intensity of 2.0 A was listed in Table 1. It can be found that the content of the oxygenous aromatic products obtained by Mo-modified SO_4^{2-}/Fe_2O_3 catalyst were higher than that of SO_4^{2-}/Fe_2O_3 without molybdenum modification catalyst at the same conditions, indicating that the catalytic activity of SO_4^{2-}/Fe_2O_3 catalyst was enhanced by modification of molybdenum. With the increasing of the dosage of molybdenum oxide from 0% to 20% in the catalysts, the selectivity of the main product 1-(methoxymethyl) benzene was increased from 17.455% to 51.341%, and the valence of molybdenum in the catalysts have no changes before and after the electrochemical reaction detected by XPS, indicating that the various products can be acquired by controlling the reaction conditions, namely controlling molybdenum content [13].

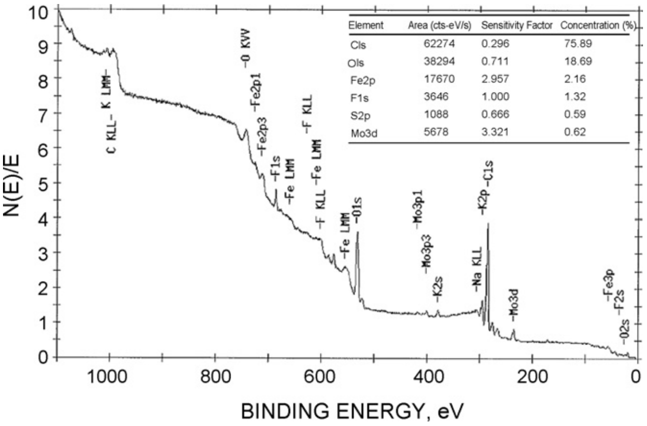
The results also showed that this catalytic electrolysis can yield different methoxyl benzene products from conventional catalytic process (benzyl aldehyde or benzoic acid). Depending upon the reaction conditions and the catalysts used, different products are also formed, which are mainly 2-*tert*-butyl-4-(2-phenylpropan-2-yl) phenol (SO_4^{2-}/Fe_2O_3 as the catalyst) or 1-(methoxymethyl) benzene ($SO_4^{2-}/Fe_2O_3–20\%\ MoO_3$ as the catalyst), indicating that the mechanism of this catalytic electrolysis process was more complex.

Although the catalytic efficiency of the process was not much high, fortunately, various oxygenous aromatic products have been successively accomplished in this simple process, it may be predicated that a simple and feasible electrochemical catalytic oxidation reaction at room temperature and standard atmosphere may be possible.

3.3. IR spectra

The representative infrared spectra of SO_4^{2-}/Fe_2O_3 and modified catalyst $SO_4^{2-}/Fe_2O_3–xMoO_3$ were also investigated. After modified by molybdenum, a new characteristic peak at 829.63 cm^{-1} maybe attributed to M–O has been observed in the IR of modified catalyst $SO_4^{2-}/Fe_2O_3–xMoO_3$, indicated that the structures of these modified $SO_4^{2-}/Fe_2O_3–xMoO_3$ catalysts are almost the same with that of SO_4^{2-}/Fe_2O_3.

In general, for the metal oxides modified with sulfate ions followed by evacuation above 673 K, bands at 1392 cm^{-1} assigned to the S=O stretching frequency of sulfate ion bonded to Fe_2O_3 are a little weak, due to the strong attracting electrons from metal ions via two covalent S=O bonds, the center metal atom lacks electrons severely, thus the strong Lewis acidic strength is generated. When a Lewis acid site absorbs water, it converts to a Brønsted acid site [13,14].

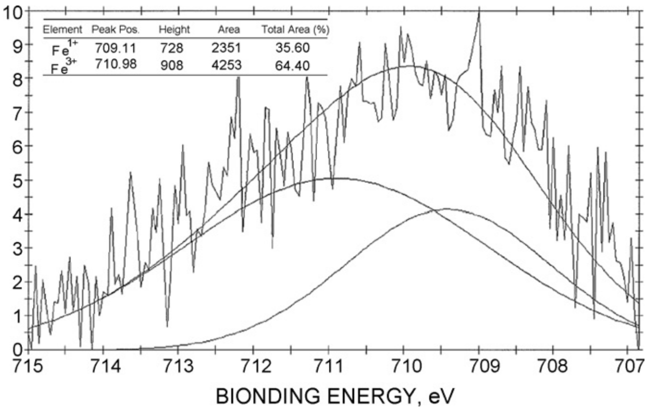


Element	Area (cts-eV/s)	Sensitivity Factor	Concentration (%)
Cls	62274	0.296	75.89
Ols	38294	0.711	18.69
Fe2p	17670	2.957	2.16
F1s	3646	1.000	1.32
S2p	1088	0.666	0.59
Mo3d	5678	3.321	0.62

Fig. 4. XPS of $SO_4^{2-}/Fe_2O_3–20\%\ MoO_3$ catalyst after the reaction.

3.4. XPS analysis

After the coupling reaction, $SO_4^{2-}/Fe_2O_3–xMoO_3$ catalyst was dried in vacuo and tested by XPS. The binding energy and its composition of the catalyst were shown in Fig. 4. XPS Fe 2p(3/2) peak of 20% MoO_3 solid superacid catalyst after the reaction was shown in Fig. 5.



Element	Peak Pos.	Height	Area	Total Area (%)
Fe^{1+}	709.11	728	2351	35.60
Fe^{3+}	710.98	908	4253	64.40

Fig. 5. XPS Fe 2p(3/2) peak of $SO_4^{2-}/Fe_2O_3–20\%\ MoO_3$ catalyst after the reaction.

The XPS Fe 2p(3/2) peak has been deconvoluted to two different valent components (FeO and Fe_2O_3) and the ratio of two atoms is 35.60:64.40 (molar ratio), inferred that the iron was the mixture of FeO and Fe_2O_3 in the catalyst after the reaction. Compared to that Fe^{3+} occupied 100% of the total iron element before the coupling reaction, it can be illuminated that Fe^{3+} was reduced to Fe^{2+} during the coupling reaction process [15].

4. Conclusion

One-step production of methoxymethyl benzene by electrochemical coupling reaction of toluene with methanol cooperated with molybdenum-modified solid superacid was investigated. From the results it can be concluded that the catalytic activity of $SO_4{}^{2-}/Fe_2O_3$–$x$$MoO_3$ catalyst were higher than that of $SO_4{}^{2-}/Fe_2O_3$ catalyst without modification at the same conditions in the coupling reaction of toluene and methanol. The various products can be obtained by controlling the reaction conditions, namely controlling the oxidation extent such as the molybdenum content.

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