

Cobalt modified solid superacid assisted electrochemical reaction of toluene with methanol

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Received 24 September 2006; received in revised form 25 January 2007; accepted 25 January 2007
Available online 2 February 2007

Abstract

The electrochemical catalytic reaction of toluene with methanol, assisted with a pair of porous graphite plate electrodes, catalyzed by solid superacid of cobalt modification catalyst with chemical conversion higher than 81%, was described and investigated by UV–vis spectrum, scan electron microscopy (SEM), powder X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and gas chromatography–mass spectrometry (GC–MS). A possible free radical reaction mechanism was proposed. It may be concluded that a simply and feasible electrochemical catalytic coupling oxidation reaction at room temperature and air pressure may be possible.

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Keywords: Electrochemical catalytic oxidation; Toluene; Methanol; Solid superacid

1. Introduction

Electrochemical synthesis has a prominent advantage over regular chemical method in as much as that they do not require large quantities of noxious or corrosive reagents, it has been widely used in many areas such as synthesis of pharmaceutical drugs, amino acids, dyestuffs, pesticides, spicery and organic reagents [1–3] and has received much attention in recent years [4–6].

Acid catalysts play a predominant role in organic synthesis and transformations. Many organic reactions such as alkylation, acylation, isomerization, esterification and rearrangements like pinacol, Beckman, etc. are accomplished by acid catalysts. In view of environmental and economical reasons, there is an ongoing effort to replace the conventional catalysts with new solid acids [7–10]. Owing to its high reactivity, ease of handling, recovery, low waste generation and environmental friendliness, heterogeneous solid acid catalysts are emerging as very attractive alternatives to the conventional homogenous acidic reagents [11–14].

Toluene is the most important aromatic hydrocarbon, oxidation of the side chain of toluene and substituted aromatic hydrocarbons can be the source of alcohols, aldehydes, and acids, which often are of commercial interest and usually are prepared by chemical process [15]. No much attention has been paid on the electrochemical catalytic oxidation, acylations or esterification researches at room temperature and air pressure.

Here, we report the preparation of solid superacid catalyst of cobalt modification and its catalytic properties on coupling reaction of toluene with methanol in electrochemical reaction system. The catalysts were detected by scan electron microscope (SEM), X-ray photoelectron spectroscopy (XPS) and powder X-ray diffraction (XRD), the electrochemical process was inspected by UV–vis spectra and the products were checked by gas chromatography/mass spectrometry (GC/MS). The effect of the cobalt dosage in solid acid was also discussed.

2. Experiment

2.1. Materials and general methods

All chemicals used in the experiment were analytical grade and used without any further purification. $\text{Fe}(\text{OH})_3$ was provided

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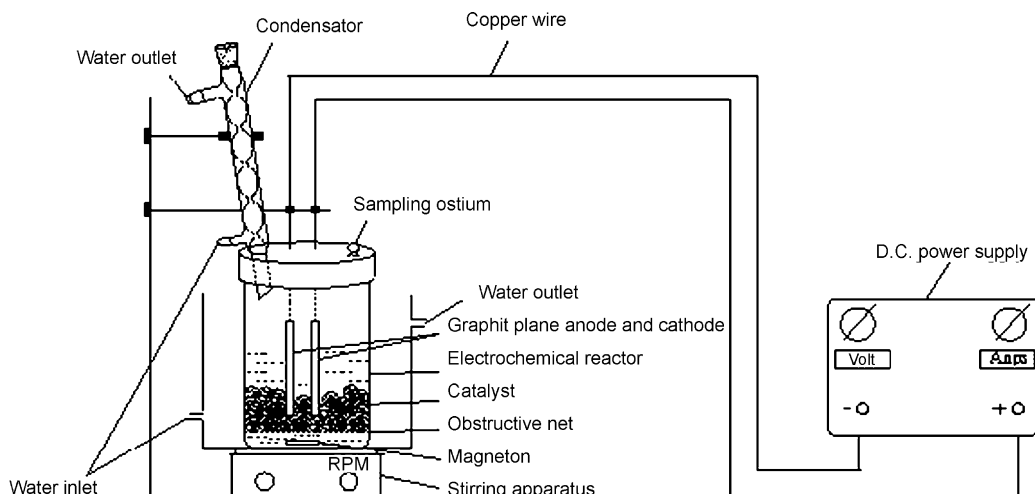


Fig. 1. Experimental setup for the electrochemical catalytic oxidation.

by Tianjin Dengfeng Reagent Co., H_2SO_4 (Xi'an Reagent Co.) and Co_2O_3 (Shanghai Colloid Reagent Co.), China. CH_3OH , KF and ArCH_3 were obtained from Xi'an Reagent Co. The effects of time and the cobalt dosage in solid acid was inspected by UV–vis 7504 spectrum made in Shanghai Xinmao Co. The component and its distribution of the products were analyzed by GC/MS (QP2010, Japan). The catalyst was detected by XRD (Rigaluc, Japan), SEM (Quanta 200, Holland) and XPS (Perkin Elmer PHI-5400).

2.2. Preparation of solid superacid catalyst ($\text{SO}_4^{2-}/\text{Fe}_2\text{O}_3-x\text{Co}_2\text{O}_3$)

Mixing a certain amount of $\text{Fe}(\text{OH})_3$ and Co_2O_3 and sulphated this mixture with 200 ml 1.0 mol/l H_2SO_4 solution for 12 h, finally calcined at 550°C for 3 h to obtain the final $\text{SO}_4^{2-}/\text{Fe}_2\text{O}_3-x\text{Co}_2\text{O}_3$ ($x=0, 10, 20$ and 30%) catalyst.

2.3. Experimental set-up

Fig. 1 shows the schematic diagram of the experimental set-up for electrochemical catalytic oxidation of toluene. The experiments were conducted in a single cell of 0.25 l capacity at 12.0 V and 2.0 A. The reaction cell was airproofed to prevent the volatilization of methanol and cooled by the cooling water in a trough to maintain the room temperature condition. The anode and cathode both were the porous graphite plate (Supplied by Spring Chemical Industrial Company Limited, Shaanxi, China, 50 mm \times 50 mm \times 6 mm) and were positioned vertically and paralleled to each other with a constant inter gap of 1.0 cm. 15 g catalyst of solid superacid and 3 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.

2.4. Electrolysis procedures

The electrolysis was carried out in cells without compartments. The anode and cathode (graphite plate) were activated by methanol solution with metal ion before using. The solvent-supporting electrolyte system was formed as follows: 3 g KF and 50 ml toluene were added in 80 ml anhydrous methanol with $\text{SO}_4^{2-}/\text{Fe}_2\text{O}_3-x\text{Co}_2\text{O}_3$ ($x=0, 10, 20$ and 30%) solid superacid catalyst. The resulting solutions were placed in the cells and electrolyzed at a current intensity of 2.0 A with stirring at room temperature. The conversion of starting material was investigated by UV–vis spectra 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 recorded at the range of 200–400 nm with methanol as blank. The current was interrupted at the moment of higher yield of the products.

2.5. 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 mm \times 30 m). The catalyst was washed with water for several times and dried in vacuo, then analyzed by XPS.

3. Results and discussion

3.1. UV spectroscopy

Fig. 2 shows the effect of time on the coupling reaction with 30.0% Co_2O_3 solid superacid catalyst detected by UV–vis adsorption spectrophotometer. With the time prolong (0–120 min), the K adsorption band (221 nm) of the benzene ring shifted but changed unobscurely, and the B adsorption band of the benzene ring hypsochromic shifted from 262 to 255 nm (arrowhead area) and the shoulder appeared

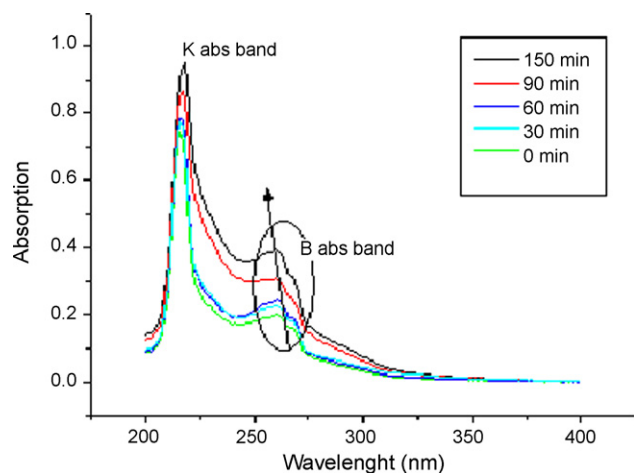


Fig. 2. Effect of time on the coupling reaction with 30.0% Co_2O_3 solid superacid catalyst.

between 232 and 256 nm after 120 min, maybe due to the interaction between the methyl of the toluene and hydroxyl group, indicating the methyl of the toluene was substituted by a methoxyl group or a hydroxyl group, which leading to the conjugation between the methyl group in the toluene 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 with different Co_2O_3 dosage at the same reaction time of 120 min and identical current intensity of 2.0 A shows in Fig. 3. It can be found that the K absorption band shifted unobviously; the B absorption band hypsochromic shifted and decreased as follows: 30.0% Co_2O_3 solid superacid catalyst > 20.0% Co_2O_3 solid superacid catalyst > 10.0% Co_2O_3 solid superacid catalyst > 0% Co_2O_3 solid superacid catalyst, suggesting that the reaction extent of the electrochemical catalytic oxida-

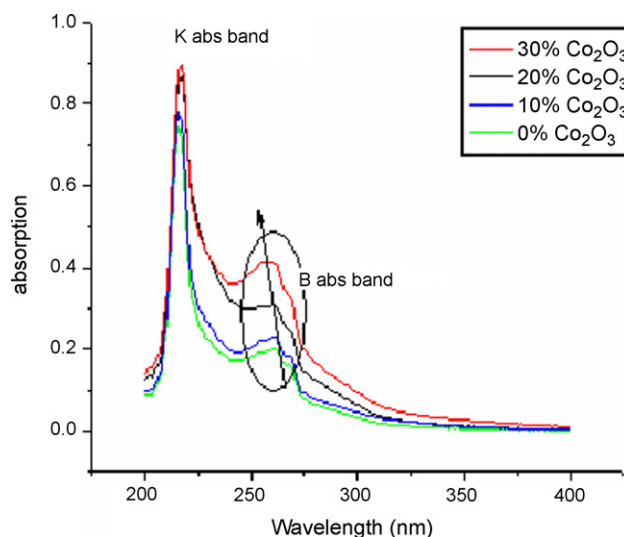


Fig. 3. Effect of Co_2O_3 content on the reaction system (120 min).

tion enhanced with the increasing of cobalt element content [16].

3.2. GC/MS spectrum

The GC of the products shows in Fig. 4 (the peak of the solvent was taken off). Table 1 compares the percentage of the products in different medium at the same reaction time of 120 min and identical current intensity of 2.0 A. It can be found that the content of the oxygenous aromatic products obtained using the solid superacid of cobalt modification catalyst as medium were higher than that of the solid superacid without cobalt modification catalyst at the same condition, indicating that the catalytic activity of solid superacid catalyst was enhanced by the promotion of cobalt. With the increasing of the percent of cobalt oxide from 0 to 30% in the catalysts, the main product 1-(methoxymethyl)benzene increased from 17.455 to 37.173%, indicating that

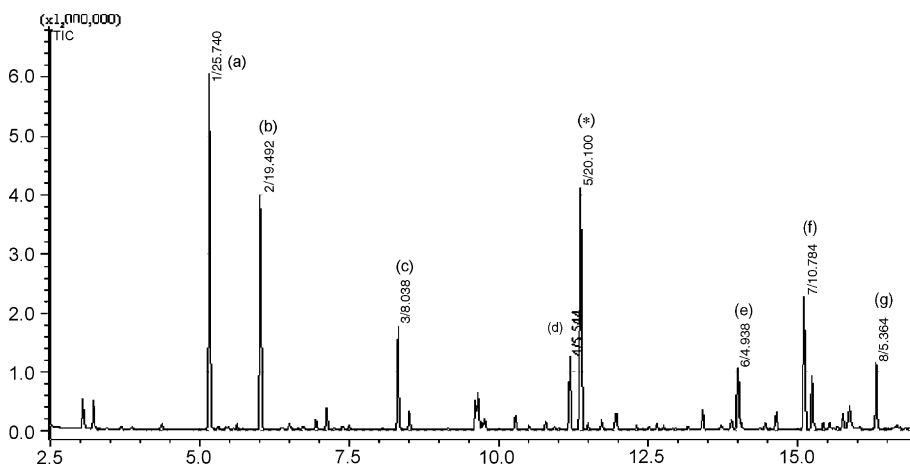


Fig. 4. GC of the products (20.0% Co_2O_3 solid superacid catalyst) (*) impurity peak: 1,2-dimethoxy-4-nitrobenzene; (a) 1-(methoxymethyl)benzene; (b) 4-methylbenzenesulfonic acid; (c) 3,6-dimethoxy-3,6-dimethylcyclohexa-1,4-diene; (d) 1,2-dimethoxy-3-methylbenzene; (e) 3,3,6,6-tetramethoxycyclohexa-1,4-diene; (f) 1-benzyl-4-methylbenzene; (g) methyl 2-(3,4-dimethoxyphenyl)-2-hydroxy-2-phenylacetate.

Table 1
The electrolysis of toluene in methanol solvent by the different catalysts^a

Catalyst	Products percentage (mass%) ^b							Total (mass%)
	(a)	(b)	(c)	(d)	(e)	(f)	(g)	
0% Co ₂ O ₃	17.455	18.877	5.931	3.170	5.931	17.418	9.903	78.685
10.0% Co ₂ O ₃	19.012	19.827	8.126	8.736	6.044	11.427	8.804	81.976
20.0% Co ₂ O ₃	25.740	19.492	8.038	5.544	4.938	10.784	5.364	79.900
30.0% Co ₂ O ₃	37.173	20.324	7.562	6.196	7.747	3.765	3.618	86.385

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

^b GC/MS spectrum, 70 eV, M/e (relative intensity)—1-(methoxymethyl)benzene (a): 122 M⁺ (50), 105 (8), 91 (100), 77 (32), 65 (24), 51 (22), 39 (22), 15 (15), 12 (2); 4-methylbenzenesulfonic acid (b): 155 M⁺ (2), 126 (2), 123 (87), 107 (27), 91 (100), 79 (28), 65 (31), 45 (22), 39 (19), 27(3); 3,6-dimethoxy-3,6-dimethylcyclohexa-1,4-diene (c): 168 M⁺(1), 153 (100), 137 (88), 122 (82), 105 (22), 91 (47), 77 (42), 65 (23), 43 (35), 39 (27), 31 (10); 1,2-dimethoxy-3-methylbenzene (d): 152 M⁺(100), 137 (54), 122 (5), 109 (26), 91 (32), 77 (22), 65 (18), 51 (5), 39 (18), 27 (2); 3,3,6,6-tetramethoxycyclohexa-1,4-diene (e): 185 M (13), 169 (100), 153 (2), 138 (43), 123 (22), 105 (2), 95 (9), 75 (6), 63 (2), 52 (7), 41 (13), 15 (8); 1-benzyl-4-methylbenzene (f): 182 M (78), 168 (13), 167 (100), 152 (25), 128 (9), 115 (10), 104 (32), 91 (15), 77 (13), 65 (14), 51 (11), 39 (13), 27 (5); methyl 2-(3,4-dimethoxyphenyl)-2-hydroxy-2-phenylacetate (g): 302 M⁺ (1), 243 (15), 165 (7), 149 (1), 128 (2), 120 (2), 105 (100), 92 (2), 77 (32), 59 (7), 51 (9), 29 (2), 15(40).

the various products can be acquired by controlling the reaction conditions, namely controlling the cobalt content in the catalyst.

3.3. XRD

The solid superacid catalyst detected by XRD before and after reaction show in Fig. 5. It can be seen that iron in the catalyst

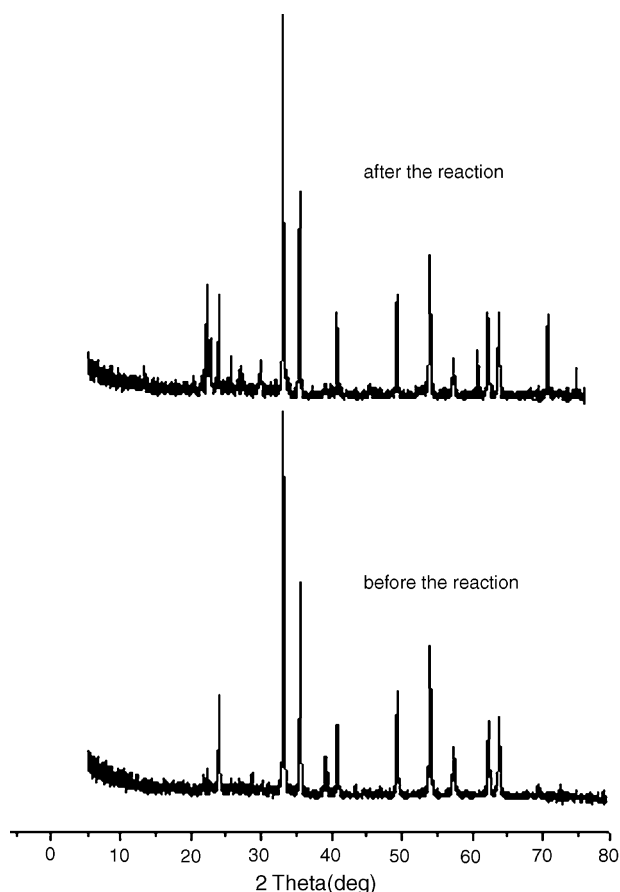


Fig. 5. XRD patterns of solid superacid catalyst before and after the reaction.

presented itself as the formation of Fe₂O₃ ($2\theta = 23.90^\circ, 33.12^\circ, 49.54^\circ, 53.87^\circ, 63.06^\circ$ and 64.76°) before the reaction and as the mixture of Fe₂O₃ and FeO ($2\theta = 42.05^\circ, 36.23^\circ, 60.90^\circ, 72.84^\circ$ and 76.61°) after the reaction, indicating that iron in the solid superacid were related with the electrochemical reaction system.

3.4. SEM

The morphology of solid superacid catalysts were examined by SEM and representative photograph of no modification and cobalt modification of solid superacid show in Fig. 6. It can be observed that the massive sandwich of no modification solid superacid (Fig. 6a) had changed into the disorder fragment (Fig. 6b) after the modified process, which maybe due to the interposition of cobalt element.

3.5. XPS analysis

After the coupling reaction, solid superacid catalyst was dried in vacuo and tested by XPS. The binding energy and its composition of the catalyst show in Fig. 7. XPS Fe 2p_{3/2} peak of 20% Co₂O₃ solid superacid catalyst after the reaction shows in Fig. 8.

The XPS Fe 2p_{3/2} peak has been deconvoluted to two different valent components (FeO and Fe₂O₃) and the ratio of two atoms is 35.88:64.12 (molar ratio), inferred that the iron was the mixture of FeO and Fe₂O₃ in the catalyst after the reaction. Compared to that Fe³⁺ occupied 100% of the total iron element before the coupling reaction, it can illuminated that Fe³⁺ was reduced to Fe²⁺ during the coupling reaction process, which is consistent with the XRD result.

3.6. Assumed mechanism [15–18]

The assumed mechanism of the reaction was proposed. A part of the hydroxyl anions were adsorbed near the anode, forming a thin layer between the solvent and the anode; the other part of the hydroxyl anions were adsorbed at the surface of the catalyst.

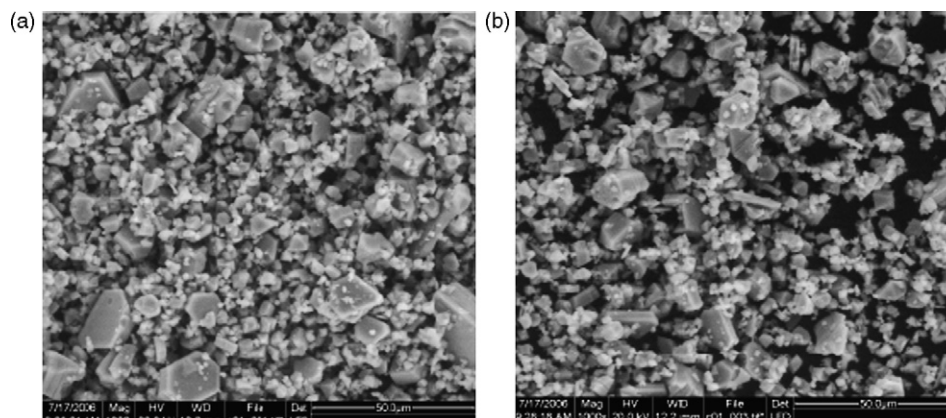
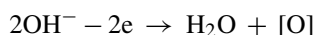


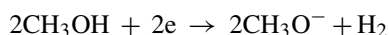
Fig. 6. Representative SEM of solid superacid (1000×): (a) no modification; (b) cobalt modification.

The anode reaction:



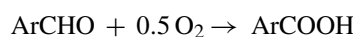
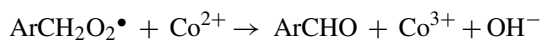
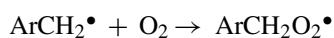
occurred at the thin hydroxyl anions layer near the anode.

The cathode reaction:

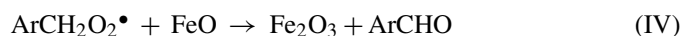
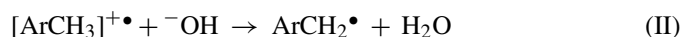
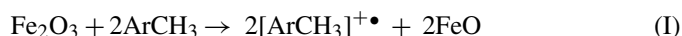


occurred near the cathode.

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 [15,16]:



The possible catalytic reaction mechanism was speculated:



A toluene free radical cation formed in the oxidation of side-chain of toluene by the catalyst was combined with a hydroxyl anion to produce a free radical. All products were obtained 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 proposed show in Fig. 9. The formation of toluene free radical cation was the rate-determining step in the coupling reaction. Hereby, the spectra of the different medium and reaction time were various.

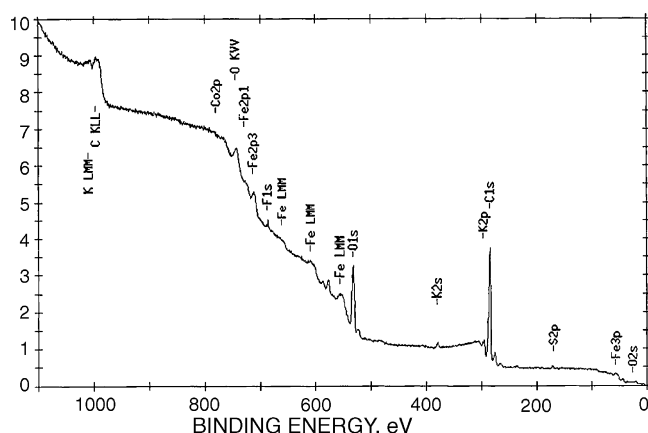


Fig. 7. XPS of 20.0% Co_2O_3 solid superacid catalyst after the reaction.

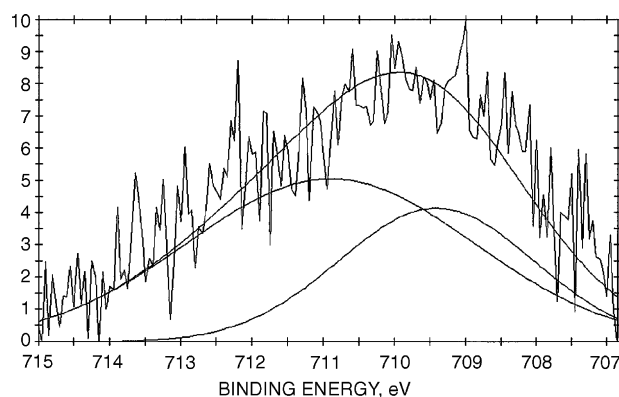


Fig. 8. Fe 2p_{3/2} binding energy of 20.0% Co_2O_3 solid superacid catalyst after the reaction.

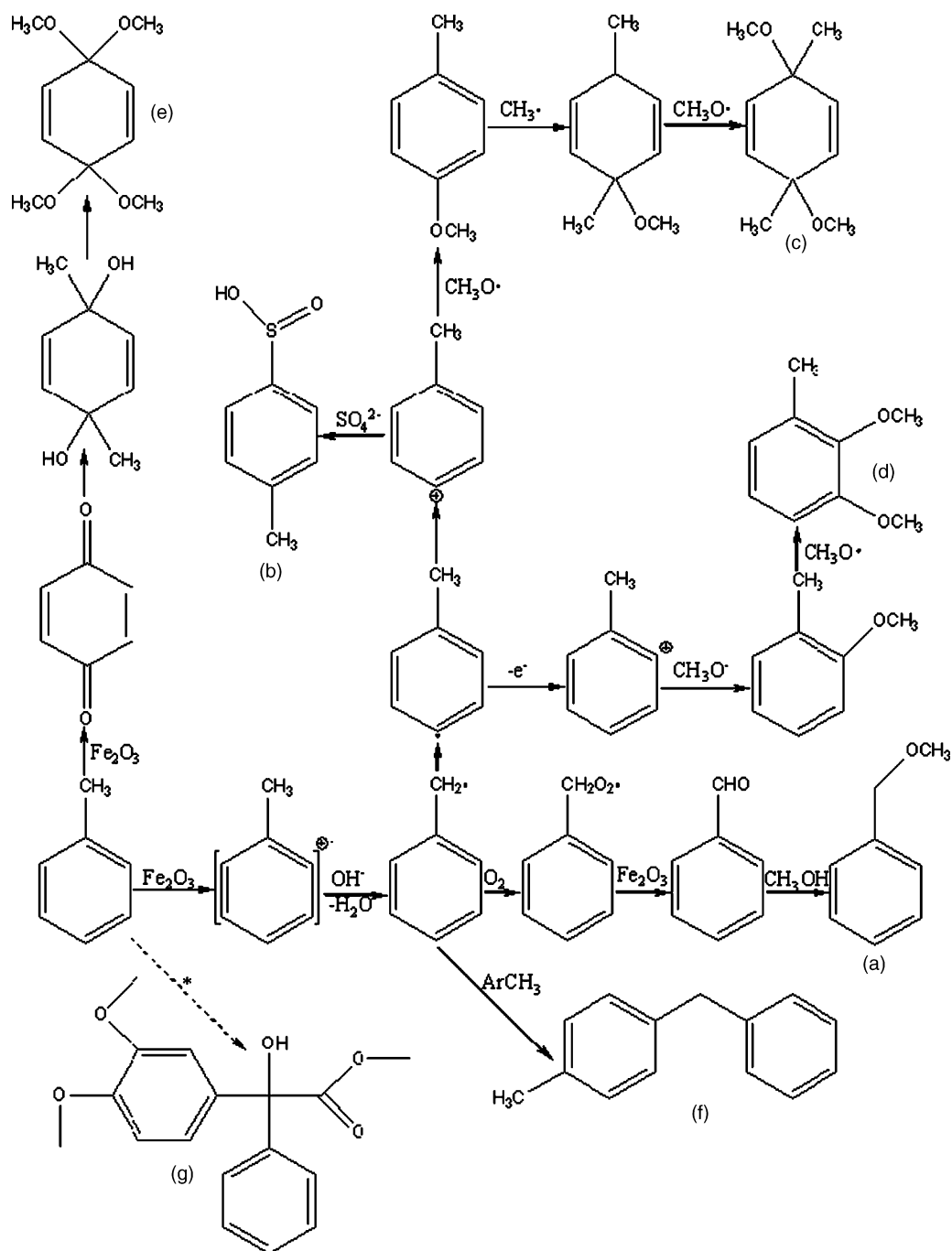


Fig. 9. The possible mechanism for the main reactions (*): the reaction mechanisms have been unknown so far.

4. Conclusion

Some toluene derivatives: 1-(fluoromethyl)benzene; 1-(methoxymethyl)benzene; 3,6-dimethoxy-3,6-dimethylcyclohexa-1,4-diene; 1,2-dimethoxy-3-methylbenzene; 3,3,6,6-tetramethoxycyclohexa-1,4-diene; 1-benzyl-4-methylbenzene and (R)-methyl 2-(3,4-dimethoxyphenyl)-2-hydroxy-2-phenylacetate were obtained by electrochemical oxidation of toluene with methanol cooperated with solid superacid of cobalt modification. The catalytic activity of solid superacid catalyst of cobalt modification was higher than that of solid superacid

catalyst without cobalt modification at the same condition in the coupling reaction of toluene and methanol. The various products can be obtained by controlling the reaction conditions, namely controlling the oxidation degree such as the cobalt dosage in the catalyst. In addition, the possible mechanism of the reaction was assumed and it fell into the free radical cation mechanism.

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