ELSEVIER

Modified SO_4^{2-}/Fe_2O_3 solid superacid catalysts for electrochemical reaction of toluene with methanol

H.Zh. Ma [*], F.T. Chen, B. Wang, Q.F. Zhuo

Institute of Energy-Chemistry, College of Chemistry and Materials Science, Shaanxi Normal University, 710062 Xi'an, PR China

Abstract

A series of sulfate, different metal promoted SO_4^{2-}/Fe_2O_3 catalysts were prepared and investigated by means of Fourier transform infrared (FT-IR) and X-ray photoelectron spectroscopy (XPS). All catalysts exhibit good catalytic activity for the electrochemical reaction of toluene with methanol assisted with a pair of porous graphite plane electrodes and chemical conversion higher than 80% was observed. In particular, molybdate promoted catalysts exhibited excellent catalytic activity.
© 2006 Elsevier B.V. All rights reserved.

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

1. Introduction

The term 'superacid' was first proposed by Conant in 1923 to describe acid systems that are stronger than conventional mineral acid. Later, Gillespie define the superacid as "an acid system stronger than that of 100% sulfuric acid, i.e., $H_0 \leq -12$" [1]. The catalytic activity of superacids for many reactions of hydrocarbon transformations is surprisingly high. They can even activate methane at low temperature [2,3].

Conventional acids such as H_2SO_4, HF, $AlCl_3$, BF_3, SbF_5, H_3PO_4 and HCl used in organic reactions pose significant risks in handling, containment and disposal due to their toxic and corrosive nature. As catalysts, solid acids have some additional advantages such as ease of separation from reaction mixture, no corrosion for the reactor, and free from pollution, etc. So they are worthy of attention in theoretical research and in synthetic application [3–8]. Owing to 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. Among various solid acid catalysts such as zeolites, clays and heteropolyacids, the sulfated metal oxides, based on iron oxide have emerged as powerful catalysts due to their super-acidity,

high reactivity at low temperatures and reusability [9,10]. The activity, selectivity and stability of sulfated iron oxide catalysts were also improved by the addition of noble metals and transition metal oxides such as Cu and Co.

Acid-catalyzed organic reactions are numerous and the usage of solid acid catalysts is very rampant in several industrial and environmental processes [11–13]. 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 [14,15]. It clearly indicates the significance of their 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 [3,8–10].

As an important chemical raw material toluene was mostly used in alkylation synthesis of *p*-xylene and its derivatives were prepared by chemical process with higher temperature (200–500 °C), longer time (12.4 h), environmental pollution and in the presence of ZSM-5 type zeolites catalyst [16]. However, no much attention has been paid on the electrochemical catalytic oxidation, acylations or esterification researches at room temperature and air pressure.

Electrochemical synthesis, an interdisciplinary science of organic chemistry and electrochemistry technology, have received considerable attention in recent years, because of its

* Corresponding author. Tel.: +86 29 85308442; fax: +86 29 85307774.
  E-mail address: mahongzh@126.com (H.Zh. Ma).

potential applications in the synthesis of pharmaceutical drugs, amino acids, dyestuffs, pesticides, spicery and organic reagents [17,18]. In industrialized production about 100 organic compounds were synthesized by electrochemical synthesis methods because of its efficiency and lower environmental contamination.

Here, we report a series of solid acids of different metal modification and its catalytic activities in the electrochemical reaction of toluene with methanol were also investigated. The catalysts were detected by X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FT-IR) and the products were checked by UV-spectrum and 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 used in the experiment were analytical grade and without any further purification.

The effect of the medium was inspected by UV–vis 7504 spectrum apparatus which made in Shanghai Xinmao Co. Products were identified and product distributions were determined by GC/MS (QP2010, Jp). The catalyst was detected by FT-IR (Eouinx55, Germany) and XPS (Perkin-Elmer PHI-5400).

2.2. Preparation of SO_4^{2-}/Fe_2O_3–20.0%M_xO_y catalysts

Mixed a certain amount of $Fe(OH)_3$ and metal oxide according to the ratio and triturated, then sulphation of this mixture was done by percolating 200 ml 1.0 mol/L H_2SO_4 solution through it for 12 h, finally calcined at 550 °C for 3 h to obtain the final SO_4^{2-}/Fe_2O_3–20% M_xO_y catalysts.

2.3. Experimental set-up

Fig. 1 shows the schematic diagram of the experimental set-up for electrochemical catalytic oxidation. The experiments were conducted in a single cell of 0.25 L capacity at 12.0 V voltage and 2.0 A current intensity. The reaction cell was cooled by 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). Fifteen-gram 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. Uniform concentration of the electrolyte was maintained by constantly stirring the solution at 200 rpm using a magnetic stirrer. 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 paste plate) were activated by methanol solution before using. The solvent-supporting electrolyte system was formed as follows: KF (3.0 g) and toluene (50 ml) were added in 80 ml anhydrous methanol with SO_4^{2-}/Fe_2O_3–20% M_xO_y ((1) no metal modification solid superacid catalyst; (2)–(7) MoO_3, CuO, CrO_3, Co_2O_3, MnO_2, V_2O_5, respectively). The resulting solutions were placed in the cells with stirring, then electrolyzed at a current intensity of 2.0 A at room temperature, detecting 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 recorded at the range of 200–400 nm using methanol as blank. The current was interrupted in the moment of higher yield in the products. The methanol used for the research of UV–vis spectrum was reclaimed for the next experiment without pollutions and waste.
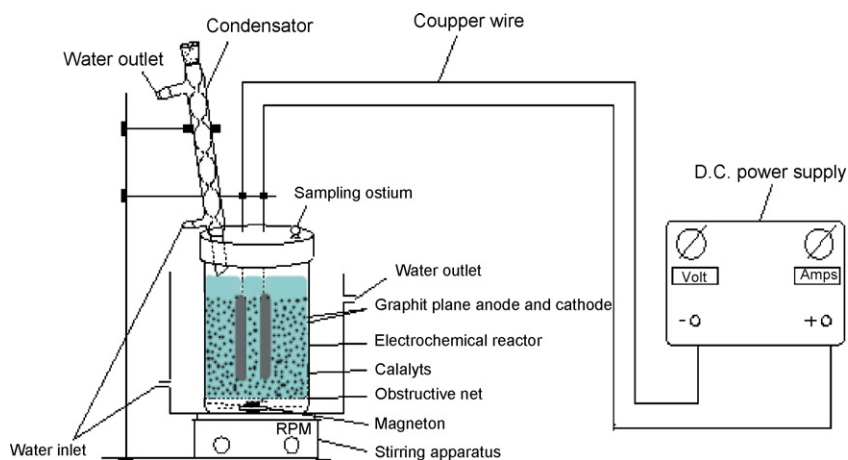

Fig. 1. Experimental set-up for the electrochemical catalytic oxidation.

2.5. Characterization of the products and the catalyst

After the reaction finished, the solution was distilled at atmospheric 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. IR

Fig. 2 shows the representative infrared spectra of SO_4^{2-}/Fe_2O_3 and modified catalyst $SO_4^{2-}/Fe_2O_3–20\%$ MoO_3. According to the literature [4,5,19,20], the vibration peak of Fe–O in Fe_2O_3 was at 539.13 cm^{-1}, after impregnating with SO_4^{2-}, this peak was divided into two peaks (571.75 cm^{-1} and 457.80 cm^{-1}). The shape and relative intensity of the peak at 1103.51 cm^{-1} assigned to S=O asymmetric vibration characteristic peak were almost unchanged, suggesting that the structure of SO_4^{2-}/Fe_2O_3 solid superacid remains stable in the catalyst even when many other components were promoted.
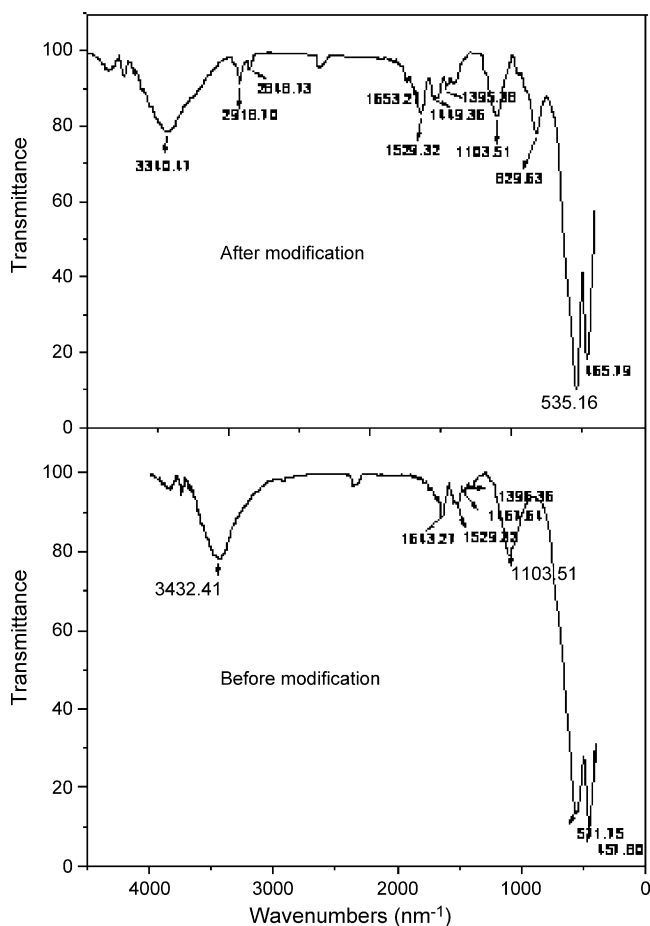

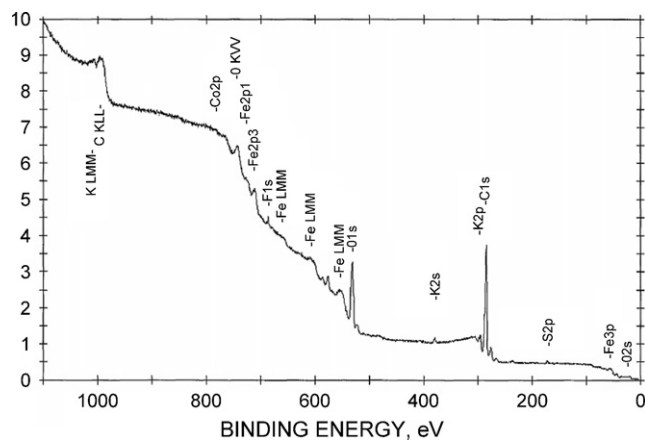Fig. 2. Representative infrared spectrum of SO_4^{2-}/Fe_2O_3 before and after modification.

Fig. 3. XPS of $SO_4^{2-}/Fe_2O_3–20\%$ CoO_3 catalyst after the reaction.

The peak at 1529.32 cm^{-1} can be assigned to the Bronsted acidity characteristic absorption, and peaks at 1467.54 cm^{-1} and 1396.35 cm^{-1} can be assigned to the mixture absorption of Bronsted acidity and Lewis acidity, the strong absorption peak at 3432.47 cm^{-1} and weak peak at 1643.27 cm^{-1} maybe assigned to the dissociative hydroxyl of H_2O absorbed on the solid superacid, indicating that the prepared solid superacid catalysts can both acted as Bronsted acid and Lewis acid in the catalytic reaction.

Compared with SO_4^{2-}/Fe_2O_3, only a new characteristic peak at 829.63 cm^{-1} has been observed in the IR of modified catalyst $SO_4^{2-}/Fe_2O_3–20\%$ MoO_3, which maybe attributed to M–O. The infrared spectrum of the other modified solid superacid catalysts are the same with that of $SO_4^{2-}/Fe_2O_3–20\%$ MoO_3 approximately, indicated that the structures of these modified solid superacids are almost the same.

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 Fe 2p3/2 peak of 20% CoO_3 solid superacid catalyst after the reaction was shown in Fig. 4. Because a mass of the organic compounds and the electrolyte were adsorbed on the surface of the cata-
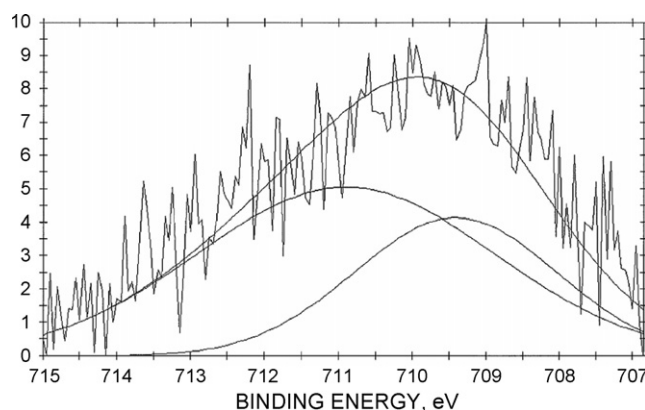

Fig. 4. Fe 2p3/2 binding energy of $SO_4^{2-}/Fe_2O_3–20\%$ CoO_3 catalyst after the reaction.

lyst, carbon element, oxygen element and fluorine element were detected by XPS.

The XPS Fe 2p3/2 peak has been deconvoluted to two different valent components (FeO and Fe_2O_3) and the ratio of two atoms is 35.88:64.12 (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.

We also studied XPS of other solid superacid catalysts, the results indicated that most metal ions were concerned with the coupling reaction and were reduced to lower valent (Fig. 5 and Table 1), respectively.

3.2. Liquid products

3.2.1. UV spectroscopy analysis

The effect of time on coupling reaction catalyzed by solid superacid catalyst was detected by UV–vis adsorption spectrophotometer. With prolong time, the K adsorption band of benzene ring shifted but changed unconspicuously, maybe due to the interactions of toluene alkylation with methanol to p-xylene. The electronic cloud of benzene ring was enlarged by $n \rightarrow \pi^*$ transition because the methyl group was an electron donor, moreover, the B adsorption band of the benzene ring hypsochromic shifted and shoulder appeared, owing to the interaction between the methyl of the toluene and hydroxyl group enlarged the energy band of $\pi \rightarrow \pi^*$ contrast to that of the ben-
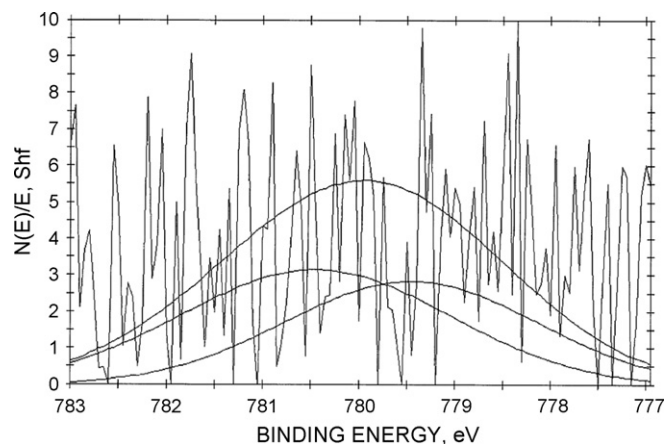

Fig. 5. Co 2p3/2 binding energy of SO_4^{2-}/Fe_2O_3–20% CoO_3 catalyst after the reaction.

zene ring that hydrogen atom in the methyl of the toluene was substituted by a methoxyl group or a hydroxyl group, 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 adsorbed peak height enlarged, indicating the reaction degree was directly proportional to the reaction time and the content of the oxygenous aromatic products.

The electronic spectra of the reaction system in different media at the same reaction time (120 min) and identical current intensity of 2.0 A were shown in Fig. 6. It can be found that K adsorption band shifted unconspicuously; B adsorption

Table 1
Simulation curve data for different metal ions

Catalyst	Element	Peak pos.	Area	Of total area %
SO_4^{2-}/Fe_2O_3	Fe^{3+}	710.98	3875	78.63
	Fe^{2+}	709.19	1053	21.73
SO_4^{2-}/Fe_2O_3–20% MoO_3	Fe^{3+}	710.98	4253	64.40
	Fe^{2+}	709.11	2351	35.60
	Fe^{3+}	711.00	2595	68.50
SO_4^{2-}/Fe_2O_3–20% CuO	Fe^{2+}	709.31	1193	31.49
	Cu^{2+}	933.85	792	55.70
	Cu^+	932.45	630	44.30
	Fe^{3+}	710.85	4136	77.11
	Fe^{2+}	709.35	1228	22.89
SO_4^{2-}/Fe_2O_3–20% CrO_3	Cr^{6+}	577.90	916	34.01
	Cr^{4+}	575.16	1372	50.95
	Cr^{3+}	576.35	405	15.04
	Fe^{3+}	710.90	3501	64.12
SO_4^{2-}/Fe_2O_3–20% Co_2O_3	Fe^{2+}	709.41	1959	35.88
	Co^{6+}	780.45	689	54.17
	Co^{3+}	779.45	583	45.83
	Fe^{3+}	711.35	5996	77.86
SO_4^{2-}/Fe_2O_3–20% MnO_2	Fe^{2+}	709.35	1705	22.14
	Mn^{4+}	642.65	1545	69.59
	Mn^{2+}	640.09	675	30.41
	Fe^{3+}	710.95	1766	46.79
SO_4^{2-}/Fe_2O_3–20% V_2O_5	Fe^{2+}	709.25	2008	53.21
	V^{5+}	517.55	735	55.81
	V^{3+}	516.04	582	44.19
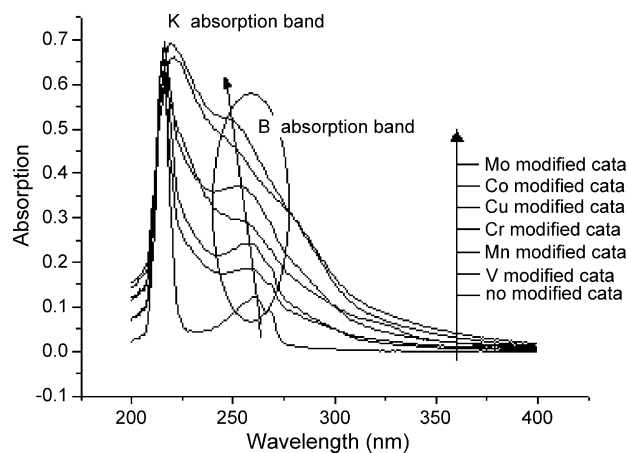
Fig. 6. The effect of the medium on the reaction system (120 min).

Fig. 7. The gas chromatography of the products (SO_4^{2-}/Fe_2O_3–20% Co_2O_3 as catalyst). [(a) p-xylene; (b) 1-(methoxymethyl)benzene; (c) 4-methylbenzenesulfinic acid; (d) 1,2-dimethoxy-3-methylbenzene; (e) methyl-4-methoxybenzoate; (f) 1-benzyl-4-methylbenzene; (g) 1-(1,2,2-trimethoxyethyl)benzene; (h) 2-tert-butyl-4-(2-phenylpropan-2-yl)phenol; (i) methyl-2-(3,4-dimethoxyphenyl)-2-hydroxy-2-phenylacetate].

band hypsochromic shifted and the adsorbed peak height was decreased as follows:

SO_4^{2-}/Fe_2O_3–20%MoO_3 catalyst

> SO_4^{2-}/Fe_2O_3–20%Co_2O_3 catalyst

> SO_4^{2-}/Fe_2O_3–20%CuO catalyst

> SO_4^{2-}/Fe_2O_3–20%CrO_3 catalyst

> SO_4^{2-}/Fe_2O_3–20%MnO_2 catalyst

> SO_4^{2-}/Fe_2O_3–20%V_2O_5 catalyst

> SO_4^{2-}/Fe_2O_3 catalyst.

This suggested that the electrochemical catalytic oxidation degree enhanced with the enhancing of catalytic activity by the different metals modification.

3.2.2. GC/MS spectrum

The GC of the products was shown in Fig. 7 (the peak of the solvent was taken off). Table 2 compared the percentage of the products in different mediums at the same reaction time of 120 min and identical current intensity of 2.0 A. It can be found that the yield of the oxygenous aromatic products were higher when SO_4^{2-}/Fe_2O_3–20%M_xO_y were used than that of SO_4^{2-}/Fe_2O_3 catalyst; moreover, the highest yield was obtained

Fig. 8. Yields of 1-(methoxymethyl)benzene over SO_4^{2-}/Fe_2O_3–20% M_xO_y.

with SO_4^{2-}/Fe_2O_3–20% MoO_3 as catalyst at the same condition (Fig. 8), indicating that the catalytic activities of solid superacid catalyst were largely promoted by the introduction of metals, especially with molybdenum element.

It was assumed from the case of electrochemical reaction of toluene with methanol that the activity enhancement would be

Table 2
The electrolysis of toluene in methanol solvent by the different catalysts

Catalyst 20.0%	Products concentration (mass%)[a]							Total (mass%)
	(a) + (b) + (c)	(d)	(e)	(f)	(g)	(h)	(i)	
Blank	34.574	Little	46.418	Little	Little	9.903	Little	90.895
MoO_3	55.982	Little	2.532	Little	Little	10.948	Little	69.462
CuO	55.282	5.463	4.692	Little	Little	22.633	8.821	96.891
CrO_3	52.399	11.496	4.272	4.183	7.202	Little	5.926	85.478
Co_2O_3	68.074	6.196	7.747	3.765	2.410	5.796	3.618	97.606
MnO_2	37.849	12.628	4.195	4.330	8.523	6.107	8.495	82.127
V_2O_5	63.610	5.113	Little	2.461	Little	Little	3.816	75.000

[a] (a) p-xylene; (b) 1-(methoxymethyl)benzene; (c) 4-methylbenzenesulfinic acid; (d) 1,2-dimethoxy-3-methylbenzene; (e) methyl-4-methoxybenzoate; (f) 1-benzyl-4-methylbenzene; (g) 1-(1,2,2-trimethoxyethyl)benzene; (h) 2-tert-butyl-4-(2-phenylpropan-2-yl)phenol; (i) methyl-2-(3,4-dimethoxyphenyl)-2-hydroxy-2-phenylacetate.
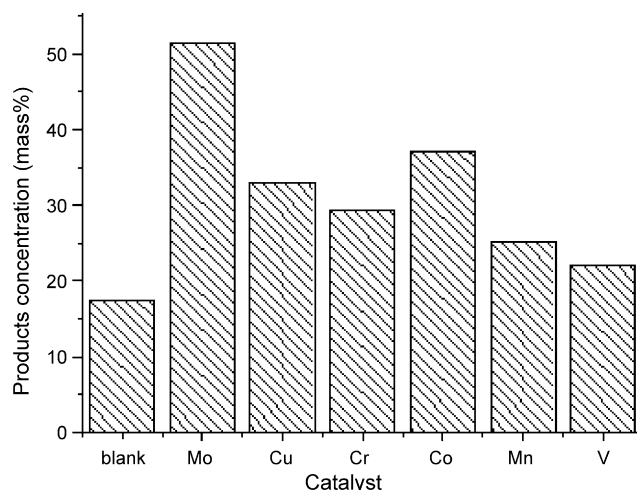
uncertain because it was reported that the promotion by the introduction of metals was not based on acidity but on the metallic effect [21].

4. Conclusion

A novel method that electrochemical oxidation of toluene in methanol solvent catalyzed by SO_4^{2-}/Fe_2O_3–20% M_xO_y solid superacid of different metal modification at room temperature and atmospheric pressure was studied. Toluene derivatives such as p-xylene, 1-(methoxymethyl)benzene were obtained effectively, indicating that SO_4^{2-}/Fe_2O_3–20% MoO_3 solid superacid can act as an effective electrochemical catalytic oxidation catalyst in the electrochemical oxidation of toluene in methanol solvent.

References

[1] R.J. Gillespise, T.E. Peel, J. Am. Chem. Soc. 95 (1995) 5173.
[2] G.A. Olah, G.K.S. Prakash, J. Sommer, Science 13 (1978) 206.
[3] G.A. Olah, G.K.S. Prakash, J. Sommer, Superacids, Wiley, New York, 1985.
[4] G. Magnacca, G. Cerrato, C. Morterra, M. Signoretto, F. Somma, F. Pinna, Chem. Mater. 15 (2003) 675.
[5] M.M. Mohamed, B.M. Abu-Zied, Thermochim. Acta 359 (2000) 109.
[6] B.M. Reddy, P.M. Sreekanth, P. Lakshmanan, A. Khan, J. Mol. Catal. A: Chem. 244 (1–2) (2006) 1–7.
[7] B.M. Reddy, P.M. Sreekanth, Y. Yamada, T. Kobayashi, J. Mol. Catal. A: Chem. 227 (1–2) (2005) 81–89.
[8] K. Tanabe, Solid Acids and Bases, Their Catalytic Properties, Tokyo Kodansha, Academic Press, New York, 1970.
[9] K. Arata, Adv. Catal. 37 (1990) 165.
[10] K. Arata, Appl. Catal. A: Gen. 146 (1996) 3.
[11] H.L. Yin, Z.Y. Tan, Y.T. Liao, Y.J. Feng, J. Environ. Radioact. 87 (2) (2006) 227–235.
[12] A. Corma, H. Garcia, Chem. Rev. 103 (2003) 4307.
[13] J.R. Sohn, S.H. Lee, J.S. Lim, Catal. Today 116 (2) (2006) 143–150.
[14] B.M. Reddy, P.M. Sreekanth, P. Lakshmanan, J. Mol. Catal. A: Chem. 237 (2005) 93.
[15] A. Corma, Chem. Rev. 95 (1995) 599.
[16] J. Utley, Chem. Soc. Rev. 26 (1997) 157.
[17] C.J. Chang, Y. Deng, C. Shi, C.K. Chang, F.C. Anson, D.G. Nocera, Chem. Commun. 5 (2000) 1355.
[18] H. Vinek, Appl. Catal. 68 (1991) 277.
[19] P. Salas, J.G. Hernandez, J.A. Montoya, J. Navarrete, J. Salmones, I. Schifter, J. Morales, J. Mol. Catal. A: Chem. 123 (1997) 149–154.
[20] W.S. Li, Zh.Q. Shen, Y.F. Zhang, Eur. Polym. J. 37 (2001) 1185–1190.
[21] A. Kazushi, N. Hideo, S. Miyuki, Appl. Catal. A: Gen. 97 (2000) 213–219.