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Recent development of mixed metal oxide anodes for electrochemical oxidation of organic pollutants in water

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ABSTRACT

Mixed metal oxides (MMOs) have been extensively employed for heterogeneous catalysis. In recent years, MMOs have received an intensive interest as anode materials for electrochemical treatment of wastewaters which contain recalcitrant organics. This review article gives an overview of the classification of MMO anodes systems, synthesis methods, characterization techniques, and recent advance of removing or alleviating various recalcitrant organic pollutants using MMO anodes, highlighting areas of consensus and currently unresolved issues. Practical issues pertinent to modification to the catalytic activities of MMO anodes are discussed, including nano- and microstructured deposits, doping and polymer composites. Electrogenerated reactive oxygen species (ROS) with MMO anodes and their determination by various techniques have also been reviewed. In addition, this article discusses several important factors which could affect the electrochemical oxidation of recalcitrant organics with MMO anodes, and critically identifies the shortcomings in current research including discrepant results and ambiguous conclusions. Finally, the challenges and possible improvement of MMO anodes for their future application are also proposed.

Contents

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Nomenclature

Abbreviation

AFM	atomic force microscopy
AOP	advanced oxidation process
BDD	boron doped diamond
COD	chemical oxygen demand
CA	carbon aerogel
CV	cyclic voltammetry
CVD	chemical vapor deposition
DRS	diffuse reflectance spectroscopy
DSA	dimensionally stable anode
EAOP	electrochemical advanced oxidation process
EIS	electrochemical impedance spectroscopy
FR	fluorine resin
FTIR	Fourier-transform infrared spectroscopy
FTO	fluorine doped tin oxide
ICE	instantaneous current efficiency
MMO	mixed metal oxide
NT	nanotube
OEP	oxygen evolution potential
OER	oxygen evolution reaction
PED	pulse electrodeposition
PVD	physical vapor deposition
PTFE	polytetrafluoroethylene
SCE	standard camel electrode
SEM	scanning electron microscopy
SHE	standard hydrogen electrode
TEM	transmission electron microscopy
TOC	total organic carbon
TGA	thermalgravimetric analysis
XAS	X-ray adsorption spectroscopy
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

Symbols

$C_{d,i}$	internal differential capacitance
C_d	total differential capacitance
C_{dl}	pseudo-capacitance
φ_{morph}	morphology factor

1. Introduction

Metal oxides represent one of the most important categories of solid catalysts which are widely used either as active phases or supports [1]. Because of their acid-base and redox properties, metal oxides have been extensively employed for heterogeneous catalysis. Among all kinds of metal oxide catalysts, those which contain more than one kind of metal cations are known as mixed metal oxides (MMOs). By mixing different metal oxides, new stable compounds can be formed, and some of them exhibit significant improvement in catalytic activity than their respective single-component metal oxides. This could be due to an increase in the surface area, an increase of active acidic or basic sites or a change in the chemical states of the metal ions. Some important applications of MMOs as heterogeneous catalyst include Al_2O_3 supported MMOs for $(CH_3)_2S_2$ degradation [2], TiO_2-ZrO_2 for nonoxidative dehydrogenation of ethylcyclohexane [3], Mg-V-Al MMOs for oxidative dehydrogenation of propane [4], $Fe_xCe_{1-x}O_2$ for N_2O degradation [5], V-Sb-Nb MMOs for ammoxidation of propane [6], $LaNiO_3$ for ethanol reforming [7] and RuO_2-IrO_2-SnO_2 for chloralkali process [8].

Besides their applications as catalysts, MMOs have also been studied for a wide range of other purposes, i.e. semiconductors, sensors, photoconductive thin films, and electrode materials for lithium battery, fuel cell and environmental application [9–12]. Remarkable progress has been achieved in the research of MMOs' application as the anode material for electrochemical oxidation of recalcitrant pollutants in aqueous environment, since the treatment of water and wastewater has become a more challenging issue due to the ineffective degradation of those pollutants by conventional treatments which rely on biological process [13,14]. Several reviews have described the removal or alleviation of recalcitrant organic pollutants in water by electrochemical oxidation, with regard to the various MMO anodes employed and different mechanisms involved [15–18]. Typically, MMO anodes are prepared by depositing the MMOs layer on inert substrates (titanium, carbon, stainless steel, etc.). Indeed, increasing efforts have been put forward to evaluating the ability of MMO anodes to remove or alleviate various types of recalcitrant organic pollutants including dyes, pesticides and herbicides, phenolic compounds, pharmaceuticals, antibiotics and hormones, plasticizers, perfluorinated chemicals, surfactants and derivatives, chelating agents and microcystin toxins.

Table 1 summarizes various types of recalcitrant organic pollutants which have been investigated for their electrochemical oxidation with different MMO anodes. The organic pollutants can be degraded by either direct oxidation or mediated oxidation with MMO anodes. In the mediated oxidation, the reactive chlorine generated from chlorides is the most commonly employed mediator. The reactive chlorine has the merit to treat landfill leachate [19,20] and reverse osmosis (RO) concentrate from water reclamation plant [21–24], both of which have high salinity. In general, MMO anodes are effective to abate aqueous pollution caused by recalcitrant organics, even for those which have extraordinary strong C–F bond (490 kJ mol^{-1}) [25–28]. With appropriate MMO anodes chosen and suitable operating condition for electrochemical oxidation, most recalcitrant organics can be completely removed, or alleviated to their acceptable levels before biological treatment [29].

In this review, several aspects of MMO anodes are discussed, i.e. the classification of MMO anodes, their synthesis and characterization, and the surface modification of MMO anodes, with specific emphasis on the improvement of their catalytic activity to degrade aqueous organics pollutants by electrochemical oxidation. Several factors which have important effects on the process efficiency are