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Review

Progress in research on catalysts for catalytic oxidation of formaldehyde

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ABSTRACT

Formaldehyde (HCHO) is carcinogenic and teratogenic, and is therefore a serious danger to human health. It also adversely affects air quality. Catalytic oxidation is an efficient technique for removing HCHO. The development of highly efficient and stable catalysts that can completely convert HCHO at low temperatures, even room temperature, is important. Supported Pt and Pd catalysts can completely convert HCHO at room temperature, but their industrial applications are limited because they are expensive. The catalytic activities in HCHO oxidation of transition-metal oxide catalysts such as manganese and cobalt oxides with unusual morphologies are better than those of traditional MnO_2, Co_3O_4, or other metal oxides. This is attributed to their specific structures, high specific surface areas, and other factors such as active phase, reducibility, and amount of surface active oxygens. Such catalysts with various morphologies have great potential and can also be used as catalyst supports. The loading of relatively cheap Ag or Au on transition-metal oxides with special morphologies potentially improves the catalytic activity in HCHO removal at room temperature. The preparation and development of new nanocatalysts with various morphologies and structures is important for HCHO removal. In this paper, research progress on precious-metal and transition-metal oxide catalyst systems for HCHO oxidation is reviewed; topics such as oxidation properties, structure–activity relationships, and factors influencing the catalytic activity and reaction mechanism are discussed. Future prospects and directions for the development of such catalysts are also covered.

1. Introduction

Formaldehyde (HCHO) is a colorless gas with a strong irritating smell at atmospheric pressure. Outdoor HCHO mainly comes from the production of materials such as paints, textiles, printing materials, pesticides, and adhesives, and from motor vehicle exhausts. Indoor HCHO mainly comes from decorating materials, plywood, fiberboard, particleboard, and other artificial boards [1]. HCHO has serious adverse effects on human health and causes conditions such as edema, eye irritation, headaches, allergic dermatitis, and dark sports. Inhalation of HCHO at high concentrations can induce bronchial asthma, and HCHO can combine with protein amino groups to cause cell mutation. The damage caused by HCHO to human health is

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closely related to its concentration in air and contact time. It has been classified as carcinogenic and teratogenic by the World Health Organization [2,3]. HCHO is also a volatile organic compound (VOC) and has strong photochemical activity, e.g., it can react photochemically with nitrogen oxides (NO_x) [4–7]. HCHO removal is therefore necessary to protect human health and the atmospheric environment.

The main techniques used in the elimination of VOCs are adsorption, and photocatalytic and catalytic oxidation methods [8–21]. Adsorption usually uses activated carbon or molecular sieves as adsorbents for HCHO removal [22–33]. The use of this method is restricted because of the limitations of adsorption capacity and adsorbent regeneration. Photocatalytic methods often use TiO_2-based catalysts to remove HCHO [34–41]. In actual applications, wall paints containing modified TiO_2 catalysts are used. However, under light, such paints can produce secondary pollution of toxicity similar to that of HCHO. Catalytic oxidation is a promising technique, and has advantages such as high removal efficiency, low light-off temperature, wide application scope, simple equipment, and no secondary pollution. HCHO can be directly converted to CO_2 and H_2O [42].

The development of catalytic oxidation techniques is important. The catalytic materials for HCHO oxidation are mainly divided into noble-metal and transition-metal oxide catalyst systems. In this paper, we review progress in research on these two systems in detail, and future directions and potential hotspots in research on catalysts for HCHO oxidation are discussed.

2. Noble-metal catalysts

Noble-metal catalyst attract much attention because of their excellent low-temperature oxidation activities. They are loaded on supports because precious metals themselves are easily volatilized, oxidized, and sintered. The loading of precious metals on supports enables HCHO conversion at low temperatures. The specific catalytic properties are related to factors such as precious-metal and support types, and structure. The precious-metal catalysts currently used for HCHO oxidation mainly contain Pt, Pd, Au, and Ag as the active components [43]. Other precious metals are not suitable for catalytic combustion because of their high volatilities and ease of oxidation at high temperatures. The supports for precious-metal catalysts for HCHO oxidation can be divided into three types. The first type is materials with no oxidation activities and large specific surface areas, such as SiO_2, Al_2O_3, TiO_2, and molecular sieves; these are common catalyst supports and are commercially available. The second type is single or mixed metal oxides without special morphologies, with high-temperature oxidation activities, but low specific surface areas; examples are bulk CeO_2 and MnO_2; these are traditional metal oxide supports. The third type is metal oxides with special morphologies such as nanorods and

Table 1
Overview of catalytic activities in HCHO oxidation of supported noble-metal catalysts.

Catalysts	Reaction conditions	T_{50} (°C)	Ref.
Common supports			
Pt/TiO_2	100 ppm HCHO, 20 vol% O_2, 50000 h^{-1} SV	R.T.	[44,45]
Rh/TiO_2		50	
Pd/TiO_2		70	
Au/TiO_2		90	
$Na\text{-}Pt/TiO_2$	600 ppm HCHO, 20 vol% O_2, 300000 h^{-1} SV, 50% relative humidity	R.T.	[46]
$Na\text{-}Pt/TiO_2$	105 ppm HCHO and 315 ppm toluene	R.T.	[47]
Pt/TiO_2(C)	36 ppm HCHO, 21 vol% O_2, total flow 500 mL/min	R.T.	[48]
$Pt/f\text{-}SiO_2$	300 ppm HCHO, 20 vol% O_2, 30000 mL/(g·h) SV	R.T.	[49]
Pt/SBA-15		40	
$Pt/p\text{-}SiO_2$		90	
Pt/TiO_2	100 ppm HCHO, 22 vol% O_2, 300000 mL/(g·h) SV	R.T.	[50]
Pd/TiO_2		80	
Rh/TiO_2		90	
Pt/SiO_2		60	
Pt/carbon	100–300 ppm HCHO, 22 vol% O_2, 1120 h^{-1} SV	<100	[51]
Pt/TiO_2	10 ppm HCHO, 80000 h^{-1} SV, 50% relative humidity	R.T.	[52]
Pd/TiO_2	10 ppm HCHO, 120000 h^{-1} SV, 50% relative humidity	R.T.	[53]
Pd/Bata	40 ppm HCHO, 20 vol% O_2, 50000 h^{-1} SV, 3% H_2O	<40	[54]
Pd/USY		<40	
Pd/ZSM-5		70	
Pd/HM10		>140	
Pd/Zeo-13X		<40	
Pd/Al_2O_3		<40	
$PdMn/Al_2O_3$	0.5% HCHO, 0.2% CH_3OH, 0.7% H_2O, 75.6% N_2, 23% O_2	60	[55]
Ag/SBA-15	1000 ppm HCHO, 15 vol% O_2, 15000 mL/(g·h) SV	50	[56]
Ag/Al_2O_3	1.2% HCHO, 14.8% O_2, 1000 or 7000 h^{-1} SV	—	[57]
Ag/SiO_2			
Ru/Al_2O_3	900 ppm HCHO, 160 ppm CH_3OH, 18% H_2O, 82% air, 20000 h^{-1} SV	198	[58]
Ru/zeolite		210	
Ru/TiO_2		212	

(To be continued)