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Solid catalysts for wet oxidation of nitrogen-containing organic compounds

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Abstract

Several solid catalysts (Co_3O_4/γ-Al_2O_3, Fe_2O_3/γ-Al_2O_3, Mn_2O_3/γ-Al_2O_3, Zn–Fe–Mn–Al–O, Pt/γ-Al_2O_3, Ru/CeO_2, Ru/C) have been prepared and used to remove N-containing organic contaminants while processing toxic and hazardous industrial waste waters using wet oxidation by air (WAO). The autoclave tests of catalysts were done to reveal the main advantages of catalysts in water presence at high pressures and temperatures. Catalyst activity was determined with regard to oxygen interaction with model mixtures (water–organic contaminant: acetonitrile, carbamide, dimethyl formamide, or multi-component mixture of aliphatic alcohols). Activity tests were done in a static reactor under ideal mixing regime. Reagents and products were monitored using gas chromatograph Cvet-560, Millichrom-1 HPLC, and routine chemical analysis. Optimum process conditions for the best catalyst (Ru/graphite-like carbon) are as follows: partial oxygen pressure – 1.0 MPa, temperature – 473–513 K. At 0.5–5.0 MPa total pressure and 433–523 K catalysts show high water-resistance and high activity level (residual content of toxic compounds is less than 1%, and no NO_x and NH_3 are detected). There are no legal restrictions on catalysts operation, since they are harmless to environment. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Recent catalytic studies using WAO of various N- and O-containing organic compounds [1–6] show ammonia and acetic acid to be the most difficult to oxidize. The most active solid catalysts are transition metal oxides (Mn/Ce, Cu/Zn, Co/Bi oxide systems) and supported noble metals (Pt, Ru). At present activity of the most widely used catalysts allows one to convert organic compounds to neutral gases at 533 K and $P_{O_2} = 2\,\text{MPa}$ in 1 h. Nevertheless, catalysts, designed for commercial application, possess at least two disadvantages. First, they show relatively low activity. Second, they are not stable enough. (Note that there are few data in the literature on catalyst durability.) However, new materials and procedures used to prepare catalysts open new ways of catalyst improvement.

The present paper is concerned with the design of new heterogeneous catalysts free from the disadvantages mentioned above. These catalysts, when applied, are expected to (i) save energy, (ii) decrease the apparatus size and metal content, and (iii) reduce emission of toxic gases. There are no data on manufacturing of such type of catalysts for WAO. Catalysts may show good performance in WAO of N- and O-

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containing organic compounds in water solutions. Therefore, they may be of interest for pharmaceutical and petrochemical enterprises.

2. Experimental

2.1. Catalyst preparation

1. *Supports*. Commercial γ-Al_2O_3 (BET surface area $230\,m^2\,g^{-1}$), γ-Al_2O_3 ($12\,m^2\,g^{-1}$), and active carbon AG-3 ($750\,m^2\,g^{-1}$) were used. Graphite-like carbon materials (90–$230\,m^2\,g^{-1}$) were manufactured [7,8] by the Institute of Technical Carbon.
2. *Catalysts*. Metal-oxide catalysts 10%-Co_3O_4/γ-Al_2O_3, 2.8%-Fe_2O_3/γ-Al_2O_3, 10%-Co_3O_4/α-Al_2O_3, 2.8%-Fe_2O_3/α-Al_2O_3, 0.9%-MnO_x/γ-Al_2O_3, and 3.5%-Zn-3%-Fe-3.5%-Mn-O_x/γ-Al_2O_3 were prepared using incipient wetness impregnation with metal nitrates solution. Then catalysts were dried and calcined at 673 K (4 h). New thermally stable catalyst Mn–Al–O_x (4.2 wt% Mn) was manufactured by AO "Katalizator". Ru-containing (0.5–4.5 wt% Ru) catalysts Ru/C, Ru/CeO_2 and Ru/CeO_2/γ-Al_2O_3 were prepared by impregnation with $RuOHCl_3$, then were dried in air at 393 K for 1 h, and reduced in hydrogen at 673 K for 5 h. Procedure used to prepare 0.50%-(Pt–Pd)/γ-Al_2O_3 and 0.56%-Pt/γ-Al_2O_3 was described elsewhere [9].

2.2. Reactor system and testing

Basic tests were performed in the ideal mixing setup equipped with high-pressure stainless steel reactor (Fig. 1). Reactor design allows liquid and gas sampling on the run. O_2, CO_2, CO, N_2, N_2O, NO, NH_3, organic compounds were analyzed with gas chromatograph Cvet-560; liquid phase was studied with Millichrom-1 HPLC, Cvet-560 GC, and routine chemical analysis.

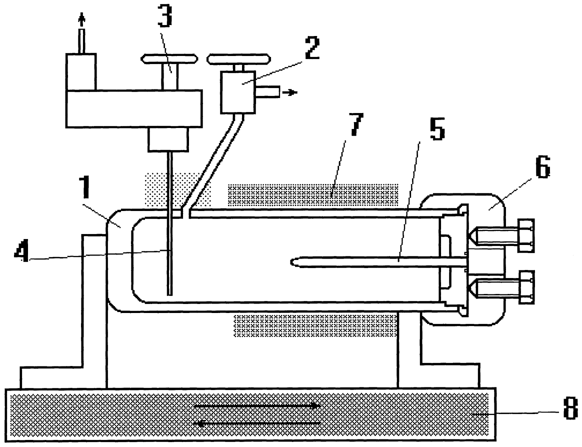

Fig. 1. Schematic view of reactor: 1 – reactor body; 2 – gas sampling valve; 3 – liquid sampling valve, 4 – capillary; 5 – thermocouple; 6 – cover; 7 – heater; 8 – vibrato-device.

Table 1
WAO test conditions

Reactor volume (ml)	200
Solution volume (ml)	150
Concentration of $CO(NH_2)_2$ ($g\,l^{-1}$)	15
Initial O_2 pressure (MPa)	1.0
Temperature (K)	473
Time (h)	2
Catalyst load (g)	1
Total pressure (MPa)	~3.5

Autoclave tests of various supports and catalysts were done at 473 K (1.55 MPa, 5 h) to reveal catalyst material performance in water presence at high pressures and temperatures. Promising samples were tested for activity in the reaction of oxygen with model mixtures (water–organic contaminant: acetonitrile, $CO(NH_2)_2$, dimethyl formamide, or multi-component mixture of aliphatic alcohols). The concentrations of contaminants ranged within 2.5–$15\,g\,l^{-1}$, oxygen ratio was stoichiometric, if not mentioned otherwise. Acetonitrile, carbamide, and dimethyl formamide were used without additional purification. Catalyst selection experiments were done in carbamide excess (Table 1).

3. Results and discussion

Oxide catalysts selected for the study are known to be active in the deep oxidation of organic compounds in the gas phase [10,11]. Ru–Ce-supported catalysts have been described in the literature as active in WAO of various substances, including acetamide and acetic acid. However, according to recent publications

Table 2
Test in butane oxidation at 573 K (0.2% C_4H_{10}/air mixture)

Catalyst	BET surface area (m^2g^{-1})	Supported metal content (wt%)	Activity, $W\cdot10^2$ ($ml^3_{C_4H_{10}}\ g^{-1}\ s^{-1}$)
Pt/γ-Al_2O_3			
(1)	166	0.56	0.14
(2)	141	0.55	0.13
Mn–Al–O_x			
(1)	33	4.2	0.48
(2)	30	4.2	0.30
Co_3O_4/γ-Al_2O_3			
(1)	168	7.3	0.009
(2)	123	6.9	0.011

[2,12], up to now all attempts to develop solid catalysts stable in water solutions failed. As a rule, existing WAO catalysts quickly decompose because of a strong chemical interaction between catalyst support and water. Moreover, their active component is washed away. Therefore, at first we tried each catalyst towards the influence of pure water at high temperatures and pressures. We have found that all catalysts appear to be stable, and do not decompose during the 5 h autoclave treatment at 473 K (1.55 MPa). Activity tests in deep oxidation of butane show negligible activity changes at 573 K, as we compare fresh samples (1) and those after exposure to water (2). Table 2 summarized the results obtained for three typical complete oxidation catalysts.

However, beside general stability, catalysts for WAO of N-containing organics need also to be active in the complete oxidation of hydrocarbon chain, and to be selective in the conversion of N-containing groups to the molecular nitrogen. As we have noted elsewhere [13,14], oxygen-containing compounds (for example, mixtures of alcohols) are most suitable model mixtures to test catalysts with respect to complete oxidation of organic molecules. The reason is that many intermediates form in the reaction course depending on (i) active component nature, (ii) chemical composition of oxidized molecules, (iii) process conditions, and (iv) support chemical composition. Table 3 summarized the results of catalyst testing in WAO of saturated alcohols mixture. Apparently, graphite-like carbon and supported Ru/C-catalyst are most active.

The catalysts provide practically complete alcohols oxidation at 423 K in 1 h. However, in some cases partial oxidation products form, especially over Pt/γ-Al_2O_3 and Pt–Pd/γ-Al_2O_3. Activated carbons AG-3 (including the hydrophobilized samples) demonstrate comparatively low catalytic activity. Unlike graphite-like carbon, carbons AG-3 undergo essential partial oxidation under WAO conditions.

Table 3
Testing of catalysts in wet oxidation of alcohols mixture (T=473 K, t=1 h, 0.02% ROH/water mixture)

Catalyst	C/C_o EtOH	C/C_o n-C_3H_7OH	C/C_o i-BuOH
C (graphite-like carbon)	0.05	<0.01	<0.01
C (activated carbon AG3)	0.22	0.08	<0.01
Ru-Ce/C	0.04	<0.01	<0.01
Mn_2O_3/γ-Al_2O_3	0.44	0.2	0.3
Ru/C (graphite-like carbon)	$\ll$0.01	$\ll$0.01	$\ll$0.01
Ru–Ce/γ-Al_2O_3	0.01	<0.01	<0.01
Pt–Pd/γ-Al_2O_3	0.32	0.11	0.15

C/C_o the ratio of final and initial concentrations.

Table 4 compares the activities of catalysts in the selective oxidation of carbamide (as N-containing compounds). Selectivity towards N_2 is a key factor characterizing catalyst work. In special experiments catalysts were tested for active component washout, and for catalyst resistance to water. Catalyst mechanical damage was prevented by using a specially designed basket. If compared to oxide catalysts, system Ru/graphite-like carbon appears to be most suitable for WAO of carbamide. It shows a high selectivity towards N_2 (about 70% at 473 K), and almost no active component washout (activity of fresh catalyst and reused catalyst remains unchanged).

Same catalyst (Ru/graphite-like carbon) shows high activity in WAO of acetonitrile and N,N-dimethyl formamide. In both cases, CO_2 and N_2 are present in the gas phase. Conversion of N-containing com-

Table 4
Catalysts testing in carbamide wet oxidation

Catalyst	Yield of CO_2 (vol%)	Selectivity towards N_2 (%)
Ru/ graphite-like carbon	50.5	70.5
Fe_2O_3/γ-Al_2O_3	38.2	6.0
Mn–Al–O_x	24.3	7.4
0.56% Pt/γ-Al_2O_3	20.3	25.0
K–Mn–O_x/γ-Al_2O_3	47.8	14.4
K–Mn–O_x/α-Al_2O_3	23.0	9.4
CeO_2/graphite-like carbon	28.3	12.0
Ru–Ce–O_x/graphite-like carbon	40.3	48.4
Zn–Fe–Mn–O_x/γ-Al_2O_3	25.3	11.1

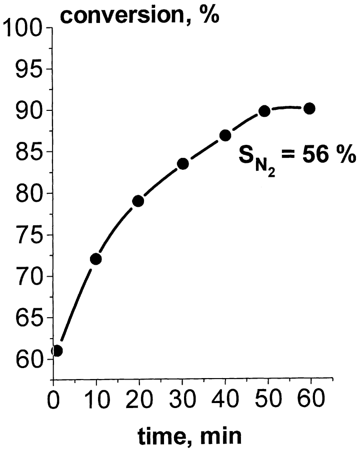

Fig. 2. Acetonitrile conversion at 473 K as a function of time (P_{total}=3.0 MPa, Ru/C-catalyst).

pound ranges within 91–95%, but selectivity towards N_2 is not higher than 55–60% at 473 K (see Fig. 2). Most likely, the reason is that partial oxidation products form. When the process is operated under more severe conditions (513 K, 4.5 MPa), the conversion of mixture organics/oxygen is almost complete.

There is no doubt that Ru/graphite-like carbon is highly stable in WAO of N-containing organic compounds mainly due to the support properties. Some unusual features of the graphite-like carbon material used to prepare Pd/carbon catalyst are well described in [15]. Further reaction mechanism studies are required to explain the Ru/carbon catalyst performance.

4. Conclusions

Various solid catalysts (oxide and Me-supported systems) have been prepared and tested to remove N-containing organics on waste water treatment using WAO. Optimum process conditions for the best catalyst (Ru/graphite-like carbon) are: partial oxygen pressure – 1.0 MPa, temperature range – 473–513 K. At 0.5–5.0 MPa total pressure, 433–523 K, catalyst shows good resistance to water, and high activity (residual content of toxicants is less than 1% from the initial one). No NO_x and NH_3 are detected. There are no legal restriction to catalyst use, since it is harmless to environment.

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