

Water depollution and the odor control by Wet air catalytic oxidation of ammonia, sulfides and mercaptans of industrial wastewaters

N. M. Dobrynkin, M. V. Batygina, A.S. Noskov

Boreskov Institute of Catalysis of Siberian Branch of Russian Academy of Sciences,

Pr. Ak. Lavrentieva, 5, Novosibirsk-90, 630090, RUSSIA

Catalytic properties of the carbon material Sibunit (commercial samples) and ceria-and zirconia-promoted precious metals (Ru, Pt, Pd) supported on carbon were studied in the processes of the catalytic wet air oxidation (CWAO) of number toxic odour compounds at elevated pressures and temperatures ($T=160 - 250\text{ }^{\circ}\text{C}$, $P_{\text{O}_2}=0.3 - 1.0\text{ MPa}$).

A possibility of the creation of effective ruthenium catalysts Ru-CeO₂/Sibunit and Ru-ZrO₂-CeO₂/Sibunit with a low ruthenium content ($\sim 0.6\%$ Ru) for the deep cleaning of the polluted waters at the moderate temperatures and the odor prevention is demonstrated.

1. Introduction

Many industrial plants produce the large amount of wastewaters containing the odorous toxic substances in forms of persistent inorganic and organic compounds. For instance, wastewater of coke enterprises contains ammonia, cyanides and thiocyanates, and wide set of organic pollutants: nitrogen-, sulfur- and oxygen-containing heterocyclic compounds, phenols and other aromatic substances (Ganczarzyk and Benedek, 1983, V'azquez, et.al, 2007). Other powerful sources of nitrogen-, and sulfur-contaminated wastewater are chemical plants and refineries, pulp and paper enterprises which manufactures various odorous compounds, such as methylamines, isothiocyanates, sulfides, disulfides, mercaptans, etc. (Fang, 1993, Mishra, et.al., 1995, Luck, 1999, Debellefontaine and Foussard, 2000). Several technologies are used to treat and/or remove such substances directly in medium of wastewater in order to minimize emissions of odour pollutants in environment.

Biological, chemical, thermal treatments and liquid oxidation and photocatalytic oxidation are most widely spread, but unfeasible for many concrete cases due to their evident drawbacks and limitations for use (Wang, 1992, Wilhelmi and Knopp, 1979, Halmann, 1996). Present technologies of the liquid-phase oxidation of multy-component polluted water systems by oxygen mainly perform in the conditions at which formed desirable harmless products are only the part of the numerous products of oxidation (Martin, et.al., 2005). Among the oxidative wastewater treatments, catalytic wet air oxidation (CWAO - catalytic oxidation in liquid phase at elevated pressures and temperatures) appears as one of the most promising, a low-cost and an effective way of

the odor-control (Béziat et.al., 1997, Gallezot et.al., 1997, Michèle Besson and Pierre Gallezot, 2005, Stüber et.al., 2005). CWAO in the presence of solid catalysts allows one to eliminate the odorous molecules and to convert them into environmentally friendly products (e.g. CO₂, N₂, H₂O, and sulfates). Besides, CWAO is particularly cost effective for treatment of industrial wastewaters with medium chemical oxygen demand ($10 \text{ gO}_2 \text{ L}^{-1} < \text{COD} < 150 \text{ gO}_2 \text{ L}^{-1}$, Mikulová, et.al., 2007).

This paper focuses on the catalytic and adsorptive properties of catalytic systems prepared of the carbon material Sibunit (porous graphite-like materials; Likholobov, et.al., 1995) and ceria-and zirconia-promoted precious metals (Ru, Pt, Pd) supported on carbon in the processes of the catalytic wet air oxidation of mentioned above odour pollutants, such as ammonia, sulfides and mercaptans of industrial wastewaters.

2. Materials and methods

2.1 Preparation and Characterization of catalysts

Supports were commercial Sibunit-3 and Sibunit-4 samples manufactured at the Institute of Hydrocarbon Processing (Omsk, Russia). BET surface areas (S_{BET}) equal to 360 – 380 m²/g were determined from single-point adsorption of nitrogen at 77 K.

Ru/C. A pre-washed and dried commercial Sibunit samples were impregnated with a solution of carbamide complex of Ru(II), evaporated to air-dry state in a water bath, dried in air at 120°C for an hour and reduced in flowing hydrogen at 450°C for 4 hours.

(Ru + CeO₂ + ZrO₂)/C, (Ru+CeO₂)/C samples were prepared by successive supporting ZrO₂, CeO₂ and Ru, which involved impregnation by aqueous Ce(NO₃)₃·6H₂O, ZrO(NO₃)₂·2H₂O and, after drying at 100°C, calcinations in an atmosphere of argon at 460° C for 4 h. Ru was supported as described above.

Procedural details for the other samples are given elsewhere (Dobrynkin et. al., 2005).

Principally, three aims were identified and solved: (1) minimization of Ru loading in the catalyst, (2) introduction of promoters to provide complete oxidation of organic compounds adsorbed on the catalyst surface, and (3) prevention of the leaching of active component.

Active component concentrations were determined by X-ray fluorescent technique using a VRA-20 instrument with a W anode in the X-ray tube. TEM micrographs were recorded on a Hitachi H-600 transmission electron microscope and used for determination of dimensions and distribution of nanoparticles.

Perfect-mixing batch stainless steel reactor of 200 ml volume was used for experiments (Batygina, et.al., 2000). Sample weight was ca. 1 g. When the same catalyst sample was used for a series of experiments, the catalyst was not taken out of the basket but washed with hot (60 °C) distilled water. Pure oxygen batches fed to the reactor from a balloon was used for oxidation in all the experiments.

2.2 Solutions and Analysis

Catalytic wet air oxidation reactions were carried out with model solutions (MS) of typical contaminants: ammonia, aniline, phenol ($C=1.0 \text{ g l}^{-1}$) prepared from commercial products (analytical purity grade), and real wastewaters were used from industrial coke plant (WW1), refinery (WW2) and pulp plant (WW3).

Gas chromatographic analysis (a gas chromatograph CVET –560, TCD + FID) was used to determine both the concentrations of the organic substances in aqueous solutions and the gas phase composition (O_2 , CO_2 , CO , N_2 , N_2O , NO , NH_3). Liquid samples to be analyzed were filtered to remove suspended matters. Intermediates formed during the liquid-phase oxidation were studied by chromat-mass-spectrometry using a VG-7070 gas chromatograph; samples of the aqueous solution and samples obtained by extraction of organic substances with diethyl ether from the aqueous solution were analyzed. Additionally routine procedure was applied to determine the chemical oxygen demand (COD) and total content of the organic contaminants (TOC) via oxidation with potassium dichromate $K_2C_2O_7$ (Bitton, 1998). A standard pH-meter was used to measure pH of solutions.

3. Results and Discussion

The catalytic results can be seen in Table 1. In general, the blank CWAO experiments performed on the carbon support indicates clearly the self-activity of Sibunits in any cases. This phenomenon has been pointed and the nature of Sibunit catalytic activity has been investigated by various methods by authors of present paper early (Batygina, et.al., 2003, and Dobrynkin et.al., 2005).

The most promising results presented in Table 1 show that the Sibunit-supported catalysts have the highest catalytic activity for oxidation of different molecules (which are hard for biodegradability due to their high toxicity) and transformation of all the intermediate organic compounds to CO_2 . Rather important results for Ru- CeO_2 /Sibunit and Ru- CeO_2 - ZrO_2 /Sibunit systems is the found out high selectivity (up to 93-99%) of formation of ecologically friendly compounds from heteroatomic fragments of oxidable molecules, e.g. N_2 formation from nitrogen- containing groups, SO_4^{2-} - from sulfides. The highest activity values are obtained for Ru- CeO_2 /Sibunit and Ru- CeO_2 - ZrO_2 /Sibunit samples, in which Ru nanoparticles (d~1-5 nm, according to our TEM data) are closely located to CeO_2 (d~ 1-5 nm and aggregates) and ZrO_2 (d~ 1 nm) (Figure 1).

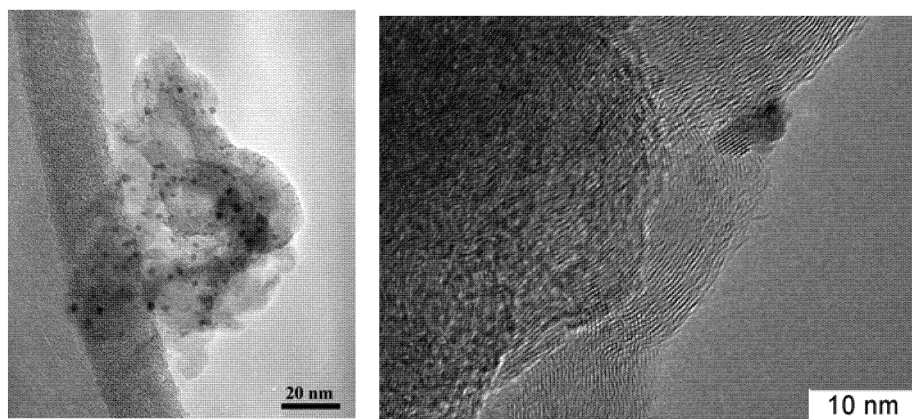


Figure 1. TEM images of Ru- CeO_2 /Sibunit (left) and Ru- CeO_2 - ZrO_2 /Sibunit active catalysts.

Table 1 Performance of Sibunit, Me /Sibunit, Ru-CeO₂/Sibunit and (Ru +CeO₂ + ZrO₂) /Sibunit catalysts in CWAO reactions of contaminants in model solutions and industrial wastewaters

Contaminant, C ₀ , gL ⁻¹	Catalyst	Temperature, °C	Time, h	Conversion, %	Selectivity, %
Sodium Sulfide / WW3, 75	Sibunit-3	100	1	100	to Na ₂ SO ₄ 99.3
Sodium Sulfide / WW2, 14.1	Sibunit-3	100	1	100	to Na ₂ SO ₄ 99.8
Mercaptans and Disulfides / WW2, 1.22	Sibunit-3	250	1	100	to Na ₂ SO ₄ 99.9 to CO ₂ 92.2
Ammonia /MS, 1.0	4.8%Ru/ Sibunit-4	260	1	100	to N ₂ 100
Sodium Sulfide / WW3, 75	4%Pd/Sibunit-3	100	1	99.3	to Na ₂ SO ₄ 96.8
Aniline /MS, 1.0	5%Ru /Sibunit-4	160	3	71.0	to CO ₂ 13.2
Phenol/ MS, 1.0	(0.5%Ru+ 0.5%Pt)/ Sibunit-4	160	3	100	to CO ₂ 20.5
Phenol/ MS, 1.0	4%Pd / Sibunit-4	160	3	94.0	to CO ₂ 1.0
Ammonia /WW1, 0.32	(0.6% Ru+8%CeO ₂) /Sibunit-4	250	1	100	to N ₂ 100
Mercaptans and Disulfides / WW2, 1.22	(0.6% Ru+ 2.5%CeO ₂ + 2.5% ZrO ₂)/ Sibunit-4	230	1	100	to Na ₂ SO ₄ 99.9 to CO ₂ 97.5
Aniline / MS 1.0	(0.6% Ru+ 8%CeO ₂) / Sibunit-4	160	3	99.7	to CO ₂ 69.3
Aniline / MS 1.0	(0.6% Ru+ 2.5%CeO ₂ + 2.5% ZrO ₂)/ Sibunit-4	160	3	98.8	to CO ₂ 71.2
Phenol/ MS, 1.0	(0.6%Ru+5%CeO ₂) / Sibunit-4	160	3	100	to CO ₂ 96.3
Phenol/ WW1, 0.47	(0.6%Ru+5%CeO ₂) / Sibunit-4	160	3	100	to CO ₂ 88.2
Phenol/ WW1, 0.47	(0.6% Ru+ 2.5%CeO ₂ + 2.5% ZrO ₂)/ Sibunit-4	160	3	100	to CO ₂ 94.1

Additional experiments were performed in a batch reactor for checking of possibilities to use the catalytic system of Ru-CeO₂/Sibunit as adsorbent and either as catalyst

simultaneously for deep oxidation of aniline and phenol, taken as examples of pollutants. Thus there is a capability to realize an adsorption, regeneration and oxidation, by means of combination of them carried out in solution of cleaned fluid. So for aniline and phenol adsorption on carbon catalysts at room temperature (1 h) we have observed a decrease of concentrations of these substances on 74 % and 92% accordingly. The further temperature rise with simultaneous oxygen supply (3 h) results in oxidation both of adsorbed and desorbed species on a surface of catalyst. At periodic repeated realization of process it results in a 99.99% degree of cleaning of water solutions with initial concentrations of aniline and phenol of 1.00 g/l.

Full cleaning (more than 99, 99) is possible at continuous realization of process in unsteady conditions. The experimental results indicate that there is another way for mount to high level of cleaning solutions by use two-stage process.

So, design of more active catalytic systems allow to oxidize typical hard-mineralized aniline and phenol almost completely at 160 °C in wet air oxidation process (Table 1), that is applicable for sharp abatement of pollutants concentration at first stage and use catalytic - adsorptive technique for further deep cleaning of the solutions at second stage. The comparisons of our data with previously published results on ruthenium/carbon catalysts shows that promoted Ru/Sibunit supported catalysts are much more active and selective. Possible reasons of high activity of Ru-CeO₂/Sibunit and Ru-CeO₂-ZrO₂/Sibunit catalysts are seems to be explained by i) influence of Sibunit and ii) interaction of Ru nanoparticles with CeO₂ particles supported on carbon. This interaction is probably very beneficial to the activity of the catalysts.

4. Conclusions

A possibility of the creation of effective ruthenium catalysts Ru-CeO₂/Sibunit and Ru-ZrO₂-CeO₂/Sibunit with a low ruthenium content (~0.6% Ru) for the deep cleaning of the polluted waters at the moderate temperatures and the odor prevention is demonstrated.

The described catalysts and method are solving the problem of the development of the environmentally reliable method for the treatment of the fluids and allow carrying out the adsorption of the pollutants on the carbon catalyst with the following regeneration of the carbon catalyst without the loss of adsorptive qualities. The experiments have shown a principal capability simultaneously to use the carbon catalyst as the adsorbent and either as the catalyst, or as the catalyst support for oxidation of the odorous substances in water solutions.

The catalysts allow: a) to decrease the mineralization temperature for typical organic pollutants from 200–240 °C to 160 °C, and b) to increase the activity of the low ruthenium content catalyst. The full cleaning (more than 99, 99 %) is possible at the continuous realization of the process in the unsteady conditions.

References

- Batygina M., Dobrynkin N., Noskov A., 2003, Catalytic Liquid-Phase Oxidation by Oxygen for Purification of Industrial Wastewater, *Studies in Surface Science and Catalysis*, 145, 359-362.

- Besson M., Gallezot P., 2005, Stability of ruthenium catalysts supported on TiO₂ or ZrO₂ in catalytic wet air oxidation *Topics in Catalysis*, 33, 101-108.
- Béziat J.C., Besson M., Gallezot P., Juif S. and Durécu S., 1997, Catalytic wet air oxidation of wastewaters, 3rd World Congress on Oxidation Catalysis, Elsevier, Amsterdam, 110, 615-622.
- Bitton G., 1998, Formula handbook for environmental engineers and scientists, Wiley-Interscience, New York.
- Debellefontaine H. and Foussard J.N., 2000, Wet air oxidation for the treatment of industrial wastes. Chemical aspects, reactor design and industrial applications in Europe, *Waste Management*, 20, 15-25.
- Dobrynkin N.M., Batygina M.V., Noskov A.S., Tsyrlunikov P.G., Shlyapin D. A., Schegolev V.V., Astrova D.A., Laskin B.M., 2005, Catalysts Ru-CeO₂/Sibunit for catalytic wet air oxidation of aniline and phenol, *Topics in catalysis*, 32, 69-76.
- Fang H.-Y., Chou M.-S. and Huang C.-W., 1993, Nitrification of ammonia-nitrogen in refinery wastewater, *Water Research*, 27, 1761-1765.
- Gallezot P., Chaumet S., Perrard A., Isnard P. 1997, Catalytic Wet Air Oxidation of Acetic Acid on Carbon-Supported Ruthenium Catalysts, *Journal of Catalysis*, 168, 104-109.
- Ganczarczyk J.J. and Benedek A., 1983, State-of-the-art in coke-plant effluent treatment, *Critical Rev. in Environmental Science and Technology*, 13: 2, 103 — 115.
- Halmann M., 1996, Photodegradation of Water Pollutants, CRC Press, Boca Raton.
- Likholobov V. A., Fenelonov V. B., Okkel L. G., Goncharova O. V., Avdeeva L. B., Zaikovskii V. I., Kuvshinov G. G., Semikolenov V. A., Duplyakin V. K., Baklanova O. N., Plaksin G. V., 1995, New carbon-carbonaceous composites for catalysis and adsorption, *React. Kinet. Catal. Lett.*, 54, 381-411.
- Luck F., 1999, Wet air oxidation: past, present and future, *Cat. Today*, 53, 81-91.
- Martin A.; Luck F.; Armbruster U.; Patria L.; Radnik J.; Schneider M., 2005, Ammonia removal from effluent streams of wet oxidation under high pressure, *Topics in Catalysis*, 33, 155-169.
- Mikulová J., Rossignol S., Barbier Jr. J., Mesnard D., Kappenstein C., Duprez D., 2007, Ruthenium and platinum catalysts supported on Ce, Zr, Pr-O mixed oxides prepared by soft chemistry for acetic acid wet air oxidation *Applied Catalysis B: Environmental*, 72, 1-10.
- Mishra V., Mahajani V., Joshi J., 1995, Wet Air Oxidation, *Ind. Eng. Chem. Res.*, 34, 2-48.
- Stüber F.; Font J.; Fortuny A.; Bengoa C.; Eftaxias A.; Fabregat A., 2005, Carbon materials and catalytic wet air oxidation of organic pollutants in wastewater, *Topics in Catalysis*, 33, 3-50.
- Vázquez I., J. Rodríguez-Iglesias, E. Marañón, L. Castrillo'n, M. A'lvarez, 2007, Removal of residual phenols from coke wastewater by adsorption, *J. Hazard. Mater.* 147, 395-400.
- Wang J.T., 1992, Effect of chemical oxidation on anaerobic biodegradation of model phenolic compounds, *Water Environ. Res.*, 64, 268-273.
- Wilhelmi A.R. and Knopp P.V., 1979, Wet air oxidation: an alternative to incineration, *Chem. Eng. Progress*, 75, 46-52.