

# Ruthenium Catalyst for Treatment of Water Containing Concentrated Organic Waste

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*The catalytic wet oxidation process (CWOP) is a promising technique for the treatment of highly concentrated organic wastewater that is difficult to degrade biochemically. This technique is based on the wet air oxidation (WAO) method of treating industrial effluent – in use for many years. WAO is a thermal liquid-phase process whereby organic substances in highly concentrated wastewater are oxidised by air at high temperatures and pressures, for long periods of time. Removal of ammoniac nitrogen and cyanide is, however, difficult. The CWOP aims to improve on the disadvantages of the WAO method. Tests were conducted to find the best catalysts. Catalyst CWO-II reduced the severity of the reaction required and improved the chemical oxygen demand and the total nitrogen conversion of organic wastewater.*

With advancing industrial development in China, water pollution is becoming an increasingly serious problem. The chemical, petroleum, pharmaceutical, pesticide, electroplating and coke industries, paper manufacture and sugar refining all produce large quantities of organic wastewater. Efficient processing of wastewater is important to prevent water sources from becoming polluted. Processing highly concentrated organic wastewater is difficult, even by biochemical methods; direct burning is very expensive, and high temperature oxidation has a low conversion percentage and fails to eliminate ammonia. Other technologies have looked at destroying organic waste and cleaning ground water (1, 2).

Wet air oxidation (WAO) is a thermal liquid-phase process in which organic substances are oxidised in wastewater by air at high temperature and pressure for long treatment times (3–6). Ammoniac nitrogen and cyanide, are difficult to remove. With WAO, the chemical oxygen demand (COD) conversion percentage of organic wastewater is 60 to 96%. The conversion of phenol and sulfur-containing organic compounds is nearly 99 %.

## Catalytic Wet Oxidation Process

The CWOP is a liquid-phase oxidation process using a solid catalyst in which organic compounds in aqueous solution are oxidised by oxygen or air at

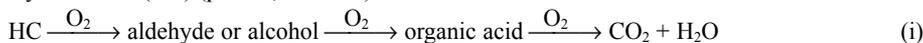
elevated temperatures and pressures. Aqueous-phase deep oxidation can be carried out at comparatively low temperatures and pressures (7). Various catalysts have been tested to reduce the severity of the reaction conditions and to improve the rate of the oxidation reactions of WAO (8, 9). Heterogeneous platinum group metal (pgm) catalysts are the ones generally selected.

For successful implementation of CWOP technology it is necessary to use efficient and durable catalysts and to determine the optimal process conditions. Ruthenium was selected as it is strongly resistant to corrosion from both acidic and basic solution at comparatively high temperatures and pressures. Catalyst deactivation can be related to the dissolution of metal on the catalyst surface due to pH changes in the reaction solution; however, although the pH of wastewater changes, the performance of Ru-based catalysts remains steady. Alumina and titania were examined as catalyst support materials. Titania was favoured because of its chemical stability, and the strong metal-support interaction in Ru/TiO<sub>2</sub> catalyst. Attention was also paid to the active components and manufacturing technology (10–14).

In CWOP technology, both pgms and non-noble metals are the active catalyst ingredients. Active ingredients are prone to run off the surface of non-noble catalysts due to changes in pH in the

Oxidation reactions typically taking place by catalysis in a CWOP reactor

Hydrocarbon (HC) (phenol, benzene):



NH<sub>3</sub>, ammoniac nitrogen, cyanide and N-containing organic compounds:



*Scheme*

reaction solution. However, pgm catalysts have a higher stability and activity.

Tests were conducted to find the best catalyst. Activity tests were undertaken in a batch reactor operated at 250°C, with a stirrer, using air as oxidant. Titania-supported catalyst was found to have higher activity than alumina-supported catalyst. Addition of a Group IIIB (rare earth) element to the pgm improved catalytic performance (15, 16). The rare earth element acted as an auxiliary catalyst.

In the industrial tests the chemical oxygen demand (COD) and total nitrogen (TN) conversion percentage of organic wastewater by the catalysts approached 99%. A catalyst with good performance (CWO-11) was selected and compared with a commercial catalyst of the same type using industrial wastewater. CWO-11 was found to be efficient at converting organic compounds in industrial wastewater that are difficult to convert biochemically to CO<sub>2</sub>, N<sub>2</sub> and H<sub>2</sub>O, see the Scheme. The CWOP equipment occupies less space than the biochemical method, and the energy produced during the oxidation can be recycled.

## Experimental Work

The carriers comprised mini-balls of 5 mm diameter TiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub>, of specific surface area 10–20 m<sup>2</sup> g<sup>-1</sup>, prepared by mechanical means. The carriers were soaked with active components of platinum group metals and auxiliary components,

such as Ce, La, etc. The catalyst was then dried, calcined and reduced. All catalysts were prepared in this way.

The organic wastewater used to evaluate the catalyst comprised:

- Simulated organic wastewater composed of ammonium sulfate and oxalic acid in amounts 28.3 g l<sup>-1</sup> and 7.4 g l<sup>-1</sup>, respectively, in distilled water.
- Organic wastewater produced by a coke oven plant (in Kunming). The COD and TN (total nitrogen, including ammoniac nitrogen, cyanide, and so on) are 4000 to 5000 mg l<sup>-1</sup> and 2000 to 3000 mg l<sup>-1</sup>, respectively. This wastewater typically also contains hydrocarbons, benzene, phenol and its derivatives, cyanide, ammoniac nitrogen, sulfur-containing organic compounds, NH<sub>3</sub> and H<sub>2</sub>S dissolved in aqueous phase.

## Simulated Laboratory Evaluations

The reaction conditions were kept constant throughout the tests. Temperature was at 250°C. The reaction vessel was equipped with a mechanical stirrer with a fixed stirring rate of 1000 rpm.

Organic wastewater was poured into the 500 ml flask. Catalyst (16 g) was then added, and air was introduced at a pressure of 28 kg cm<sup>-2</sup>. The reaction was free from external diffusion limitations. Diffusion is an indispensable procedure in a heterogeneous catalytic reaction. An improved flow rate for the reaction solution can eliminate the effect of external diffusion. If the reaction rate

$$\text{COD conversion, \%} = \frac{\text{COD of wastewater before reaction} - \text{COD of wastewater after reaction}}{\text{COD of wastewater before reaction}} \times 100\% \quad (\text{a})$$

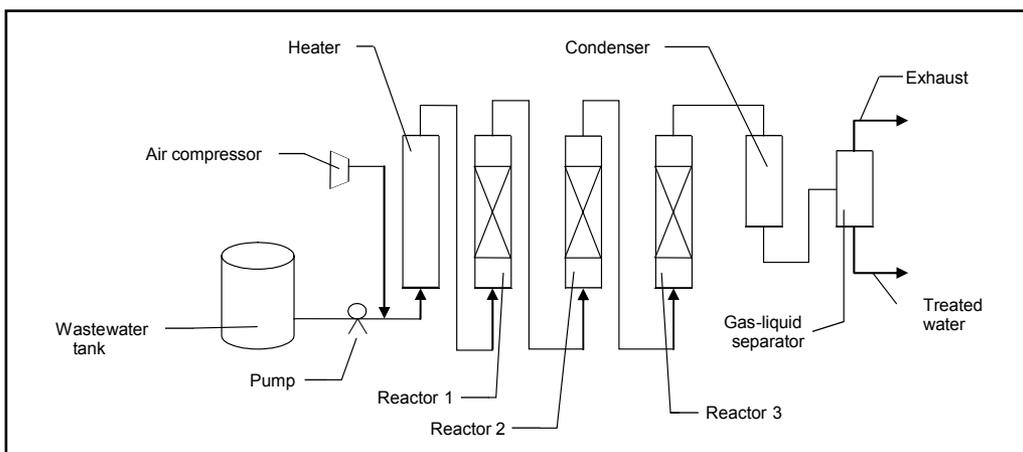


Fig. 1 Flow diagram of a simulated industrial test with three reactors where pH is measured at each reactor exit point

does not change along with the stirring rate (1000 rpm), the reaction is free from external diffusion limitations.

Catalytic runs of 30 minutes' duration were performed, after which the reaction was stopped by interrupting the air supply. The COD percentage conversion of organic wastewater was calculated according to Expression (a). Similarly, the TN content before and after the reaction can be used to give a conversion percentage.

### Simulated Industrial Conditions in A Pilot Plant

In this method 1 litre of solid catalyst was used in each of the three fixed-bed reactors; air and organic wastewater were continuously pumped in. The water flow used was  $4 \text{ l h}^{-1}$  (liquid hourly space velocity (LHSV) =  $1.3 \text{ h}^{-1}$ ) to treat the wastewater. A flow diagram of a simulated industrial test in the pilot plant is shown in Figure 1. The reactor is similar to one used for practical industrial operation. Four experiments were performed.

## Results and Discussions

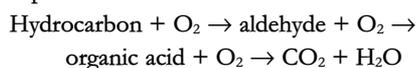
### Reproducibility of Conditions

For consistent evaluation and to differentiate between catalysts it is important to select suitable equipment and good evaluation conditions. A 500 ml batch reactor was selected. Wastewater from the coke oven plant (carbonising water containing phenol, benzene, carbon dioxide and hydrocarbons) was evaluated twice using the same catalyst.

Table I shows that the COD conversion percentages in the two experiments were very close when the same equipment and conditions were used. This confirms that equipment and catalyst evaluation conditions were comparable.

### Catalyst Evaluation by Batch Reactor

The CWOP is usually carried out at high temperature and pressure in an oxidative medium, the pH of which can vary greatly. The pH of the reaction system in the batch reactor was measured before and after the reaction, at each reactor exit point. The pH of the reaction system varies, for example with the reactions:



The catalysts tested for the purification of wastewater comprised carriers alumina or titania, and active components such as Pd, Ru and Group IIIB elements. Table II gives conversion data for wastewater from the coke oven plant. The catalyst

Number of runs	Catalyst	COD conversion, %
1	CWO-1*	83.85
2	CWO-1	83.82

\* CWO-1 is similar to catalyst CWO-11

Table II Evaluation of Different Catalyst Systems Using Wastewater from a Coke Oven Plant			
Catalyst	Catalyst system	COD conversion, %	TN conversion, %
CWO-2	Pd/Al <sub>2</sub> O <sub>3</sub>	79.8	5.6
CWO-12	Ru/TiO <sub>2</sub>	77.1	53.6
CWO-7	Ru/TiO <sub>2</sub>	78.3	43.8
CWO-8	Ru-Group IIIB/TiO <sub>2</sub>	80.4	44.8
CWO-10	Ru-Group IIIB/TiO <sub>2</sub>	74.9	33.5
CWO-11	Ru-Group IIIB/TiO <sub>2</sub>	85.2	66.5
CWO-9	Ru-Pd-Group IIIB/TiO <sub>2</sub>	76.8	48.7

system CWO-2 Pd/Al<sub>2</sub>O<sub>3</sub> is seen to be effective for COD conversion but not for TN conversion. Changing the active catalyst component to Ru and the support to TiO<sub>2</sub>, as in CWO-7 and CWO-12, increased the TN conversion percentage.

More effective catalysis was obtained when a Ru-Group IIIB catalyst was used, as in CWO-8, CWO-10 and CWO-11. CWO-11 was the most effective. Both the COD percentage conversion and the TN percentage conversion of CWO-11 were very high. The catalyst system CWO-9, which contained Ru, Pd and a Group IIIB addition/TiO<sub>2</sub> showed no advantage over the above catalysts.

### Comparison with a Commercial Catalyst

The performance of catalyst CWO-11 was compared in the batch reactor under identical reaction conditions with one of the best available commercial catalysts. This catalyst generally operates under similar conditions and with similar wastewaters. The results (Table III) show that the COD and TN percentage conversions of catalyst CWO-11 were higher than those of the commercial catalyst, with the difference for TN conversion being more pronounced.

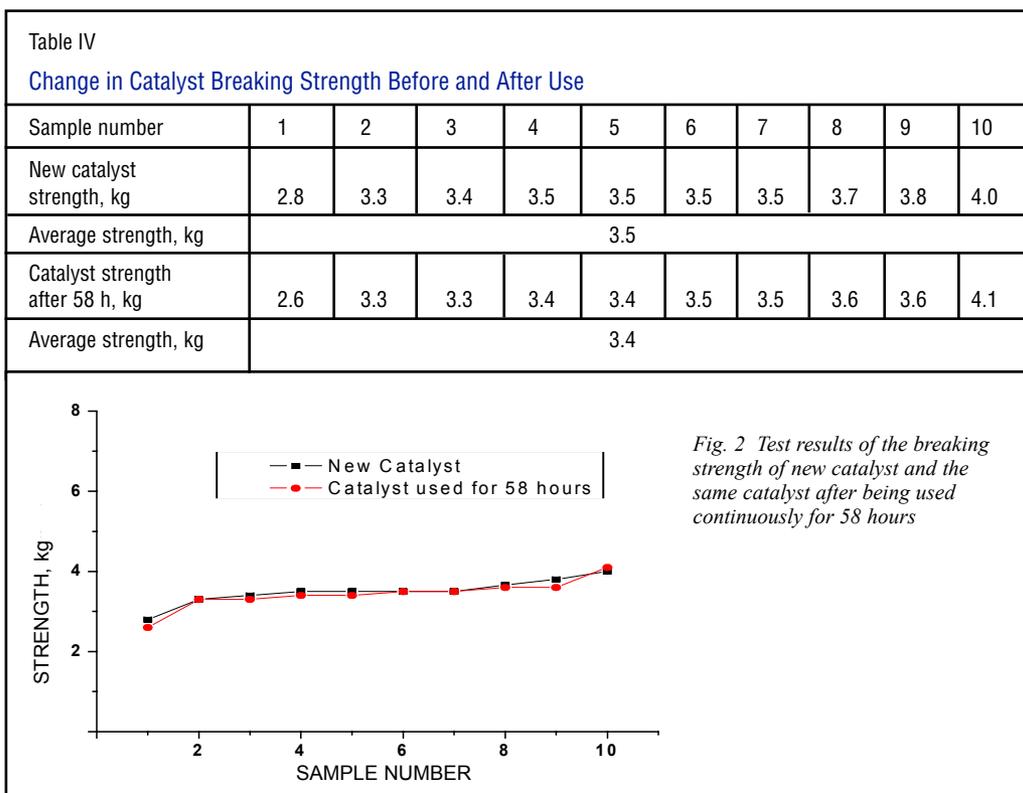
### Preliminary Examination of Changes in Catalyst Breaking Strength

Knowing the breaking strength of a catalyst is important as catalysts in fixed-bed reactors need to bear high pressures, especially in the lower part of a reactor, where catalyst could be crushed, leading to a drift of active components from the catalyst surface, and reduced catalytic activity. The breaking strength of the catalyst is defined by the pressure applied by steel plate as the catalyst is being broken. Measurements of catalyst strength were taken by a hand crusher method, during which a steel plate slowly crushes the catalyst.

The CWO-11 catalyst was tested under similar simulated conditions of reaction pressures: 90 × 2, 75, 60, 50 × 2 kg cm<sup>-2</sup>, and with large temperature increases and decreases. The processes were carried out one immediately after the other for 6 cycles for 58 hours (20 h for the reaction and 38 h for the temperature changes), see Figure 2.

The breaking strengths of the catalysts before and after being used for 58 hours were measured. Ten samples of each kind of catalyst were randomly chosen for testing. Table IV shows the results. The data indicate that catalyst strength

Table III Comparison of Catalysts		
Catalyst	COD conversion, %	TN conversion, %
CWO-11 (Kunming Precious Metals Institute)	85.2	66.5
Similar commercial catalyst (Osaka Gas Co. Ltd., Japan)	83.1	51.1



shows no obvious changes after testing over 6-cycles, each lasting for 58 hours. The catalyst could thus be used for long periods without crumbling.

### Results of Simulated Industrial Tests in a Pilot Plant on Catalyst CWO-11

As Table V shows, the COD percentage conversion for Reactor 3 exit point (R-3) is ~ 99.9%, (from 16,483.6 for raw wastewater down to 16.48)

and the TN percentage conversion has reached 100% (3528 for raw wastewater down to 0). The TN conversion percentage at Reactor 2 exit point (R-2) has also reached 100%.

Table VI shows that the TN percentage conversion at Reactor 1 exit point (R-1) has reached 100%. The COD percentage conversion at Reactor 2 exit point (R-2) is up to 99.9%.

In Table VII, the TN conversion percentage

Table V  
Tests on CWO-11 with Simulated Industrial Wastewater  
Experimental conditions: air pressure: 70 kg m<sup>-2</sup>, temperature: 250°C, water flow\*: 4 l h<sup>-1</sup>

Wastewater sample	O <sub>2</sub> , %	pH	COD, mg l <sup>-1</sup>	TN, mg l <sup>-1</sup>	Flow rate, l h <sup>-1</sup>	Exhaust volume, l h <sup>-1</sup>
Raw wastewater	20.8	9.1	16,483.6	3528	-	-
R-1 exit point**	12.2	3.5	7905.4	3.36	4.0	554.4
R-2 exit point	7.9	5.0	414.44	0	3.9	529.4
R-3 exit point	7.1	3.8	16.48	0	3.96	523.4

\* Wastewater moves smoothly and continuously, and is not recirculated. \*\* Exit points from Reactors 1, 2 and 3 are shown in Figure 1

Table VI						
Tests on CWO-11 with Simulated Industrial Wastewater						
Experimental Conditions: air pressure: 90 kg m <sup>-2</sup> , temperature: 270°C, water flow: 4 l h <sup>-1</sup>						
Wastewater sample	O <sub>2</sub> , %	pH	COD, mg l <sup>-1</sup>	TN, mg l <sup>-1</sup>	Flow rate, l h <sup>-1</sup>	Exhaust volume l h <sup>-1</sup>
Raw wastewater	20.8	8.5	16,483.6	3640.0	-	-
R-1 exit point	9.1	4.2	412.09	0	4.0	566.6
R-2 exit point	8.5	4.0	11.77	0	3.86	542.2
R-3 exit point	5.8	3.9	11.77	0	3.96	528

can be seen, at R-3 to reach 100%. However, the COD conversion percentage at R-3 is only up to 68%.

Table VIII shows, the COD percentage conversion at R-3 is up to 99.2%, while the TN percentage conversion reaches 99.9%.

Thus, experimental conditions of 70 kg cm<sup>-2</sup> and 250°C and also of 90 kg cm<sup>-2</sup> and 270°C can meet the requirements for use in the conversion of wastewater using catalyst CWO-11. An air pressure of 70 kg cm<sup>-2</sup> and reaction temperature of 250°C would be economically more desirable.

## Conclusions

We have obtained a new catalyst (CWO-11) for use in the catalytic wet oxidation process that is effective for converting organic compounds in simulated wastewater and wastewater from a coke oven plant into CO<sub>2</sub>, H<sub>2</sub>O and N<sub>2</sub>. CWO-11 has a higher activity for COD and TN conversions than a similar commercial catalyst. The COD and TN conversion percentages of organic wastewater are up to 99%.

CWO-11 been used in scaled-up reactors, in a batch reactor in the laboratory and in a continuous

Table VII						
Tests of CWO-11 with Simulated Industrial Wastewater						
Experimental conditions: air pressure: 50 kg m <sup>-2</sup> , temperature: 230°C, water flow: 4 l h <sup>-1</sup>						
Wastewater sample	O <sub>2</sub> , %	pH	COD, mg l <sup>-1</sup>	TN, mg l <sup>-1</sup>	Flow rate, l h <sup>-1</sup>	Exhaust volume, l h <sup>-1</sup>
Raw wastewater	20.8	8.5	16,483.6	3640.0	-	-
R-1 exit point	15.8	5.4	12,166.5	1372.0	3.96	548
R-2 exit point	12.3	3.5	10,890.9	2.160	3.92	518.2
R-3 exit point	8.4	3.6	5214.2	0	4.0	482.6

Table VIII							
Tests on CWO-11 with Wastewater from a Coke Oven Plant							
Experimental conditions: air pressure: 70 kg m <sup>-2</sup> , temperature: 250°C, water flow: 4 l h <sup>-1</sup>							
Wastewater sample	Reaction time, min	O <sub>2</sub> , %	pH	COD, mg l <sup>-1</sup>	TN, mg l <sup>-1</sup>	Flow rate, l h <sup>-1</sup>	Exhaust volume, l h <sup>-1</sup>
Raw wastewater	0	20.8	8.9	3000.5	756.0	-	-
R-3 exit point	45	15.5	5.4	33.21	0	4.4	269.7
R-3 exit point	45	15.0	2.5	14.53	1.12	4.04	291.6
Average value	45	15.2	4	23.87	0.6	4.2	280.6

process in a pilot plant. This method of catalyst evaluation has effectively differentiated between catalysts of different performance.

It is planned to increase and improve the mechanical strength of the catalyst and to use CWO-11 in further industrial applications.

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