

CATALYTIC REDUCTION OF NITRIC OXIDE IN AUTOMOBILE EXHAUST GASES

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ABSTRACT

The amount of nitric oxide from auto exhaust gases of engine is being reduced down to the environmental acceptable limits by means of a reactor-converter. Different prepared catalysts Ru, Os and Ir supported on γ -alumina were used to reduce nitric oxide. While Pt and Pd supported with γ -alumina were used to oxidize carbon monoxide. The impregnation technique had been used to prepare the catalysts.

Two and three layers of the selected catalysts had been employed in the reactor-converter. The three layers types are Ru-Pt-Pd, Os-Pt-Pd, and Ir-Pt-Pd, while the two layers types are Ru-Pt, Os-Pt, and Ir-Pt. The effect of temperature and gas hourly space velocity on the reduction of nitrogen oxide to nitrogen had been studied.

The prepared catalysts show high activity for NO reduction and CO oxidation. It was found that the conversion of nitric oxide to nitrogen increased with reaction increasing the temperature and decreasing the gas hourly space velocity. Also, it was noticed that the effect of temperature is more obvious than that of gas hourly space velocity.

INTRODUCTION

Automobile exhaust contains carbon monoxide, carbon dioxide, nitrogen oxides (mainly NO), water, hydrogen and nitrogen. The exhaust also can contain hundreds of hydrocarbons and particulates including carbon and oxidized carbon compounds, metal oxides, oil additives, fuel additives, and break down products of the exhaust system including the exhaust-control catalyst⁽¹⁾.

An automotive emission-control system must remove nitrogen oxides (NO_x), hydrocarbons (HC) and carbon monoxide (CO) from the exhaust.

Jones *et al.*⁽²⁾ had shown that at low temperature gaseous hydrogen is more effective than CO and will selectively reduce NO over platinum and palladium catalysts. The NO-H₂ reaction was susceptible to poisoning by lead, sulfur and carbon monoxide. At elevated temperatures, simultaneous CO oxidation and water gas shift activity influence the selectivity.

Sigg and Wicke⁽³⁾ have observed a Pd/Ag/Fe/Al₂O₃ catalyst to exhibit considerable activity for reducing NO in the presence of an excess of oxygen (NO-CO-H₂-O₂ feed stream).

Tauster and Murrell^(4,5) have described the competition as the partitioning of the reducing agent between NO and O₂:

The selective reaction of nitric oxide with hydrogen and carbon monoxide in the presence of excess oxygen has been the subject of several recent publications.

Schlatter and Taylor⁽⁶⁾ have found that the activity of a low loaded rhodium on alumina catalyst for promoting the reduction of NO in the presence of excess oxygen was improved by severe thermal aging. Interestingly, the catalysts activity for promoting the CO-O₂ reaction was greatly damaged by thermal aging.

Much of the early works on potential NO_x control focused on the rich operating condition encountered in the dual-bed approach. In the absence of oxygen, ruthenium is the most effective metal for selectively reducing NO to N₂ rather than NH₃⁽⁷⁾. However, small amounts of oxygen are detrimental to ruthenium catalysts. Certain base metal oxides have been shown to stabilize supported ruthenium against oxidation, but the long-term viability of such systems remains uncertain⁽⁶⁾.

Gandhi *et al.*⁽⁸⁾ have recently described the properties required of a three-way catalyst (Ru-Pt-Pd and Ir-Pt-Pd). One important property is the

ability to reduce NO selectively to N_2 under both rich and slightly lean operating conditions. The second requirement is oxidation activity sufficient to control CO and HC emission without the need for a separate oxidizing converter system ⁽⁶⁾.

This work deals with the use of two catalysts layers system (Ru-Pt, Ir-Pt, and Os-Pt), and three catalysts layer system (Ru-Pt-Pd, Ir-Pt-Pd, and Os-Pt-Pd) supported with γ -alumina for NO and CO removal from exhaust gases at different operating conditions.

EXPERIMENTAL WORK

Materials

1. Gamma alumina spheres (Kaiser low density γ - Al_2O_3 , 3 mm in diameter, bulk density of 0.55 g/cm^3).
2. Chloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$), Matheson, Coleman and Bell).
3. Iridium ammonium chloride ($(NH_4)_2IrCl_6$) BDH Chemical Ltd. Pool England.
4. Ruthenium ammonium chloride ($(NH_4)_2RuCl_6$) BDH Chemical Ltd. Pool England.
5. Osmium ammonium chloride ($(NH_4)_2OsCl_6$) BDH Chemical Ltd. Pool England.
6. Palladium chloride ($PdCl_2$) BDH Chemical Ltd. Pool England.

Catalyst Preparation

All catalysts were prepared by impregnation method using the apparatus shown in Fig. (1).

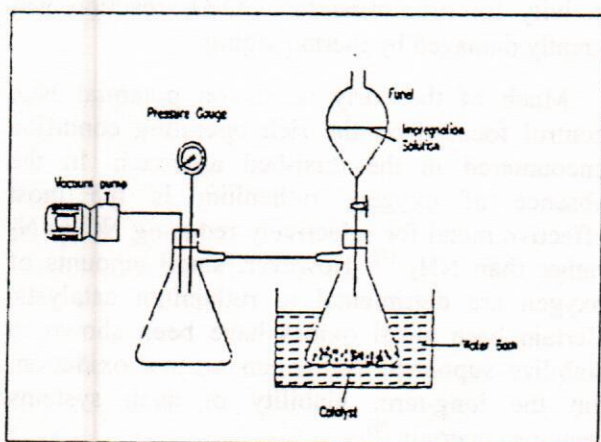


Fig. (1) Impregnation method apparatus

The carrier γ -alumina (3 mm diameter) was calcined at $600^\circ C$ for 2 hours then placed in a desiccator. The metal loading, the quantity of γ -alumina and the impregnation solution used in catalyst preparation are listed in Table (1).

Table (1) Type of Catalyst, Metal Loading, Quantity of γ -Alumina and the Impregnation Solution Used

Type of catalyst (Noble Metal)	Metal Loading (wt. %)	Quantity of γ - Al_2O_3 (g)	Impregnation Solution
Pt/ Al_2O_3	0.008	88	0.5 g of $H_2PtCl_6 \cdot 6H_2O$ in 44 ml of deionized water
Pd/ Al_2O_3	0.002	50	0.1 g of $PdCl_2$ in 25 ml of deionized water
Ru/ Al_2O_3	0.0022	29.7	0.1 g of $(NH_4)_2RuCl_6$ in 14.8 ml of deionized water
Ir/ Al_2O_3	0.0028	28	0.1 g of $(NH_4)_2IrCl_6$ in 14 ml of deionized water
Os/ Al_2O_3	0.0022	35.5	0.1 g of $(NH_4)_2OsCl_6$ in 17.7 ml of deionized water

Prior to impregnation, evacuation of the impregnation apparatus was conducted to remove the air from pores of the carrier.

The impregnation process was carried out under 5 mm Hg with shaking at fixed temperature ($70^\circ C$) for 3 hours, and the impregnation solution was added drop by drop. The impregnated alumina was dried with air overnight at room temperature, and heated slowly at $110^\circ C$ for 2 hours. Finally, the dried impregnated alumina is calcined at $580^\circ C$ for 4 hours in presence of air and then placed in desiccator.

The Experimental Unit

The reactor-converter temperature was controlled by steel jacket heater and voltage regulator (purchased from the superior Electric Company, Bristol, Connecticut, USA) and measured using two 1/8-inch chromel-alumel thermocouples.

The reactor-converter was connected with tailpipe of the engine exhaust (Volkswagen engine, 1300 Beetle, 1285 cc, model 1968). The flow diagram of the experimental unit is shown in Fig. (2).

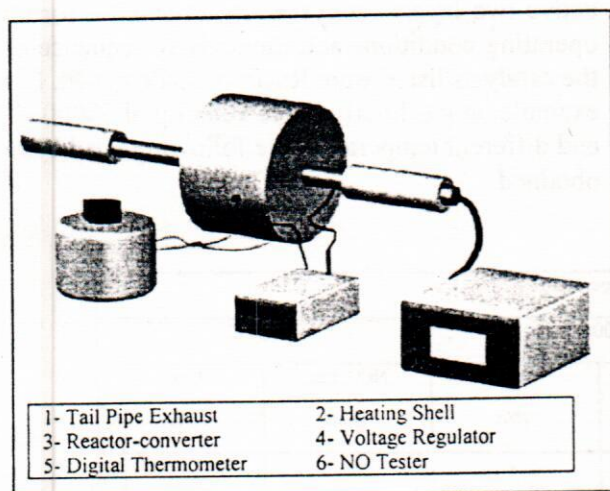


Fig. (2) The experimental Unit

The Procedure

The reactor-converter was attached to the tail pipe of the engine. Steady state operation of the engine was achieved after 5 minutes from starting then the exhaust gases were passed through a heating shell in order to raise and control the temperature of the gases prior to entering the reactor-converter.

The heating was conducted via a voltage regulator. Temperature recording of both the heating shell and the reactor-converter were performed using a digital thermometer. NO tester measures the concentration before and after the reactor-converter.

Test Methods

Nitrogen monoxide measurement

Nitrogen monoxide is determined by NO tester (portable) model EC-250 manufactured by Riken

Keike. Results of NO determination were double checked by a gas chromatography.

Carbon monoxide measurement

Carbon monoxide concentration is determined by CO indicator (testoryt, Bruno Ihtig. Pudenhofen. 6054 Rodgau Germany). The vol. % of CO is measured by a compacted Orsat analysis range (0-20 % volume).

RESULTS AND DISCUSSION

Effect of Temperature on the Conversion of Nitric Oxide to Nitrogen

Figures (3-5) present the results of the effect of temperature at different gas hourly space velocity on the conversion of NO to N₂ using three catalysts layers Ru-Pt-Pd, Os-Pt-Pd and Ir-Pt-Pd, respectively.

The temperature promotes the rate of reduction of NO to N₂ in general, and resulting in conversion increase.

These results are in good agreement with those obtained by Schlatter and Taylor⁽⁶⁾ for Ru-Pt-Pd and Ir-Pt-Pd catalysts.

The catalyst, Os-Pt-Pd, is firstly studied in this investigation and it shows higher activity than Ir-Pt-Pd catalyst. The activity sequence of the catalysts were Ru-Pt-Pd > Os-Pt-Pd > Ir-Pt-Pd. For example, at the gas hourly space velocity of 52000 h⁻¹ and at different temperature the following results are obtained:

Catalyst	Temperature					
	300 °C		400 °C		500 °C	
	NO Conc. ppm	Conv. (%)	NO Conc. ppm	Conv. (%)	NO Conc. ppm	Conv. (%)
Ru-Pt-Pd	5	86.11	-	-	-	-
Os-Pt-Pd	6	83.33	-	-	-	-
Ir-Pt-Pd	18	50.00	7	80.55	4	88.88

Figures (6-8) present the results of the effect of temperature at different gas hourly space velocity on the conversion of NO to N₂ using two catalysts layers Ru-Pt, Os-Pt and Ir-Pt, respectively.

Two catalyst layers are firstly studied in this investigation and show high activity. The more

active two layers catalyst is Ru-Pt catalyst for all operating conditions and the activity sequence of the catalysts listed were Ru-Pt > Os-Pt > Ir-Pt. For example, at gas hourly space velocity of 52000 h⁻¹ and different temperature the following results are obtained:

Catalyst	Temperature					
	300 °C		400 °C		500 °C	
	NO Conc. Ppm	Conv. (%)	NO Conc. ppm	Conv. (%)	NO Conc. ppm	Conv. (%)
Ru-Pt	7	80.55	-	-	-	-
Os-Pt	9	75.00	-	-	-	-
Ir-Pt	20	44.44	9	75.00	6	83.33

Effect of Gas Hourly Space Velocity on the Conversion of Nitric Oxide to Nitrogen

Figures (9-14) show the effect of gas hourly space velocity on the conversion of NO to N₂ at different temperatures. It is clear from these figures that the gas hourly space velocity has a slight effect on the conversion especially at higher values of gas hourly space velocity and lower

temperatures. Any way, the conversion increases at higher temperature with decreasing gas hourly space velocity. These results are in good agreement with those obtained by Taylor and Schlatter⁽⁶⁾, Taylor and Klimisch⁽⁸⁾.

Summary of the experiments at 300 °C for two and three catalysts layers is presented in Table (2).

Table (2) Comparison between Catalytic Activities of Ru-Pt-Pd, Os-Pt-Pd, Ir-Pt-Pd, Ru-Pt, Os-Pt, and Ir-Pt Catalyst at Different Gas Hourly Space Velocity and Fixed Temperature of 300 °C and Initial NO Concentration is 34 ppm.

Catalyst	Gas Hourly Space Velocity (GSHV)							
	104000 h ⁻¹		52000 h ⁻¹		35454 h ⁻¹		27857 h ⁻¹	
	ppm	Conv. (%)	ppm	Conv. (%)	ppm	Conv. (%)	ppm	Conv. (%)
Three Catalysts Layers								
Ru-Pt-Pd	11	69.44	5	86.11	3	91.66	2	94.44
Os-Pt-Pd	8	77.77	6	83.33	5	86.11	4	88.88
Ir-Pt-Pd	23	36.11	18	50.00	15	58.33	12	66.66
Two Catalysts Layers								
Ru-Pt	13	63.88	7	80.55	5	96.11	4	88.88
Os-Pt	4	69.44	9	75.00	6	83.33	3	91.66
Ir-Pt	25	30.55	20	44.44	16	55.55	14	61.11

Table (2) shows that catalyst Ru-Pt-Pd at 300 °C and gas hourly space velocity of 52000 h⁻¹ decreases NO concentration from 34 ppm to 5 ppm, which is less than the required level (10 ppm) ⁽⁵⁾. Anyway, two catalysts layers system, Ru-Pt, at 300 °C and 52000 h⁻¹ decreases NO concentration from 34 ppm to 7 ppm, which is also less than the required level.

It is preferable to use two catalysts layers, namely Os-Pt because it is easier to prepare than three catalysts layers in the converter and it satisfies the environmental requirement of NO in exhaust gases although Os-Pt gives slightly lower activity as compared with three catalyst layers

It is worthwhile to investigate the action of nitric oxide and carbon monoxide on these tetroxides at the experimental conditions. These species provide some of the unusual features of the catalyzed reactions. Usually the reduction of nitric oxide is occurred on exhibited on solid surface through chemisorption adsorption to form the adsorbed activated complex. The complex then decomposes and the products are desorbed as nitrogen and oxygen. Furthermore it well known that "the activation energy of a surface reaction should be less than for the corresponding homogenous reaction". Therefore, the catalytic reaction of these oxides with carbon monoxide and nitric oxide is homogenous.

CONCLUSIONS

- 1- The effect of temperature in the range of 50-450 °C and the gas hourly space velocity in the range of 27857-104000 h⁻¹ were studied and the results show that the temperature has a pronounced effect on the conversion while the gas hourly space velocity shows a slight effect especially at higher values of gas hourly space velocity and lower temperature.
- 2- The activity sequence toward NO reduction of the three catalysts layers tested were Ru-Pt-Pd > Os-Pt-Pd > Ir-Pt-Pd.
- 3- The activity sequence toward NO reduction of the two catalysts layers tested were Ru-Pt > Os-Pt > Ir-Pt.

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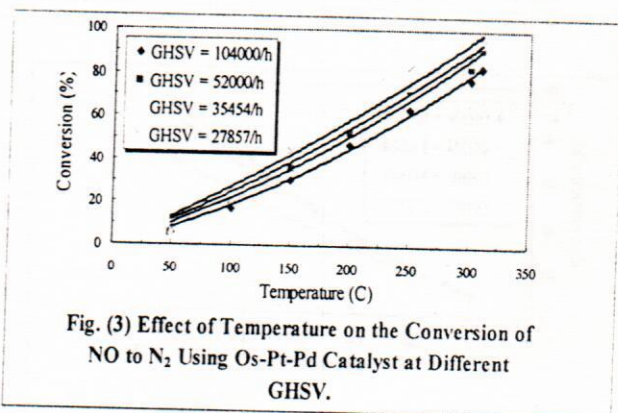


Fig. (3) Effect of Temperature on the Conversion of NO to N₂ Using Os-Pt-Pd Catalyst at Different GHSV.

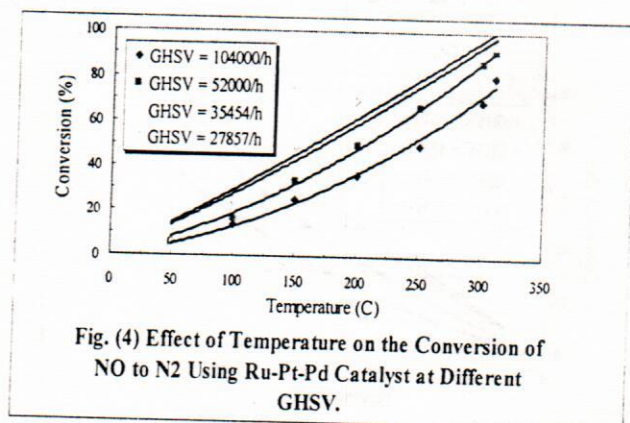


Fig. (4) Effect of Temperature on the Conversion of NO to N₂ Using Ru-Pt-Pd Catalyst at Different GHSV.

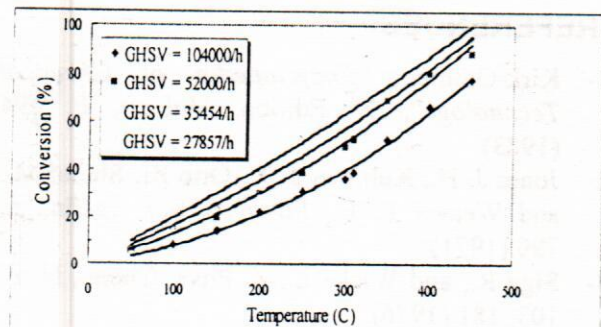


Fig. (5) Effect of Temperature on the Conversion of NO to N2 Using Ir-Pt-Pd Catalyst at Different GHSV.

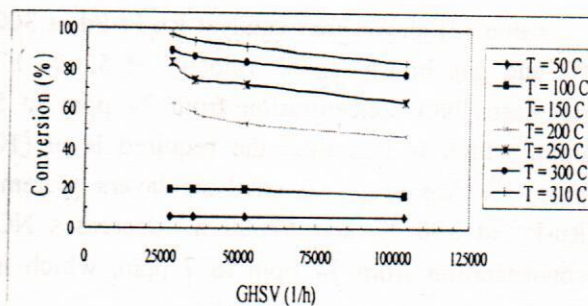


Fig. (9) Effect of GHSV on the Conversion of NO to N2 Using Os-Pt-Pd Catalyst at Different Temperatures

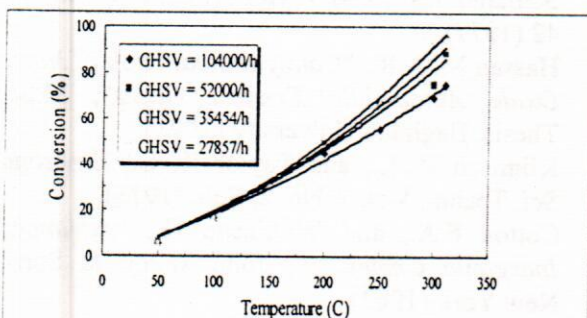


Fig. (6) Effect of Temperature on the Conversion of NO to N2 Using Os-Pt Catalyst at Different GHSV.

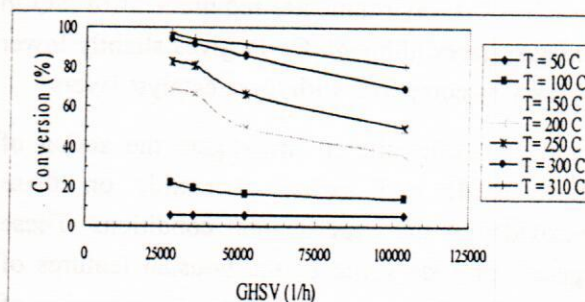


Fig. (10) Effect of GHSV on the Conversion of NO to N2 Using Ru-Pt-Pd Catalyst at Different Temperatures

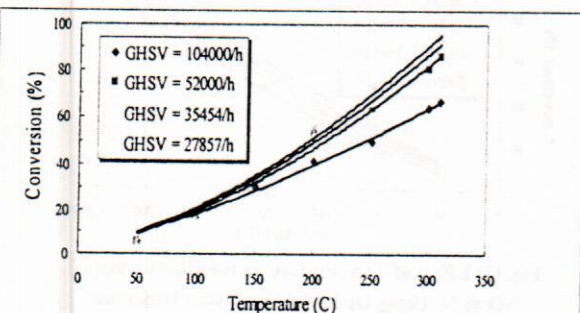


Fig. (7) Effect of Temperature on the Conversion of NO to N2 Using Ru-Pt Catalyst at Different GHSV.

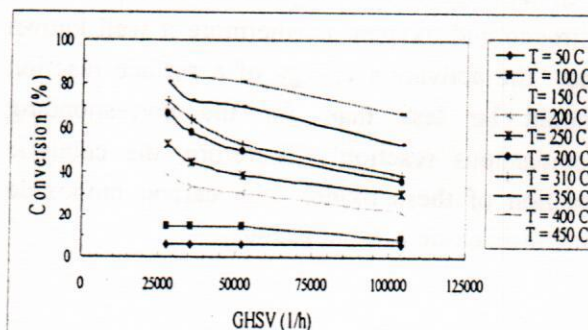


Fig. (11) Effect of GHSV on the Conversion of NO to N2 Using Ir-Pt-Pd Catalyst at Different Temperatures

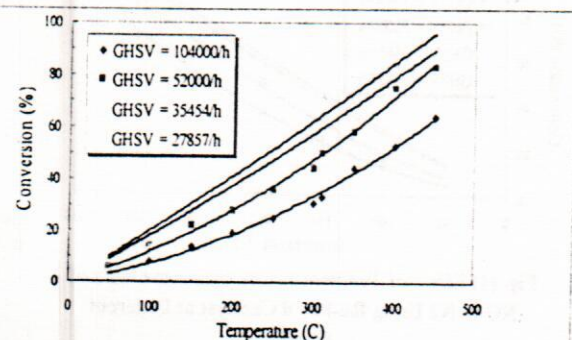


Fig. (8) Effect of Temperature on the Conversion of NO to N2 Using Ir-Pt Catalyst at Different GHSV.

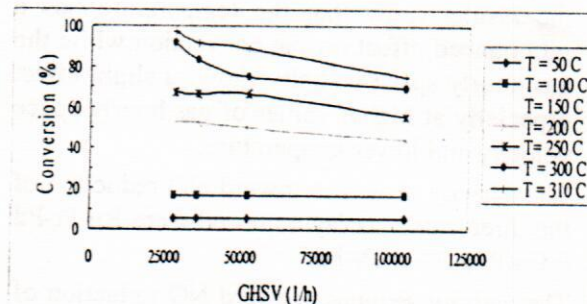


Fig. (12) Effect of GHSV on the Conversion Using of NO to N2 Os-Pt Catalyst at Different Temperatures

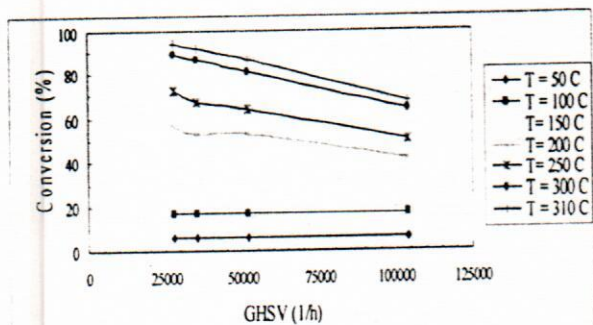


Fig. (13) Effect of GHSV on the Conversion of NO to N₂ Using Ru-Pt Catalyst at Different

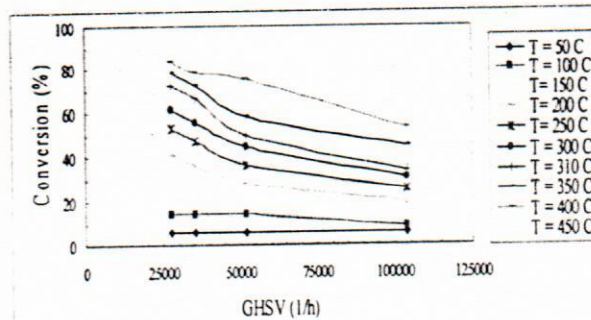


Fig. (14) Effect of GHSV on the Conversion of NO to N₂ Using Ir-Pt Catalyst at Different Temperatures