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# RESEARCH NOTE

# Microwave-Assisted Purification of Automotive Emissions

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**By coupling microwave heating with the catalytic action of a catalyst, the purification of simulated automotive exhaust was investigated over a noble metal catalyst. The effects of microwave heating on the lighting-off temperature and operation window were observed. By comparing the activity of the catalyst in the microwave heating mode with that in the conventional heating mode, it was found that microwave heating caused the lighting-off temperature of the catalyst to decrease remarkably. Even when 10% of $H_2O$ was added to the simulated exhaust, the lighting-off temperature could still be lowered more than 50°C. Meanwhile, the activity of the catalyst increased greatly at the low reaction temperatures, and the operation window was also enlarged, obviously by microwave irradiation.** © 2002 Elsevier Science (USA)

*Key Words:* **microwave-assisted catalysis; noble metal catalyst; local heating; simulated automotive exhaust; lighting-off temperature; operation window.**

## INTRODUCTION

The simultaneous control of nitrogen oxides (NO), carbon monoxide (CO), and hydrocarbon (HC) emissions from automobile exhaust can be achieved by the use of a three-way catalyst (TWC) in connection with an $O_2$ sensor and a closed-loop feedback control mechanism of the air–fuel ($A/F$) ratio (1–3). Standard TWC formulations are those containing mainly noble metals, such as platinum (Pt), rhodium (Rh), and palladium (Pd) (4–6).

The TWC has been in use since 1979. But its operation window (namely, the temperature range where the conversions of NO, CO, and HC are not less than 80%) is very narrow; i.e., its activity is too sensitive to $O_2$ concentration (7). With increased $O_2$ concentration, three-way action of the catalyst decreases quickly. However, in order to improve fuel economy, the focus for future automobiles is lean-burn engines, which will produce exhaust with a high $O_2$ concentration. TWC will not be able to function effectively in such conditions (8). Moreover, if the lighting-off temperature of the TWC is too high, it will cause a large quantity of exhaust gas to escape into the atmosphere without any purification before reaching the lighting-off temperature. Accordingly, future regulations of automotive emissions will require the control of emissions in the cool state of the engine.

In order to adapt to the future requirement of automotive emissions as depicted above, new techniques or new catalysts must be explored. Many new catalysts, such as Cu–ZSM-5 (9) and Co–ZSM-5 (10), have been found. However, these catalysts all have the same basic limitations (11), making supported noble metal catalysts still the most promising candidates for coping with this problem, by combining reasonable activities with good thermal stability and resistance to $SO_2$ (12).

Microwave-assisted reactions have been carried out in organic synthesis since 1986, and many novel results have been observed (13, 14). The preparation of catalysts by microwave heating has also been reported, with the catalysts obtained by this technique showing an obvious advantage compared with those treated by conventional heating (15). We have reported studies on microwave heating and discharge-assisted removal of NO (16–18). Conner and co-workers also found some advantages to microwave-assisted conversion of CO in automotive exhaust (19, 20). As microwave heating is a kind of “internal heating,” it possesses many characteristics, such as uniformity, quickness, and high-energy efficiency. Moreover, microwaves are easily absorbed by polar species, and automotive exhaust has many polar species, such as $H_2O$ and NO. So microwave-assisted catalytic reaction (MACR) of automotive exhaust was investigated in the present paper over noble metal catalysts containing Pt, Pd, and Rh. The effects of different heating modes on the lighting-off temperature were investigated. Interesting results from variations in the operation window as well as from the performance of the catalysts after addition of $H_2O$ to the simulated exhaust in MACR were obtained.

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## EXPERIMENTAL

### *Catalyst Preparation*

TWC was prepared by a conventional impregnation method. Aiming at the practicality of the method, honeycomb ceramic was used as a carrier, which had about 400 cells per in.$^2$ and a 0.3-mm wall thickness. First, high-surface-area alumina ($\gamma$-$Al_2O_3$) was coated on the honeycomb carrier, and then the honeycomb was dried at 80°C for 2 h and at 120°C for 4 h, and calcined at 600°C for 3 h. The honeycomb ceramic coated by $\gamma$-$Al_2O_3$ was the substrate. The substrate was impregnated with a complex solution containing $PdCl_2$, $RhCl_3$, and $H_2PtCl_6 \cdot 6H_2O$. The sample was dried at room temperature for 48 h, dried at 120°C for 2 h, and then calcined at 550°C for 3 h. Finally, the sample was reduced by $H_2$ at 500°C for 5 h. The resulting catalyst had 1 g noble metal loading per liter, in which the ratio of Pt/Pd/Rh was 3/5/10 (weight ratio). BET surface area of the catalyst was determined by nitrogen adsorption at 77 K; the value obtained was 90 m$^2$/g.

### *Catalyst Test*

Details of the MACR have been described elsewhere (16, 17). In all the experiments, microwave effective power ranged from 0 to 200 W. Catalyst tests were carried out in a steady-state plug-flow mode, using a quartz tubular reactor of 20-mm i.d. (inner diameter). Catalyst (5.3 ml) was used to evaluate catalytic activity. The flow rate of the simulated exhaust was 4417 ml/min (ca. GHSV = 50,000 h$^{-1}$). The simulated exhaust was composed of 1000 ppm NO, 1000 ppm $C_3H_8$, 0.5% $H_2$, 1.5% CO, 12% $CO_2$, variable $O_2$ (0.8–1.6%), and $N_2$ carrier gas. Each of these component gases was independently controlled with a mass flow meter. When observing the effect of $H_2O$ on the purification, 10% $H_2O$ vapor was introduced into the simulated gas by $N_2$ carrier gas. The reactants and products were all analyzed with an online five-gas analyzer for analyzing $C_3H_8$, NO, CO, $CO_2$, and $O_2$ (FGA4005, Foshan Instrument Corp., China). All product gases were measured after 30 min time on stream at each experimental temperature. The conversion of each reactant was calculated by its concentration in the gas streams before and after the reactor.

The stoichiometry number, $S$, used to identify the redox characteristics of the simulated gas is defined as (6)

$$S = \frac{2[O_2] + [NO]}{[H_2] + [CO] + 10[C_3H_8]}, \qquad [1]$$

where $[i]$ is the concentration of the reactant $i$ in the feedstream. In the case of $S < 1.0$, $S = 1.0$, $S > 1.0$, the feedstream is reducing, stoichiometric, and oxidizing, respectively.

The experiments were run in the conventional reaction (CR) mode and the MACR mode. In the CR mode, the experiments were carried out in the quartz reactor. The simulated exhaust was preheated first by a tubular oven, then passed into the catalyst bed, where the catalyst was heated by another tubular oven. The temperatures of the two ovens were controlled independently by a temperature-programmed regulator. The temperature of the simulated exhaust 10 mm from the upper surface of the catalyst bed was measured by an EU-2-type thermocouple (NiCr–NiAl thermocouple), which was regarded as the exhaust temperature in CR.

MACR was carried out in the same quartz reactor, which was aligned perpendicularly at the center of the waveguide and parallel to the electric field direction. Microwave energy was delivered continuously to the catalyst. Not all reactants were preheated, except in the case of added $H_2O$. In other words, room temperature reactants passed directly into the catalyst that was irradiated by microwaves. When $H_2O$ was added to the exhaust gas, the gas was preheated to 110–115°C by a tubular oven to ensure that $H_2O$ entered evenly into the reactor. In MACR, the average temperature of the catalyst was measured by an IR pyrometer located on the radial direction of the reactor. In order to verify the temperature, a thermocouple was inserted immediately into the catalyst bed along a guide tube to measure the catalyst temperature, as Perry *et al.* did after the microwave generator was turned off (21, 22). By using the error correction (as in Perry's report, considering the decreased temperature induced while inserting the thermocouple at the bottom of the guide tube), the dependence of the temperature measured by the thermocouple on that measured by the IR pyrometer could be drawn. Then the correction factor of the IR pyrometer could be calculated. In the IR pyrometer, there was a calibration button with which the correction factor could be inputted. Therefore, the real temperature of the catalyst could be measured by the IR pyrometer in our work; the temperature agreed well with that measured by the thermocouple (18, 23, 24). The dependence of IR temperature on microwave input power is presented in Fig. 1.

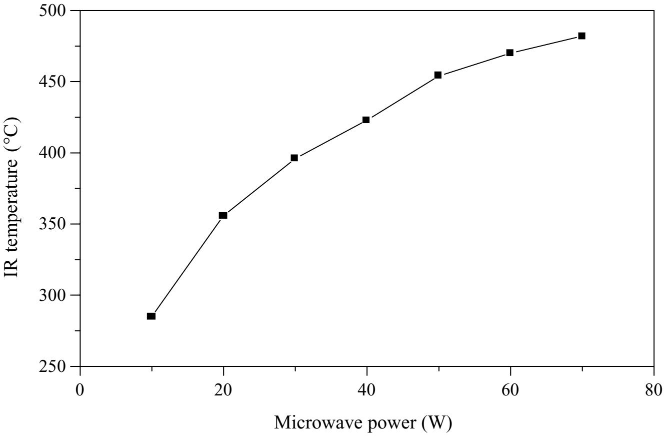

**FIG. 1.** Dependence of IR temperature on microwave power.

## RESULTS AND DISCUSSION

The lighting-off temperature (e.g., the temperature for 50% conversion of each reactant) is one of the important standards for evaluating the catalyst of automotive exhausts. We first investigated the lighting-off temperature in the CR and the MACR mode with dry exhaust, which consisted of 1000 ppm NO, 1000 ppm $C_3H_8$, 1.5% CO, 0.5% $H_2$, 12% $CO_2$, 1.4% $O_2$, and $N_2$ carrier gas. As the range of the IR pyrometer is from 200 to 1000°C, and the lighting-off temperature of the catalyst for CO is below 200°C, the lighting-off temperature of the CO was not determined in any MACR. The results are shown in Table 1.

From the data in Table 1, it can be seen that no matter whether in the CR or the MACR mode the lighting-off temperature of the catalyst for CO was the lowest, and that for $C_3H_8$ was the highest. By the action of MACR, the lighting-off temperatures for $C_3H_8$ and NO decreased greatly when all gases were introduced into the reactor at room temperature. Unlike that in the CR mode, the temperatures decreased more than 50°C in the MACR mode, even up to 70°C. Although the lighting-off temperature for CO was not determined, it is possible that the temperature for CO also decreased. So with dry exhaust as the feedstream, microwave heating lowered the lighting-off temperature of $C_3H_8$, CO, and NO, and this is very beneficial for purifying automotive exhaust in the cool start-up stage.

The dependence of $C_3H_8$, CO, and NO conversions on temperature was also studied in the CR and the MACR mode with dry exhaust. The results are presented in Figs. 2–4, respectively. As shown in these three figures, the conversions of all reactant gases increased quickly with the increase in temperature in the CR mode. Then, with a further increase in temperature, the conversions leveled off to a stable value. In the MACR mode, the tendency of the plots was the same as that in the CR mode. It is worth noting that the conversions of all reactant gases in the MACR mode were obviously higher than that in the CR mode. This provides strong evidence that microwave heating can enhance the catalytic activity of the catalyst at low reaction temperatures. However, with a further increase in temperature, the conversions in the MACR mode all leveled off to a stable value, which was the same as that in the CR mode.

### TABLE 1

**The Lighting-Off Temperature of the Catalyst under Different Reaction Modes with the Dry Exhaust[a]**

| Reaction mode | $C_3H_8$ (°C) | CO (°C) | NO (°C) |
|---|---|---|---|
| CR | 340 | 170 | 320 |
| MACR | 275 | — | 270 |

[a] Reaction conditions: 1000 ppm NO; 1000 ppm $C_3H_8$; 1.5% CO; 0.5% $H_2$; 12% $CO_2$; 1.4% $O_2$; $N_2$ carrier gas; 5.3 ml catalyst; total flow rate, 4417 ml/min (GHSV = 50,000 $h^{-1}$).

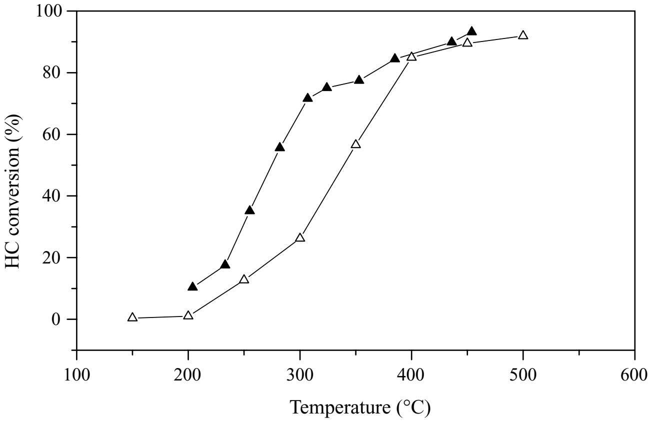

**FIG. 2.** Dependence of $C_3H_8$ conversion on the temperature in different reaction modes. Reaction conditions: 1000 ppm NO; 1000 ppm $C_3H_8$; 1.5% CO; 0.5% $H_2$; 12% $CO_2$; 1.4% $O_2$; $N_2$ carrier gas; 5.3 ml catalyst; total flow rate, 4417 ml/min (GHSV = 50,000 $h^{-1}$). CR (△), MACR (▲).

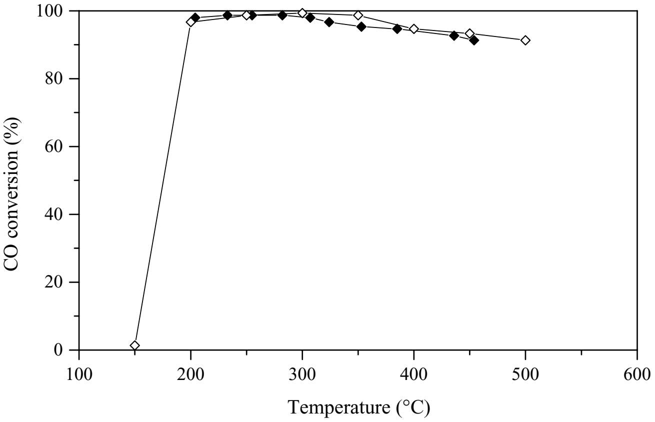

**FIG. 3.** Dependence of CO conversion on the temperature in different reaction modes. Reaction conditions: 1000 ppm NO; 1000 ppm $C_3H_8$; 1.5% CO; 0.5% $H_2$; 12% $CO_2$; 1.4% $O_2$; $N_2$ carrier gas; 5.3 ml catalyst; total flow rate, 4417 ml/min (GHSV = 50,000 $h^{-1}$). CR (◇), MACR (◆).

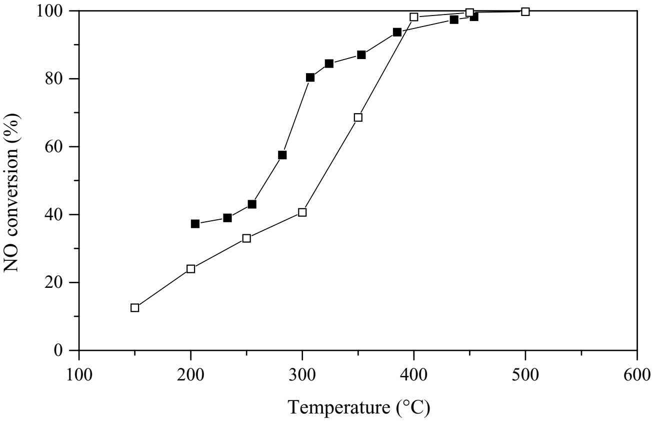

**FIG. 4.** Dependence of NO conversion on the temperature in different reaction modes. Reaction conditions: 1000 ppm NO; 1000 ppm $C_3H_8$; 1.5% CO; 0.5% $H_2$; 12% $CO_2$; 1.4% $O_2$; $N_2$ carrier gas; 5.3 ml catalyst; total flow rate, 4417 ml/min (GHSV = 50,000 $h^{-1}$). CR (□), MACR (■).

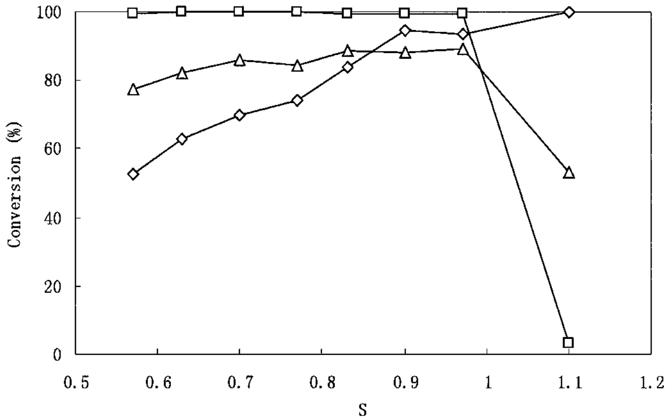

**FIG. 5.** The effect of *S* on the conversions of CO, $C_3H_8$, and NO in CR mode. Reaction conditions: 1000 ppm NO; 1000 ppm $C_3H_8$; 1.5% CO; 0.5% $H_2$; 12% $CO_2$; $N_2$ carrier gas; 5.3 ml catalyst; total flow rate, 4417 ml/min (GHSV = 50,000 $h^{-1}$). CO (◇), $C_3H_8$ (△), NO (□).

A lean-fuel (rich $O_2$) state is important for adapting to future requirements of high efficiency and low energy resource consumption in vehicles. Therefore, the effects of $O_2$ concentration on the conversions of $C_3H_8$, CO, and NO with dry exhaust were also investigated. $O_2$ concentration was indirectly presented by *S* according to Eq. [1] (the dependence of the conversions on *S* is shown in Fig. 5 for CR and Fig. 6 for MACR at 450°C). In the CR mode, in the range of *S* from ca. 0.8 to 0.99, the conversions of CO, $C_3H_8$, and NO all exceed 80%, which meets the TWC requirements (3). The optimal *S* value was 0.95 over the catalyst obtained in the CR mode, where the conversions of CO, $C_3H_8$, and NO were ca. 93, 88, and 100%, respectively. In the MACR mode, the range of *S* where the conversions of CO, $C_3H_8$, and NO exceed 80% was from ca. 0.8 to 1.05, and the optimal *S* was about 0.97, corresponding to conversions of CO, $C_3H_8$, and NO of ca. 94, 92, and 98%, respectively. Furthermore, when *S* was from 0.6 to 1.1, all conversions in the MACR mode were basically higher than that in the CR mode. For example, when *S* was 0.6, the conversions of CO, $C_3H_8$, and NO were 58, 88, and 98% in the MACR mode, respectively, while they were 55, 78, and 100% in the CR mode, respectively. When *S* was 1.1, the conversions were 100, 90, and 25% in the MACR mode, respectively, and those for CR were 100, 55, and 5%, respectively. These results indicated that microwave irradiation actually promoted the activity of the catalyst. At the same time, increasing further the value of *S*, the conversion of $C_3H_8$ leveled to a stable value in the MACR mode, while it decreased quickly in the CR mode. So, by comparing the operation window (presented by *S*) in the CR mode with that in the MACR mode, it was clear that the operating window of the latter enlarged greatly, which is beneficial for performance under lean-fuel conditions, and the optimal value of *S* was also increased.

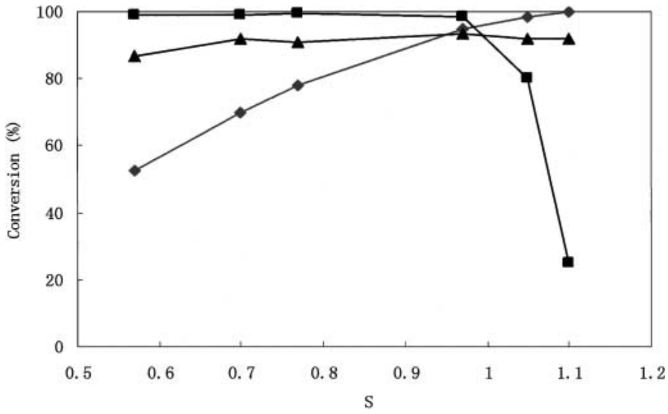

**FIG. 6.** The effect of *S* on the conversions of CO, $C_3H_8$, and NO in MACR mode. Reaction conditions: 1000 ppm NO; 1000 ppm $C_3H_8$; 1.5% CO; 0.5% $H_2$; 12% $CO_2$; $N_2$ carrier gas; 5.3 ml catalyst; total flow rate, 4417 ml/min (GHSV = 50,000 $h^{-1}$). CO (◆), $C_3H_8$ (▲), NO (■).

For the wet simulated exhaust, which consisted of 1000 ppm NO, 1000 ppm $C_3H_8$, 1.5% CO, 0.5% $H_2$, 12% $CO_2$, 10% $H_2O$, 1.4% $O_2$, and $N_2$ carrier gas, the effects of different reaction modes on the lighting-off temperature were also observed, and the results are shown in Table 2. It can be seen that the lighting-off temperatures of $C_3H_8$ and NO were clearly lower in the MACR mode than in the CR mode. Moreover, the lighting-off temperature of NO with the wet exhaust gas was lower than with the dry exhaust in the MACR mode, which indicated that $H_2O$ obviously did not influence the conversion of the exhaust gas in MACR (18). Comparing Table 1 (dry exhaust) with Table 2 (wet exhaust), we can see that no matter whether with dry or wet exhaust, the lighting-off temperature in MACR was always lower than in CR. So it is reasonable to conclude that by microwave heating, the lighting-off temperature of the catalyst was greatly lowered no matter whether dry or wet exhaust was used.

Although the mechanism of MACR is not clear, we imagine that the ability of the catalyst to absorb microwaves (19, 20), the special heating mode of microwaves, and the catalytic activity of the novel metal are important factors in the MACR mode. It is well known that many supported

**TABLE 2**

**The Lighting-Off Temperature of the Catalyst under Different Reaction Modes with the Wet Exhaust**[a]

| Reaction mode | $C_3H_8$ (°C) | CO (°C) | NO (°C) |
|---|---|---|---|
| CR | 350 | 175 | 330 |
| MACR | 300 | — | 260 |

[a] Reaction conditions: 1000 ppm NO; 1000 ppm $C_3H_8$; 1.5% CO; 0.5% $H_2$; 12% $CO_2$; 1.4% $O_2$; 10% $H_2O$; $N_2$ carrier gas; 5.3 ml catalyst; total flow rate, 4417 ml/min (GHSV = 50,000 $h^{-1}$).

metal catalysts can absorb well microwaves, which enable the formation of the local heating spots on the surface of the catalysts (19, 20, 23–25). Local heating has an ability to activate the adsorbed molecules (17, 18, 25). After NO and CO are adsorbed on the surface of the catalyst, in view of the fact that they are strongly polar molecules, they can be excited directly by microwaves (19, 20, 23, 24), or indirectly by the catalyst surface (24). Moreover, the supported noble metal components are considered to be the active sites of the $DeNO_x$ reactions (7, 12, 26). All these result in the promoting of the reactions among NO, CO, $C_3H_8$, and $O_2$. Therefore we consider that they are the possible reasons why the catalyst exerts an enhanced reactivity in the MACR mode compared to the CR mode. Further mechanisms are been investigating.

## CONCLUSION

A novel technique of microwave-assisted catalytic reactions has been used to purify simulated automotive exhaust. The catalytic activity of the catalyst increased greatly by microwave heating. The lighting-off temperatures of all reactant gases decreased obviously in the MACR mode for both dry and wet exhaust. The operation window of the catalyst was also enlarged in the MACR mode, which is beneficial for a catalyst performing in lean-fuel conditions.

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