The effect of microwave energy on three-way automotive catalysts poisoned by SO_2

Michael D. Turner [a], Robert L. Laurence [a], K.S. Yngvesson [b] and Wm. Curtis Conner [a,*]
[a] *Department of Chemical Engineering, University of Massachusetts, Amherst, MA 01003, USA*
[b] *Department Electrical and Computer Engineering, University of Massachusetts, Amherst, MA 01003, USA*

Received 10 August 2000; accepted 27 November 2000

Recent studies suggest that microwave energy can be employed in catalysis and that the results differ from “conventional” heating. The influence of microwave energy on automotive exhaust catalysis in the presence and absence of a catalyst poison (SO_2) was studied. The conclusion is that microwave energy can induce carbon monoxide (CO) lightoff (the temperature where 50% of final conversion is achieved) more efficiently than conventional heating and can reverse the poisoning by SO_2 for a commercial three-way catalyst.

KEY WORDS: microwave; three-way catalyst; auto exhaust; poisoning; sulfur dioxide; lightoff

1. Introduction

The study of sulfur poisoning on three-way automotive catalysis is of increasing importance in light of the recent amendments to the Clean Air Act of 1990. Numerous studies have demonstrated that the sulfur present in gasoline decreases the effectiveness of catalysts for the control of contaminants in auto exhaust [1]. All automotive fuels produced today have some level of sulfur-containing organic compounds present. When burned in an internal combustion engine, these compounds are converted primarily into sulfur dioxide (SO_2). When the SO_2 enters the catalytic converter, it may adsorb on the noble metals of the catalyst. The adsorbed sulfur can react to form sulfides with the noble metals under reducing conditions and sulfites or sulfates under oxidizing conditions preventing the adsorption of carbon monoxide (CO) for further oxidation reactions. In addition, the SO_2 forms sulfates with the base metal oxides, such as ceria (CeO_x) [2]. When these sulfates form, the base metal oxides may lose their oxygen storage capabilities. This results in poor performance for feed streams where the air to fuel ratio is less than stoichiometry (rich conditions). Completely removing these sulfur compounds is not economically practical with the current fuel processing technologies. For this reason, alternative methods must be developed to counter the detrimental effects of SO_2 on the three-way catalyst.

Several studies have investigated the effects of microwave radiation on catalytic reactions [3–5]. We have shown previously that microwave energy can be selectively absorbed by the surface of oxide supports [6,7]. The result was a rapid, efficient, and selective heating of the surface. It was inferred that a steady-state temperature gradient existed in a flowing gas with the temperature of the surface being the greatest, followed by the bulk solid temperature, and finally, the gas phase temperature. Consequently, desorption was induced at a lower bulk solid temperature than would be required for conventional desorption. This does not mean desorption occurred at a lower temperature, since the temperature of the surface could be greater than the normal desorption temperature. The importance is that the microwave energy is directed toward the surface of the support, and in some cases toward the adsorbate itself (if the adsorbate has a high dielectric constant). This selective absorption of the microwave energy allows the desorption to occur without heating the entire system to the isothermal desorption temperature. Therefore, microwave energy could provide a two-fold advantage in the SO_2/TWC system. Firstly, the microwave energy may be able to desorb the surface adsorbed sulfur since sulfates and sulfides are among the most polarizable bonds in the system and would be most receptive to absorb microwave energy. Secondly, if microwave energy can selectively heat the surface of the TWC, lightoff (defined here as the temperature when 50% of final conversion is achieved) may be induced at a bulk temperature lower than is normally required; although, the effective surface temperature could be much greater. This would greatly reduce overall emissions of CO since a large portion of the CO in the exhaust of an automobile is emitted prior to lightoff of the catalyst.

2. Experimental

2.1. Materials

This study used Engelhard Corporation’s state-of-the-art three-way automotive catalyst. This catalyst was supplied in the form of a 1.25 cm diameter by 3.25 cm long ceramic monolith. A summary of the catalyst composition is presented in table 1.

---

[*] To whom correspondence should be addressed.

1011-372X/01/0200-0133$19.50/0

Table 1
Engelhard three-way catalyst composition as reported in the material safety data sheet (MSDS).

>50 w/o ceramic
<20 w/o aluminum oxide
<20 w/o zirconium oxide
<10 w/o cerium oxide
<5 w/o strontium oxide
<2 w/o nickel oxide
<2 w/o neodymium oxide
<2 w/o lanthanum oxide
<2 w/o rhodium
<1 w/o palladium
<1 w/o platinum

Table 2
Reactant gas cylinder concentrations.

Cylinder	Composition
1	Ultrahigh-purity helium (99.9999%)
2	1.38% C_3H_8 and 5.25% CO in helium
3	47% O_2 in helium
4	0.283% SO_2 in helium

The reactants were purchased as premixed gases in four separate cylinders from Matheson Gas Products Incorporated. This reduces the overall operating cost while maintaining the ability to change the feed composition. The four gas mixtures are shown in table 2. Helium was chosen over nitrogen as the carrier gas for two reasons. Firstly, nitrogen and carbon monoxide have the same mass ($m/e = 28$), thus if nitrogen were used as the carrier gas, it would complicate the carbon monoxide analysis in the mass spectrometer detector. Secondly, helium has a higher thermal conductivity than nitrogen, which allows for better heat transfer to and from the catalyst.

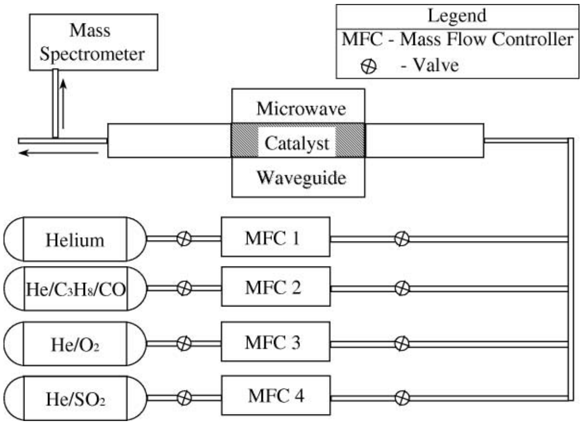

Figure 1. Inlet manifold for the three-way catalyst experiments. The on-line mass spectrometer and mass flow controllers are each computer controlled.

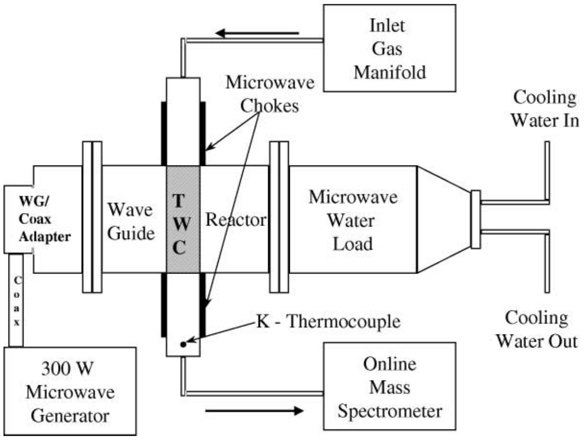

Figure 2. Schematic of the microwave waveguide exhaust reaction system. The 2.45 GHz generator was operated from 0 to 300 W of continuous power. The TWC catalyst bed passes through the short axis of the 7.2 cm × 3.4 cm rectangular waveguide.

2.2. Apparatus

The experiments were performed with an apparatus consisting of an inlet manifold connected to a reactor designed for exposure to microwave radiation, figure 1. The inlet manifold consists of four computer-operated mass flow controllers. These controllers can mix the reactants over a wide range of ratios for inlet into the reactor. All tubing in the manifold is nickel-free stainless steel for two reasons. Firstly, it is resistant to corrosion by sulfurous and sulfuric acids, which can be formed as by-products. Secondly, if stainless steel containing nickel were used, the carbon monoxide in the feed stream could react with the nickel, forming nickel carbonyl, a nerve toxin.

The microwave reactor was designed and built for these experiments. The reactor system consists of a Sairem model GMP 03 K/SM, 300 W maximum, continuous variable power microwave source operating at 2.45 GHz, a Lectronic Corporation coaxial-to-WR284 wave guide adapter, a modified section of a Lectronic Corporation WR284 wave guide, and a Raytheon Corporation 1 kW water dummy load. The reactor system is shown in figure 2. The microwave source measures both the forward and reflected power through its coaxial output cable. The calibration of the ratio of the reflected power to the forward power was checked with a Hewlett–Packard model 8753 automatic network analyzer. The main body of the reactor is the length of modified rectangular WR284 waveguide. The internal dimensions of the waveguide are 7.214 cm × 3.404 cm [8]. At 2.45 GHz, the electric field inside the waveguide is in the TE_{10} mode. This mode has uniform field strength along the short axis of the waveguide, as seen in figure 3 [8]. As a result of this field alignment, ports were drilled through the long sidewalls of the waveguide to admit a quartz sample tube, 1.80 cm in diameter, through the microwave waveguide. This modification allows the entire sample to be exposed to a uniform amount of microwave radiation. Microwave chokes (1.91 cm in diameter and 5.08 cm in length) were installed over the ports in order to prevent the operator from being exposed to any spurious microwave radiation emitted from the ports. For a given diameter port, the lengths of the chokes are calculated from standard equations [8]. The water load

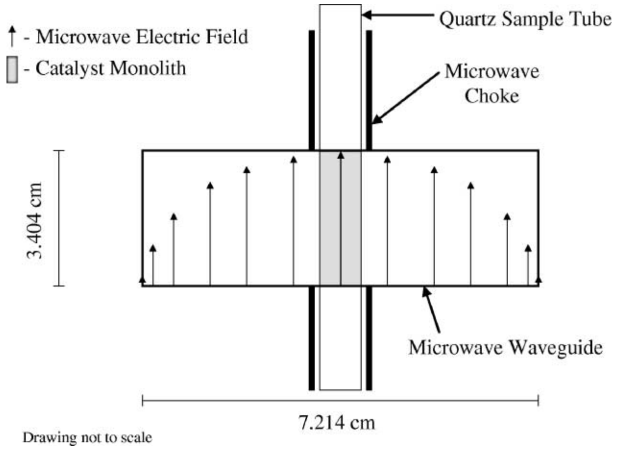

Figure 3. Microwave field orientation and relative strength in the TE_{10} mode of a cross section of a WR284 waveguide. The position of the catalyst takes advantage of the maximum in microwave electric field parallel to the short side.

was used to remove any radiation transmitted through the waveguide. In addition, the water load may be used to perform an energy balance on the system [9,10]. The water load is a sink, which minimizes reflection of the microwave radiation inside the reactor. The power supply never showed more than 3 W of power reflected to the microwave source.

The reactor has four 330 W bar heaters clamped to the exterior of the microwave waveguide. These heaters are used to heat the catalyst up to 513 K. A K-type thermocouple and an on-line Balzers QMG112A quadrupole mass spectrometer were connected to the apparatus. The thermocouple is used to measure the gas effluent and was placed at the end of the microwave chokes to avoid the microwave radiation from using the metal as an antenna, which could cause electrical arcing inside the reactor. The mass spectrometer was used to measure the concentration of the products in the effluent or reactants in the inlet by bypassing the reactor.

2.3. Procedure

2.3.1. Temperature calibration

As mentioned above, the thermocouple cannot be in physical contact with the catalyst when microwave energy is present. Therefore, in order to estimate the bulk catalyst temperature in the presence of microwave energy, a calibration was performed. Using only conventional heating, the thermocouple was placed in direct contact with the heated catalyst and the temperature was recorded. Next, a short length of tubing was added so that the thermocouple was just outside the microwave choke and this temperature was recorded for the same heating power. This calibration is used to correct the effluent gas temperature to reflect the bulk catalyst temperature in the presence of microwave radiation.

2.3.2. Sample preparation

Prior to all experiments, the catalyst was heated in a tube furnace to 773 K in the presence of oxygen to remove any adsorbed poisons or impurities. The catalyst was then allowed to stabilize at 373 K for 1 h under a flow of the reactant mixture. The reactor feed composition was chosen to simulate the exhaust of a late model 3.8 liter V-6 engine [11]. The feed concentrations and m/e of both the reactants and products monitored by the mass spectrometer are reported in table 3. The stoichiometry was cycled between net reducing and net oxidizing conditions at 0.5 Hz to simulate closed loop operation of a typical engine. This was accomplished by varying the oxygen concentration in the feed by ±3% centered about stoichiometry. The total flow rate of reactants through the catalyst for these experiments was $1.67\ \mathrm{l\,min^{-1}}$, a space velocity of approximately $20\,000\ \mathrm{h^{-1}}$. Sulfur dioxide was included in the feed at 30 ppm to study the effects of poisoning on the CO lightoff temperature.

Table 3
Feed composition and m/e of both the reactants and products monitored by the mass spectrometer.

Compound	Feed concentration (ppm)	m/e
He – helium	Balance	4
CO – carbon monoxide	1150	28
C_3H_8 – propane	300	29
O_2 – oxygen	1988–2122 (±3% step change at 0.5 Hz)	32
CO_2 – carbon dioxide	0 (product, not present in feed)	44
SO_2 – sulfur dioxide	30 (used only during sulfur studies)	64

Sets of transient experiments were performed on the three-way automotive catalyst using conventional heating and heating assisted by microwave energy. These tests were used to determine the following:

(i) the effect of microwave energy on the CO lightoff temperature of the catalyst both in the presence and absence of SO_2; and

(ii) whether microwave energy could reverse the poisoning of the CO conversion by SO_2.

2.3.3. Transient experiments

With the temperature of the catalyst stable at 373 K, the microwave energy was introduced at 300 W. Simultaneously, the bar heaters clamped on the exterior of the waveguide were turned on. This resulted in the bulk catalyst temperature being increased from 373 to 513 K. After the catalyst reaches 513 K, the heaters were turned off and the catalyst allowed to cool back to 373 K. The effluent gas was analyzed for the following m/e (species): 28 (CO), 29 (C_3H_8 fragment), 32 (O_2), and 44 (CO_2) during the experiment. The experiment was repeated in the absence of microwave energy to measure the CO lightoff temperature for conventional heating.

It is known that SO_2 shifts the CO lightoff temperature higher in temperature [11]. Therefore, these experiments were repeated with SO_2 present in the feed stream to determine whether microwave energy can shift the CO lightoff temperature back to its un-poisoned value.

3. Results and discussion

3.1. Effect of microwave energy and SO_2 on CO oxidation

For the purpose of this discussion, the CO lightoff temperature is attained when 50% of the final CO conversion is achieved. The effect of microwave energy on the CO lightoff temperature in the absence of SO_2 is shown in figure 4. The lightoff temperature using only conventional heating was 485 K. However, a combination of conventional heating and microwave energy shifts the lightoff temperature approximately 9 K lower to 476 K.

The final bulk temperature of the catalyst was 513 K regardless of the presence of microwave radiation. This is not remarkable since the monolith is mostly ceramic, a substance of low permittivity. Thus, only a fraction of the microwave energy was adsorbed in this experiment; most of the energy passed through the waveguide and was absorbed by the water load. Therefore, it is concluded that the small fraction of microwave energy was selectively adsorbed by the surface/adsorbed-layer of the three-way catalyst. Although the effective surface temperature cannot be measured, it is believed that the effective surface temperature is higher than the bulk catalyst temperature which is higher than the gas phase temperature in these steady-state flow experiments.

Therefore, the actual CO lightoff temperature may not have decreased, because the effective surface temperature is not known. However, the bulk catalyst lightoff temperature has been decreased by 9 K. This is significant because a large fraction of the pollution from automobiles is emitted prior to the lightoff of the catalyst. Therefore, if the catalyst were made to lightoff at a lower temperature, the amount of pollution generated by automobiles would be drastically reduced.

The transient experiments were performed a second time with SO_2 in the feed stream. These results, in addition to the data presented in figure 4, are reported in figure 5 for comparison. This data confirms previous reports that SO_2 shifts the CO lightoff temperature higher, from 485 K for the un-poisoned catalyst to 494 K for the poisoned catalyst when only conventional heating is used. However, if a combination of conventional heating and microwave energy is used, figure 5 shows that the lightoff temperature is reduced from 494 to 482 K. Thus, microwave energy has lowered the lightoff temperature 12 K. This is 3 K lower than the lightoff temperature of the un-poisoned catalyst using only conventional heating, 485 K.

The SO_2 poisoning not only shifts the CO lightoff temperature higher but also decreases the overall conversion of CO. Figure 5 shows that for a poisoned catalyst the overall CO conversion is 85% at the maximum temperature of 513 K when using only conventional heating. When microwave energy is used to augment the conventional heating, the conversion is 100% at a temperature of only 500 K. In addition to shifting the lightoff temperature lower, the lightoff curve is steeper when microwave energy is used compared to using only conventional heating. Thus, microwave energy does not only shift the lightoff; it reverses the influence of SO_2.

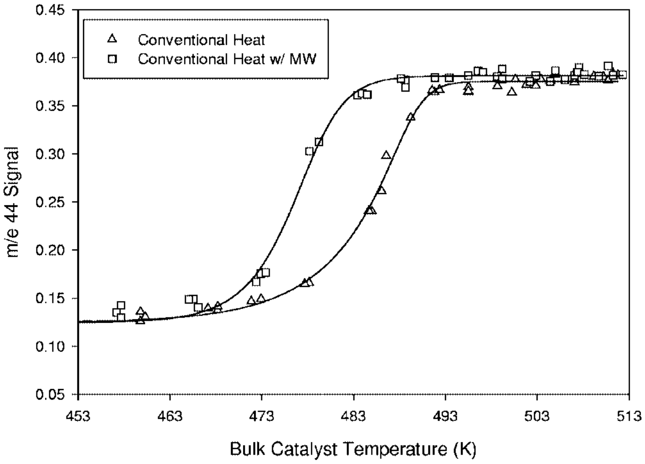

Figure 4. Carbon dioxide ($m/e = 44$) production versus bulk catalyst temperature for conventional and microwave experiments.

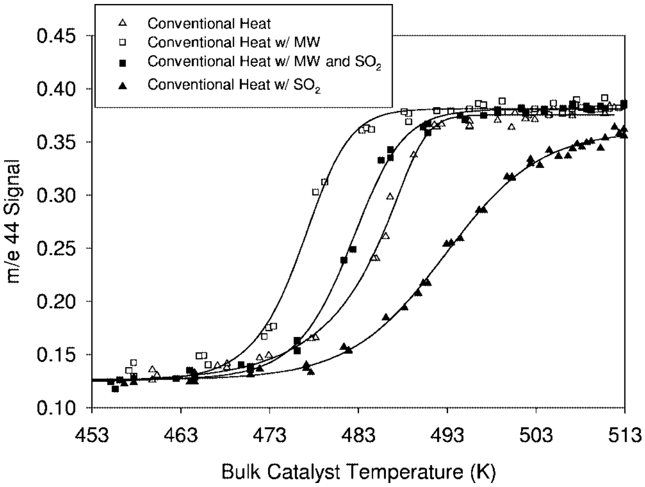

Figure 5. Carbon dioxide ($m/e = 44$) production versus bulk catalyst temperature for conventional and microwave experiments in the presence and absence of sulfur dioxide, a catalyst poison.

The most probable explanation for the results presented above is that the sulfides and sulfates formed during poisoning by the SO_2 are the most polarizable bonds in the system and are most likely to absorb microwave energy. This absorption of microwave energy causes these sulfur compounds to decompose and desorb with sulfur probably being removed as SO_2; although, we were unable to measure these species with the mass spectrometer. This leaves the noble metals and base metal oxides available for CO oxidation, leading to an increase in conversion. Any further microwave energy absorbed at the surface could then increase the effective surface temperature or interact with adsorbed species to promote lightoff at a lower bulk temperature.

3.2. Effect of SO_2 on propane oxidation

During the study on the effect of microwave energy on the three-way automotive catalyst, a result was discovered that has not yet been seen in the literature. All the previous research suggests that SO_2 increases the lightoff tempera-

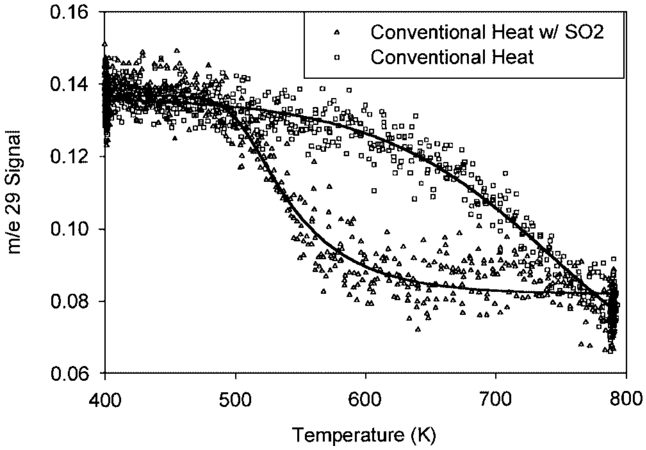

Figure 6. Propane ($m/e = 29$) production versus bulk catalyst temperature for conventional experiments in the presence and absence of sulfur dioxide, a catalyst poison.

ture of the catalyst and reduces the conversion [11,12]. Although a reduction in the hydrocarbon conversion was observed, it was noted that the SO_2 reduced the hydrocarbon lightoff temperature of Engelhard Corporation's catalyst by approximately 100 K.

These results came about while using a tube furnace to perform the conventional experiments; this was prior to the construction of the waveguide reactor, which is limited to 513 K. Other than the method of heating, the inlet and detector systems are identical to the one used in the microwave experiments. Three types of experiments were performed using the tube furnace setup. In all experiments, the temperature was cycled from 373 to 773 K and back to 373 K. In the first two experiments, the catalyst was cycled in temperature both in the presence and absence of SO_2. In the third experiment the catalyst was poisoned at low temperature, the poison removed from the gas stream, and the temperature cycle performed. The results of these experiments are presented in figure 6.

For the un-poisoned experiment, the results show that the propane conversion increases monotonically up to the final temperature of 773 K. It is possible that if the temperature were allowed to increase the conversion would increase toward 100% from 70% at 773 K. The propane lightoff temperature for this experiment is approximately 650 K. The conversion of the hydrocarbon increases rather rapidly to its final value of 70% at 773 K with a lightoff temperature close to 540 K for the poisoned experiment. The fact that the conversion has reached its maximum value at only 70% is typical; however, the decrease in the hydrocarbon lightoff temperature from 650 K for the un-poisoned experiment to only 540 K is rather surprising.

In the third type of experiment (the catalyst is prepoisoned by SO_2 at low temperature), the results are similar to those for the poisoned experiment as the temperature is increased from 373 to 773 K. However, as the temperature is decreased the results are similar to the un-poisoned experiments. Thus, as the catalyst is first heated, the poison is still adsorbed and the results are the same as if SO_2 were present. The poison desorbs when the temperature increases further. Finally, if the temperature is then decreased, the poison is no longer present and the results are the same as for an un-poisoned catalyst.

4. Conclusions

In this work, the effect of microwave energy on a state-of-the-art three-way automotive catalyst both in the presence and absence of SO_2 has been studied. The results obtained provide four general conclusions:

(i) Microwave energy can shift the CO lightoff temperature of the bulk catalyst lower when compared to the lightoff temperature using only conventional heating.

(ii) Results obtained by other research groups that SO_2 shifts the CO lightoff temperature of the bulk catalyst higher when compared to an un-poisoned catalyst were confirmed.

(iii) Microwave energy can shift the lightoff temperature of the bulk catalyst poison by SO_2 lower than the lightoff temperature of the un-poisoned catalyst using only conventional heating.

(iv) For a catalyst poisoned by SO_2, microwave energy can increase the overall conversion of CO from 85% at 513 K using conventional heating, to 100% at 500 K using microwave energy.

These studies demonstrate the ability of microwave energy to influence heterogeneous catalytic reactions. This influence will be greatest if the energy can be directed to the surface, i.e., the bulk does not interact strongly with the microwave energy. The concentration of microwave energy on the surface will depend on the nature of the surface (hydroxyls, etc.), active sites (metals), and the specific adsorbing (reacting or desorbing) species. It is also important that the reaction or desorption can occur prior to thermal equilibration; otherwise, there will be little difference for microwave induced sorption/reaction compared to conventional heating.

In addition, it should be noted that these experiments did not investigate the influence of microwave power on the reaction or the presence of water added to the feed stream. These influences will be investigated in future studies. However, using higher microwave power could cause an even more pronounced shift in the lightoff temperature. Finally, the unique result that SO_2 has lowered the propane lightoff temperature was observed. This result has not previously been published to our knowledge.

Acknowledgement

The authors would like to thank Dr. S. Tauster of Engelhard Corporation for the donation of their state-of-the-art three-way automotive catalyst and Dr. M. Deba of General Motors Corporation for providing guidance on testing procedures. Funding for this research was provided by Coordination Research Council (CRC).

References

[1] B.H. Engler, D. Lindner, E.S. Lox, A. Schafer-Sindlinger and K. Ostgathe, in: *Catalysis and Automotive Pollution Control III*, Stud. Surf. Sci. Catal., Vol. 96, eds. A. Frenner and J.M. Bastin (Elsevier, Amsterdam, 1995) pp. 441–460.

[2] S. Lundgren, G. Spiess, O. Hjortsberg, E. Jobson, I. Gottberg and G. Smedler, in: *Catalysis and Automotive Pollution Control III*, Stud. Surf. Sci. Catal., Vol. 96, eds. A. Frenner and J.M. Bastin (Elsevier, Amsterdam, 1995) pp. 763–774.

[3] B. Krieger-Brockett, M. Mingos and J. Wan, in: *Proc. Microwave-Induced Reactions Workshop*, eds. M. Burka and K.R. Amarnath (Meeting Planning Associates, Pacific Grove, 1993).

[4] C.Y. Cha and Y. Kong, Carbon 33 (1995) 1141.

[5] G. Bond and R.B. Moyes, in: *Microwave-Enhanced Chemistry*, eds. H.M. Kingston and S.J. Haswell (Am. Chem. Soc., Washington, DC, 1997).

[6] M.D. Turner, W.C. Conner, R.L. Laurence and S. Yngvesson, in: *Proc. of the 12th Int. Zeolite Conference*, eds. M.M.J. Treacy, B.K. Marcus, M.E. Bisher and J.B. Higgins (Mater. Res. Soc., Baltimore, MD, 1999).

[7] M.D. Turner, R.L. Laurence, W.C. Conner and K.S. Yngvesson, AIChE J. 46 (2000) 758.

[8] D.M. Pozar, *Microwave Engineering* (Addison-Wesley, Reading, 1990).

[9] M.D. Turner, Ph.D. Dissertation, University of Massachusetts, Amherst (2000).

[10] M.D. Turner, R.L. Laurence, S. Yngvesson and W.C. Conner, How Efficiently Does Microwave Energy Heat Zeolites? (2000), in progress.

[11] D.D. Beck and J.W. Sommers, in: *Catalysis and Automotive Pollution Control III*, Stud. Surf. Sci. Catal., Vol. 96, eds. A. Frenner and J.M. Bastin (Elsevier, Amsterdam, 1995) pp. 721–748.

[12] D.R. Monroe, M.H. Krueger, D.D. Beck and M.J. D'Aniello, in: *Catalysis and Automotive Pollution Control II*, Stud. Surf. Sci. Catal., Vol. 71, ed. A. Crucq (Elsevier, Amsterdam, 1991) pp. 593–616.