Photocatalytic oxidation in the presence of microwave irradiation: observations with ethylene and water

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Abstract

Microwave irradiation was employed in the heterogeneous photocatalytic oxidation (PCO) of a test compound, ethylene, in the gas phase on TiO_2/ZrO_2 mixed oxide thin films prepared via sol–gel processing. This approach was taken to study the rate of PCO of these compounds as a function of water concentration by perturbing the presence of water on the surface of the catalyst. PCO experiments were conducted with two types of reactor assemblies (Approaches 1 and 2). In Approach 1 when microwave plasma lighting was applied, microwave irradiation increased the rate constants by 15% ($\alpha = 1$) and 26.9% ($\alpha = 0.5$) corrected for light irradiance in studies conducted at 15% relative humidity (RH), but had a negligible effect at 0 and 5% RH. In Approach 2, with the light source external to the microwave chamber, the degradation of ethylene with 3 μl liquid water injection proceeded faster (83.9%) in the presence of the microwave irradiation than in the absence. Measurements of water adsorption indicated that microwave irradiation facilitated the removal of excess water from the catalyst surface treated with UV illumination in studies with the RH above 15%, but excess water removal was not observed in studies with the RH lower than 5%. Contact angle measurements helped to elucidate the effect of surface wettability of TiO_2/ZrO_2 catalyst films on the observed results. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Microwave irradiation; Photocatalytic oxidation; TiO_2/ZrO_2 mixed metal oxide; Water adsorption

1. Introduction

Photocatalytic oxidation (PCO) of volatile organic compounds using irradiated TiO_2 has been widely studied and generally advocated as an air purification technology [1–4]. Researchers have designed many photocatalytic reactors in order to achieve good efficiency, and they have also modified TiO_2 to improve its photocatalytic activity [5,6]. In this regard, our research group has employed TiO_2/ZrO_2 mixed oxide thin films made via sol–gel processing that have been shown to have high photocatalytic activity [7–10].

The heterogeneous PCO of ethylene has also been previously investigated [7,9–14]. Ethylene is a ripening gas that causes premature aging effects in fruits, vegetables and flowers. Therefore, the floral and food storage industries have been interested in the degradation of ethylene at low concentrations in low temperature environments. Accordingly, studies have found, both using TiO_2 and TiO_2/ZrO_2, that water molecules on the surface of the catalyst change the rate of PCO [10,13,14]. This is thought to involve two possible phenomena. First, the water molecules scavenge positive holes before they can recombine with excited electrons, producing OH radicals [15] that effectively oxidize the reactants. Second, if there is a sufficient amount of water, these water molecules cover the surface of the catalyst and prevent (i.e., compete with) the reactants from accessing the active species, OH radicals and/or reacting holes [14].

The surface coverage of water on TiO_2 is deeply related with surface wettability. The surface wettability of TiO_2 after UV illumination has recently been the focus of much attention [16–19]. In these studies, the surface of TiO_2 is hydrophobic and its contact angle varies between $15°$ and $72°$ when not exposed to UV light. However after UV illumination, TiO_2 becomes hydrophilic and its contact angle changes to less than $1°$. This phenomenon results in the surface coverage of water molecules, which likely inhibits the reactants from attaching to active sites of oxidation on the catalyst surface.

Microwaves are well known for their heating effects on high dielectric substances such as water. Therefore, microwave heating is widely employed in both industry and research laboratories. However, except for time-resolved microwave conductivity studies of charge carriers [20], there have been few studies concerned with the effect of microwaves on photocatalytic reactions. Recently, some

researchers have started to investigate photocatalytic or photochemical reactions combined with microwave irradiation [21–26]. However, most of these studies are conducted in liquid phase and they all have concluded that the diffusion of reactants is perturbed by microwave irradiation and that OH radicals are formed by microwaves [26].

In the present context, when a fluorescent bulb is located in a microwave field, the bulb emits UV light without electric power being supplied directly to the bulb (i.e., via ballasts). Instead, lighting is achieved when microwaves excite the mercury vapor inside the fluorescent bulb. However, the collision frequency of the excited mercury atoms is low because of the low pressure of mercury in the bulb. In this case, the mercury atoms discharge their energy by colliding on the phosphor-coated wall of the fluorescent bulb, emitting light. This process is called microwave plasma lighting. It has been commercialized (e.g., Environmental Growth Chambers, Chagrin Falls, OH) and recently reported for applications to photocatalytic reactions [23].

The objective of this study is to determine the influence of microwave irradiation on the PCO of ethylene and on the behavior of water on the surface of the TiO_2/ZrO_2 catalysts. In order to perform these studies, we conducted microwave photocatalytic oxidation (MWPCO) using two types of reactor assemblies. The importance of photocatalytic reactor design in the presence of microwaves is also discussed.

2. Experimental

2.1. Catalyst preparation

A mixed metal oxide (TiO_2/ZrO_2) suspension (sol) was prepared via a sol–gel processing procedure [7–10]. A TiO_2 sol and a ZrO_2 sol were mixed after synthesizing these sols separately. The mixing ratio of ZrO_2/TiO_2 was 12 wt.%. The mixed metal oxide was supported on two substrates, borosilicate glass beads, 5 mm in diameter (Kimble Glass, Deerfield, IL) (Approach 1) and circular glass slides, 12 mm in diameter (Microscope Cover Glass, Fisher, PA) (Approach 2). The substrates were dipped into the mixed oxide sol and

successively dried at room temperature for 30 min and then at 100 °C for an hour. After repeating this coating and drying process two more times, the catalyst was calcined at 350 °C for 3 h using a temperature ramping rate of 3 °C per minute.

2.2. Microwave photocatalytic reactor assemblies (Approach 1)

A schematic diagram of the entire test system as employed for Approach 1 is provided in Fig. 1(a). A microwave generator (Microwave Technologies and Applications, Glen Ellyn, IL) combined with a rectangular waveguide (8.6 cm in width, 40.8 cm in depth and 11.2 cm in height) was operated with 150 W output at a frequency of 2.45 GHz with a variable-power magnetron. Rectangular (8.6 cm × 10.2 cm) channels directly opposite to each other were cut into the top and bottom of the waveguide. Two aluminum plates (16.5 cm × 10.2 cm × 6 mm), each with a 7.1 cm diameter hole located at the geometric center of the plate, completely covered each channel opening. These plates acted as lower and upper supports for the vertically positioned reactor and also prevented radiation leakage from the waveguide. Little to no microwave radiation (less than 7 mW/cm^2) leaked from this test assembly as monitored by a microwave leak detector (HI-1801, Holaday Industries, Eden Prairie, MN).

The reactant gas mixture was circulated through the closed reactor system that consisted of the glass photocatalytic reactor (227 ml empty volume), a sampling port, a glass reservoir (48 ml volume, 5829 Connecting Adapter, Ace Glass Vineland, NJ), a humidity probe (Model HMI 41 indicator coupled with Model HMP 46 probe, Vaisala, Helsinki, Finland), and a peristaltic recirculation pump. A septum (Thermolite septa, Restek, Bellefonte, PA) was fixed in a union-T and closed with a nut and a back ferrule (SS-400-3, Swagelok, Solon, OH) for the sampling port. These components were connected with Viton^{TM} tubing (black in Fig. 1(a), MasterFlex, Cole-Parmer Instrument, Vernon Hills, IL) and stainless steel tubing (gray in Fig. 1(a), SS316, McMaster-Carr, Elmhurst, IL), which were observed to behave inertly with ethylene. The humidity probe is inserted into the reservoir by being fixed in a
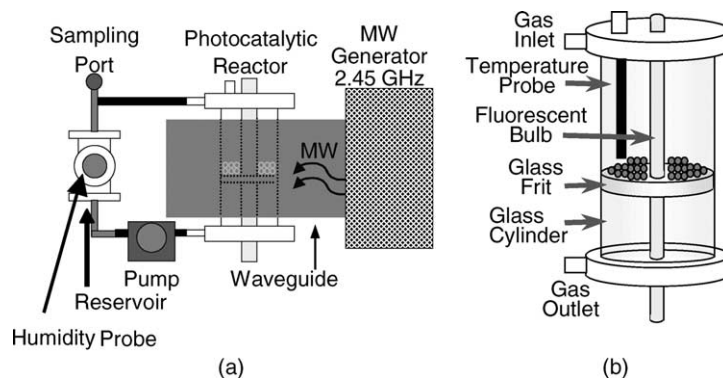

Fig. 1. Schematic diagram of the microwave photocatalytic reactor assembly in Approach 1: (a) the entire test system; (b) the photocatalytic reactor.

Teflon connector (7506 Bushing, Ace Glass, Vineland, NJ). Only the photocatalytic reactor in the system was located in the microwave field.

A schematic diagram of the photocatalytic reactor is shown in Fig. 1(b). A chromatographic column (5 cm inner diameter, 5820 Chromatograph Column, Ace Glass, Vineland, NJ) was cut to 15 cm length, and a porous coarse glass frit (5 cm diameter × 6 mm thick) was affixed (i.e., sealed with a gas-fired torch followed by an annealing process) to the inner surface of the column at approximately the midpoint along the column. The upper and lower ends of the column were sealed with Teflon^{TM} plugs fitted with an O-ring (5844 Plug, Ace Glass, Vineland, NJ). Each plug had an appropriate number of holes that were either threaded or contained O-rings allowing for insertion of and a gas-tight seal for a fluorescent bulb (F8T5/350BL, Sylvania, Danvers, MA), inlet and outlet gas ports, and an optical temperature probe (SIW-2, Luxtron, Santa Clara, CA). The fluorescent bulb was inserted along the axial centerline of the reactor without connection to an external ballast. The catalyst-coated spheres were supported on the frit in the middle of the reactor and also positioned in the middle of the waveguide. Both ends of the fluorescent bulb were located outside of the waveguide to isolate the metal parts from microwaves. When the microwave generator was powered, the fluorescent bulb emitted light in the UV range via microwave plasma lighting. Reaction temperature was measured with the optical probe, which produces no artifact during exposure to microwaves. The desired test temperature (60 °C) in the reactor was controlled by blowing cooling air over the outside of the photocatalytic reactor.

Ethylene at a concentration of 404 ppm with a balance of ultra zero air (AGA Specialty Gas, Cleveland, OH) was supplied to the system. During the course of each experiment and typically at 15 min intervals, 200 μl samples of the gaseous contents of the reactor were obtained with a gas-tight syringe. The samples were analyzed for ethylene concentration with a flame ionization detector that was coupled to a Hewlett Packard 5890 II gas chromatograph. The experiments were also conducted in the absence of microwave irradiation, and in this study external heat was supplied to the reactor in order to attain the desired temperature (60 °C). Experiments in the presence of microwave irradiation are designated as MWPCO and experiments in the absence of microwave irradiation are termed PCO. Blank experiments performed in the absence of UV light or in the absence of the catalyst confirmed that no reaction occurred under these conditions.

2.3. Microwave photocatalytic reactor assemblies (Approach 2)

A schematic diagram of the entire test system of the microwave photocatalytic reactor for Approach 2 is shown in Fig. 2(a). The combined microwave generator and waveg-
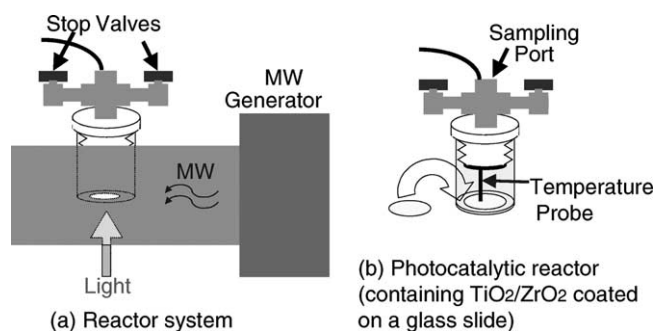

Fig. 2. Schematic diagram of the microwave photocatalytic reactor assembly in Approach 2: (a) the entire test system; (b) the photocatalytic reactor (containing TiO$_2$/ZrO$_2$ coated on a glass slide).

uide assembly was similar to the one employed in Approach 1. Again, two aluminum plates, each in this case with 2.5 cm diameter holes, were positioned over the channels of the waveguide thereby preventing microwave leakage. A batch reactor (15 ml volume) was inserted through the hole of the upper plate. UV light (Model 7825-32, 200 W medium pressure Hg vapor lamp, Ace Glass, Vineland, NJ) illuminated the reactor from below by passing light from outside the waveguide and up through the hole in the lower plate of the waveguide.

A schematic diagram of the photocatalytic reactor is shown in Fig. 2(b). A chromatographic column (5820 Chromatography Column, Ace Glass, Vineland, NJ) was cut, shielded with an optical-grade glass plate as the bottom, placed vertically through the upper plate, and operated as a batch reactor. The reactant gas mixture was isolated in the reactor. Two valves (SS-4P4T, Swagelok, Solon, OH) were fixed to tubing at the top of the column and positioned above the waveguide. These valves were closed during an experiment and opened only when the gas mixture was introduced to the reactor. A sampling port similar to the one in Approach 1 was positioned at the top of the reactor. The mixed metal oxide catalyst supported on a glass slide was positioned on the bottom of the reactor.

Reactant gas mixtures were introduced into the reactor by aid of a vacuum pump, which was connected in series to a valve. A gas-sampling bag (GSB-P-1, Calibrated Instruments, Hawthorne, NY) filled with ethylene at a concentration of 404 ppm was connected to inlet tubing at the other valve. Introduction of a reactant gas mixture was accomplished by evacuating the contents of the reactor by aid of the vacuum pump, followed by back-filling the reactor volume with the contents of the gas-sampling bag. This process was repeated three times. During the course of each experiment and typically at 15 min intervals, 200 μl samples were obtained with a gas-tight syringe from the sampling port on the top of the reactor. The concentration of ethylene was measured by the same method as in Approach 1. The desired temperature (50 °C) was monitored with the optical probe and controlled by the cooling air. Experiments were

conducted in both the presence and absence of microwave irradiation (MWPCO and PCO) as in Approach 1. In PCO, the external heat was supplied by wrapping the waveguide with heating tape to attain the desired temperature.

2.4. Kinetics of ethylene degradation

In Approach 1, light irradiance via microwave plasma lighting differed from that via ballasts (conventional lighting). The effect of microwave irradiation on the reaction rate constants was determined as follows. In each experiment, light irradiance was measured using an optical cable and a photon detector (International Light, Newburyport, MA). The effect of light irradiance was taken into account in interpreting the rate constants of these reactions. The half-order (of ethylene) reaction model was applied (Eq. (1)) and the value for the exponent of the light irradiance term (α) was taken as either 0.5 or 1 in this study (Eq. (2)). The determination of the rate constants (k_{obs} in Eq. (1)) followed the approach given in [7,8]

$$r = k_{obs}C_A^{0.5} \tag{1}$$

$$k_{obs} = k_{abs}I^\alpha \quad (\alpha = 0.5 \text{ or } 1) \tag{2}$$

where k_{obs} is the observed values of rate constants (uncorrected for the irradiance), I the associated light irradiances and k_{abs} the absolute values of rate constants (corrected for the irradiance, either $\alpha = 0.5$ or 1).

2.5. Adsorption

In the absence of irradiance (dark conditions), the adsorption of water on the mixed oxide was measured in both the presence of the microwave irradiation and in its absence. In the latter case, external heat was supplied to the system by using a heating tape to maintain constant temperature in the reactor. This adsorption elucidates the effect of microwave irradiation itself on the removal of water from the catalyst surface. In this study, a measure of the water molecules adsorbed on the catalyst surface in a microwave field was conducted by measuring the relative humidity (RH) of air in the recirculating system. This approach was used as a surrogate for measuring the water concentration on the surface of the catalyst.

During the adsorption experiments, the photocatalysts were packed into a chromatographic column (Ace Glass, Vineland, NJ). The packed-bed column was inserted in the microwave waveguide and connected to the system used in Approach 1. Next, water was injected into the system and equilibrium was established at a constant temperature (60 °C). RH in the system was measured with the humidity probe used in Approach 1. The catalyst used in the experiments was TiO$_2$/ZrO$_2$ supported on glass beads and was illuminated with UV light for 45 min (UV pre-illumination) before being packed into the column because it is known

that the wettability is preserved long after UV irradiation ceases [16–19].

2.6. Contact angle

Contact angle measurements provide information concerning the macroscopic interfacial forces between water and the mixed oxides as well as on the physical–chemical properties of the mixed oxides themselves (hydrophilicity). These measurements were taken to demonstrate the effect that microwave irradiation has on the catalyst. The mixed oxide was dip coated onto a glass slide and calcined in the same way as in Approach 2. Since contact angles change with time and condition, they were measured within 3 days after the mixed metal oxide was calcined. Between calcination and contact angle measurement, the slide was stored in a dark oven kept at 100 °C. Afterwards, the supported glass slides were treated by four separate methods: (1) irradiated with microwaves for 45 min; (2) illuminated with UV light for 45 min; (3) no irradiation; (4) irradiated both with UV light and microwaves for 45 min. A drop of water was placed on the glass slide with a micro-syringe, and the contact angle was measured with a microscope (NRL contact angle Goniometer, Ramé-Hart, Mountain Lakes, NJ).

3. Results

3.1. MWPCO (Approach 1)

These experiments were conducted under three humidity conditions: 0, 5, and 15% RH. Fig. 3(a–c) shows the fractions of unreacted ethylene C_A/C_{A0} in MWPCO and PCO. There was no significant difference between MWPCO and PCO at 0% RH, but generally, the reaction rate in MWPCO was greater than that in PCO at 5 and 15% RH. Since light irradiance using microwave plasma lighting (MWPCO) was different from the irradiance using ballasts (PCO), reaction rates were corrected for the irradiance using the formula given in Eq. (2). Table 1 shows the observed values of rate constants (k_{obs}, uncorrected for the irradiance), associated light irradiances (I), and the absolute values of rate constants (k_{abs}, corrected for the irradiance, either $\alpha = 0.5$ or 1). The absolute rate constants were determined as the average of three replicate experiments performed for each set of reaction conditions at the three different humidities. Both in MWPCO and PCO, the calculated values of k_{abs} at 0% RH were greater than at 5 and 15% RH. However, this observation does not agree with the results in Approach 2, and this discrepancy is explained in the discussion section. At 0%, k_{abs}'s were not different (−2.3% ($\alpha = 1$) or 1.3% ($\alpha = 0.5$)) between MWPCO and PCO. Similarly, at 5% k_{abs}'s were not different (−3.4% ($\alpha = 1$) or 6.2% ($\alpha = 0.5$)). Under these conditions, it would appear that MWPCO did not have any particular advantage over PCO.

Table 1
Reaction rate constants for ethylene removal under different conditions in Approach 1

Humidity (% RH)	Conditions	k_{obs} ($\times 10^5$ mol$^{1/2}$ l$^{1/2}$ g^{-1} s^{-1})	I (mW cm^{-2})	Difference (%)	k_{abs} ($\times 10^5$ mol$^{1/2}$ l$^{1/2}$ g^{-1} s^{-1} mW$^{-\alpha}$ cm$^{2\alpha}$) ($\alpha=1$)	Difference (%)	k_{abs} ($\times 10^5$ mol$^{1/2}$ l$^{1/2}$ g^{-1} s^{-1} mW$^{-\alpha}$ cm$^{2\alpha}$) ($\alpha=0.5$)	Difference (%)
0	PCO	9.55	1.10	8.2	8.80	−2.3	9.22	1.3
	MWPCO	10.4	1.19		8.60		9.34	
5	PCO	8.37	1.11	20.7	7.57	−3.4	7.96	6.2
	MWPCO	9.77	1.34		7.31		8.45	
15	PCO	6.65	1.13	22.1	5.87	15.0	6.25	26.9
	MWPCO	9.33	1.38		6.75		7.93	

However, at 15% RH, k_{abs} for MWPCO was greater (15.0% ($\alpha = 1$) or 26.9% ($\alpha = 0.5$)) than k_{abs} for PCO.

3.2. MWPCO (Approach 2)

These experiments were conducted also under three humidity conditions (dry, low and high). However, in this system, RH could not be easily measured. To achieve low humidity, 0.1 μl of water was injected into the reactor (ca. 15 ml volume), whereas 3.0 μl of water was injected to obtain the highest humidity studied. These three conditions are called 0, 0.1, and 3 μl, respectively, for convenience. Fig. 4(a–c) shows the fraction of unreacted ethylene C_A/C_{A0} in MWPCO and PCO, for which light irradiance
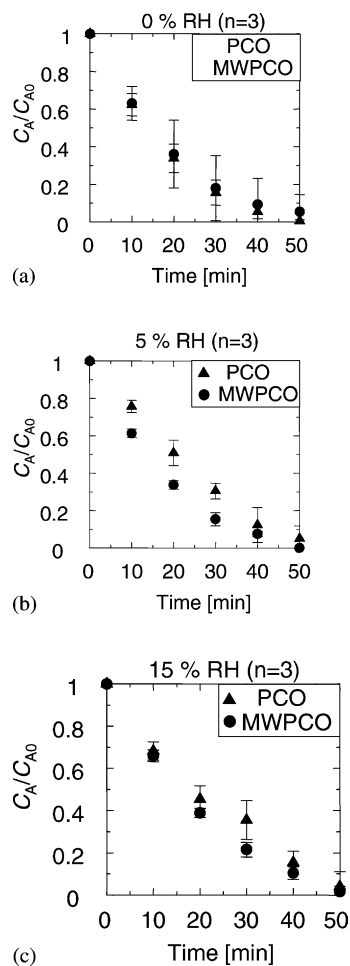

Fig. 3. PCO of ethylene at three different humidities using Approach 1 (60 °C): (a) 0% RH, (b) 5% RH and (c) 15% RH.
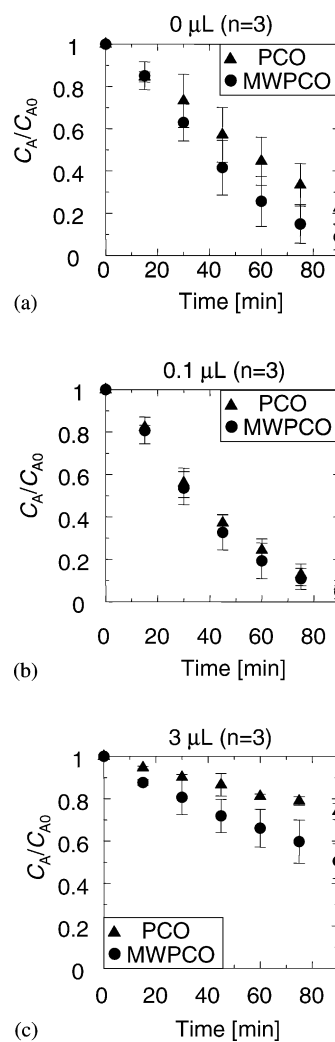
Fig. 4. PCO of ethylene at three different humidities using Approach 2 (50 °C): (a) 0 μl, (b) 0.1 μl and (c) 3 μl.

Table 2
Reaction rate constants for ethylene removal under different conditions in Approach 2

Condition	k_{obs} ($\times 10^5$ mol$^{1/2}$ l$^{1/2}$ g^{-1} s^{-1})		
	0 µl	0.1 µl	3 µl
PCO	19.9	27.6	5.16
MWPCO	26.7	28.5	9.49
Difference (%)	34.2	3.3	83.9

Table 3
Contact angles of materials

Materials	Contact angle (°)
TiO_2/ZrO_2	15
MW TiO_2/ZrO_2	4
UV TiO_2/ZrO_2	<1
UV + MW TiO_2/ZrO_2	4
TiO_2	20
MW TiO_2	20
UV TiO_2	<1
UV + MW TiO_2	4
TiO_2[a]	15
UV TiO_2[a]	<1

[a] From [15].

was constant in each case (5.7 mW/cm^2). The observed values of the rate constants (k_{obs}) were also calculated and reported in Table 2. Since the light irradiance was constant, the absolute values were not calculated. Both in MWPCO and PCO, the rates of PCO at 0.1 µl were greater than those at both 0 and 3 µl, which agrees with other reports [13]. If the mixed oxide catalyst contains a small amount of water, it provides OH radicals and provides high catalytic activity. However, if excessive amounts of water exist on the surface of the catalyst, the reaction rates decrease because the reactant molecules, ethylene and oxygen, cannot access active sites, as observed by other investigations [10,14].

If the reaction rates are compared at 0 µl, the reaction rate in MWPCO was the same at the beginning and became greater than that in PCO (Fig. 4(a)), and the difference in k_{obs} between MWPCO and PCO was not small (34.2%). At 3 µl, the reaction rate in MWPCO was greater than that in PCO throughout the reaction (Fig. 4(b)), and the difference in k_{obs} was significant (83.9%). However, at 0.1 µl, there was no difference in the reaction rate between MWPCO and PCO (3.3%).

3.3. Adsorption

Fig. 5 shows RH plotted against the amount of water injected into the system heated with either the microwave (MW) or a heating tape (Heat). When the amount of the injected water was small (0–3 µl), the relative humidities were not that divergent between MW and Heat. When the amount of the injected water increased (>3 µl), the RH in the sys-
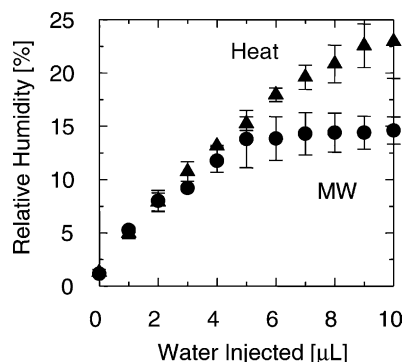
tem irradiated with MW was higher than with Heat. In this measurement, water was not adsorbed only on the surface of the catalyst, but also on the wall of the reactor, the tubing and the reservoir. Water adsorbed on the wall of the reactor in the microwave field may contribute to the difference in RH, but it is assumed that this effect was not significant due to the surface area of the catalyst compared to that of the surface area of the reactor.

In this experiment, when much water is adsorbed on the TiO_2/ZrO_2 surface, the RH is low, and when water is desorbed from the surface, the RH increases. Therefore, MW removed excess water from the surface of the catalyst.

3.4. Contact angle

Table 3 shows contact angles of TiO_2/ZrO_2 and TiO_2 with several types of treatments. TiO_2/ZrO_2 and TiO_2 without treatment have contact angles of 15° and 20°. After UV illumination, both of these oxide systems show contact angles less than 1°. This observation agrees with other reports [15–18]. It is interesting to note that the contact angle of the mixed oxide catalyst became ca. 4° after the microwave irradiation, but pure TiO_2 did not change. After UV light and microwave irradiation on TiO_2/ZrO_2 and TiO_2, their contact angles increased slightly, but did not change significantly. It is inferred that exposure of the mixed oxide (TiO_2/ZrO_2) to microwaves increased its wettability but did not have a similar effect with the single component oxide TiO_2.

4. Discussion

4.1. Microwave photocatalytic reactor design

Two types of microwave photocatalytic reactors were fabricated to study the degradation of ethylene. The effect of the microwave irradiation on the reaction did not allow for simple comparison between the two test systems (Approaches 1 and 2), because the amount of catalyst, the light irradiance, and the humidity were different. However, in both Approaches, MWPCO had an advantage over PCO at the

Fig. 5. Measurements of RH in the system as a function of the amount of water added (60 °C).

highest humidity studied, and its advantage in Approach 2 was considerably greater (83.9% increase in rate constant) as compared to that achieved in Approach 1. In Approach 1, a fraction of the microwave energy may have been absorbed by the mercury in the fluorescent bulb to generate light (since the dielectric constant of metals is infinite) and may not have coupled appreciably with water on the catalyst surface until a relatively large surface coverage was obtained at 15% RH. In contrast, the microwave energy was focused only on water and the catalyst in Approach 2. Therefore, this argument may support why the effect of MWPCO in Approach 2 was more apparent than in Approach 1.

In a practical sense that impacts reactor design engineering, light sources need to be located near the catalyst. In this case, employing microwaves to achieve plasma lighting of light sources appears to be an appropriate method for fulfilling this requirement so long as it can be implemented in a cost-effective manner. However, if one employs the microwave energy to remove water from the surface of the catalyst, it may be better to provide UV illumination from outside the microwave field (*a.k.a.*, Approach 1). These remarks are made via observation with ethylene and the humidities studied herein.

In Approach 1, the reaction rate constants at 0% RH both in MWPCO and PCO were greater than those at 5% RH, but the reaction rate constants at $0 \mu l$ of water added in MWPCO and PCO were smaller than those at $0.1 \mu l$ in Approach 2. This discrepancy can arise for two possible reasons. First, in Approach 1, microwaves were absorbed by mercury in the fluorescent bulb, and their effect on water was inconsequential. Second, the humidity conditions were not comparable between both approaches. In Approach 1, there was a sufficient amount of water to diminish the reaction rate by covering the surface, whereas the amount of water in Approach 2 may not have been sufficient to diminish the reaction rate.

Since the goal of this investigation was to initiate the study of fundamental aspects of the effect of microwaves on the PCO under humid conditions, the reactor assemblies were not designed to study the economics of the combined treatment approach (MWPCO). However, observations presented demonstrate that microwave irradiation lessened rate-limiting effect when excess water was present on the surface of the catalyst. Therefore, in applications where there are constraints on the operating conditions (e.g., one must achieve a high conversion while operating in a limited volume at high humidity and modest temperature $(50–100\,^{\circ}C)$), microwave photocatalytic reactions may be a preferable option to purely photocatalytic reactions, although one would expect higher capital and operating costs for a microwave photocatalytic reactor than for a purely photocatalytic reactor.

4.2. Microwave effect on PCO

In the adsorption experiment, there were small differences in adsorption of water between MW and Heat under the very low humidity conditions ($0–3 \mu l$ injection). However, the humidity probe is not particularly accurate under these conditions, especially when the temperature is high (over $60\,^{\circ}C$). For this reason, we could not effectively report the RH under these conditions. We did observe that microwave irradiation increases the wettability of TiO_2/ZrO_2 from contact angle experiments. In Approach 2, at $0 \mu l$, the rate in MWPCO became greater with time than that in PCO and the difference in the reaction rate constants between MWPCO and PCO was 34.2%. The increase of the wettability by the microwave irradiation may have facilitated the adsorption of water (a product), which produces OH radicals, and indirectly accelerated the rate of the PCO. This observation requires more rigorous study to prove.

In Approach 2, at $0.1 \mu l$, there is likely a sufficient amount of bound water molecules to create OH radicals on the surface of the catalyst, but not a sufficient amount of water to diminish the rate of the PCO in both MWPCO and PCO. Therefore, there was little effect of applying microwave irradiation on the overall reaction even though the presence of microwaves increased the wettability of the catalyst and aided in the removal of water.

In adsorption experiments at the higher humidity test case (the amount of water injected is more than $5 \mu l$), the microwave irradiation removed excess water from the surface (Fig. 5). This is consistent with the results obtained in both approaches at the highest humidity studied. The reaction rate of MWPCO was greater than that for PCO, and this was presumed to be caused by the removal of excess water on the surface. If a two-component (ethylene and water) Langmuir–Hinshelwood rate equation could be employed to model these results as discussed in other reports [14], the effect of the microwave irradiation on removal of excess water might become more obvious. Such a study was not conducted for this paper because of the difficulty in measuring water uptake on the catalyst in these systems.

5. Conclusions

Two types of microwave photocatalytic reactor assemblies were tested for photocatalytic reaction. At the highest humidity test case in both Approaches 1 and 2, reaction rate constants were greater for MWPCO than for PCO, and the adsorption experiment demonstrated that microwave irradiation removed water from the surface of the catalyst better than when heat was supplied by conductive means (Heat). The microwave irradiation appears to assist the PCO of ethylene at high humidity. When microwave plasma lighting was applied (Approach 1), the effect of the microwave irradiation on the removal of water was either 15% ($\alpha = 1$) or 26.9% ($\alpha = 0.5$) at the highest humidity test case as compared to the experiments when the microwave irradiation was focused on the catalyst in Approach 2 (83.9%). Approach 2 (external UV illumination) appears to be more practical for studying the effect of microwave fields on the removal of

water from the surface of the photocatalyst. Contact angle measurements indicated that microwave irradiation increased the wettability of a surface coated with a TiO_2/ZrO_2 photocatalyst.

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