

Influence of operating parameters on gas phase photocatalytic oxidation of methyl-ethyl-ketone in a light emitting diode (LED)-fluidized bed reactor

Mohammad Hajaghazadeh*, Vincenzo Vaiano^{*,†}, Diana Sannino^{**}, Hossein Kakooei^{***},
and Rahmat Sotudeh-Gharebagh^{****}

*Department of Occupational Health, Health Faculty, Urmia University of Medical Sciences, Urmia, Iran

**Department of Industrial Engineering, University of Salerno, Fisciano, Italy

***Department of Occupational Health, School of Public health, Tehran University of Medical Sciences, Tehran, Iran

****Oil and Gas Processing Center of Excellence, School of Chemical Engineering,

College of Engineering, University of Tehran, Tehran, Iran

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Abstract–The effect of operating parameters on gas phase photocatalytic oxidation of methyl ethyl ketone (MEK) has been investigated over P25 and PC500 photocatalysts. The parameters were gas flow rate, relative humidity (RH), reaction temperature, and ultraviolet intensity. The photoreactor was composed of two LEDs matrices and a fluidized bed reactor (LED-FBR). No mass transfer limitation phenomena occurred at flow rates in the range 30–70 NL/h. The oxidation of MEK over the two photocatalysts did not highly depend on the presence or absence of humidity in the air stream. Temperature was determined as an important parameter in conversion of MEK over 60 to 120 °C, influencing also the selectivity to carbon dioxide and carbon monoxide. The simultaneous influence of RH and temperature was observed in the reaction at different temperatures and RHs, evidencing the decrease in the selectivity towards CO with increase of RH. With the increase of ultraviolet intensity, the rate of MEK oxidation increased over both catalysts, with the better activity of PC500 than P25 particularly at higher light intensities. The main effect of temperature was both to promote the MEK conversion and to limit the competitive water adsorption in the PCO reaction over the tested titanias.

Keywords: Photocatalytic Oxidation, Relative Humidity, Temperature, Fluidized Bed Reactor, Ultraviolet Light Intensity, Selectivity to CO₂ and CO

INTRODUCTION

The emission of volatile organic compounds (VOCs) from the effluent of industrial processes into the environment has made imperative the treatment of polluted air [1–6] and liquid [7–14] streams. Activated carbon adsorption, as a conventional technology for the treatment of hazardous effluents, only transfers the molecules of pollutant to the porous structure of the adsorbent. By contrast, oxidation processes such as thermal catalytic oxidation (TCO) and photocatalytic oxidation (PCO) are the alternative remediation technologies in which oxidizing species allow the destruction of a wide range of chemicals. However, TCO operates at higher temperature than PCO, and hence the energy requirements might limit its wide application.

Heterogeneous PCO enjoys some advantages, such as operation at low temperature and applicability to the wide range of pollutants. Therefore, semiconductor-mediated PCO could be a promising technology in the treatment of VOC polluted streams. Following the pioneering research of Fujishima and Honda [15] on TiO₂ ability in the photocatalytic water splitting into hydrogen and oxygen, titania-assisted PCO has been successfully used for the removal of

a variety of organic pollutants for many years. The principles underlying semiconductor photocatalysis have been explained frequently in the literature. However, as a summary, the formation of electron-hole (e[−]-h⁺) pairs on the surface of irradiated titania generates highly reactive radical species, mainly hydroxyl radicals [16].

Depending on the band gap energy of the semiconductor, ultraviolet (UV) or visible light is able to generate hole-electron pairs. Due to developments in solid state semiconductor technology, lower cost, and environmentally friendly light emitting diodes (LEDs) are commercially available. Some unique features such as long-lasting, robustness, small size, energy efficient, eco-friendly have been listed for LEDs [17]. Furthermore, by reason of easy control of input DC voltage of LEDs, obtaining different photon fluxes is an operational advantage over fluorescent lamps. LEDs have been used in PCO of different pollutants such as dyes [18–20] and gas phase pollutants [21].

Among organic pollutants, methyl ethyl ketone (MEK), a typical malodorous substance, has been used to test the ability of different photocatalysts in its removal both in fixed and fluidized bed photoreactors [1,2]. With respect to a fixed bed reactor, the fluidized bed has the advantage of easy temperature control and enhanced mass transfer to and from the photocatalysts. Moreover, the increased photoactivity in a fluidized bed photoreactor could be partially associated with higher light absorption due to utilization of scattered lights by the catalyst particles and to photocatalyst recircula-

[†]To whom correspondence should be addressed.

E-mail: vvaiano@unisa.it

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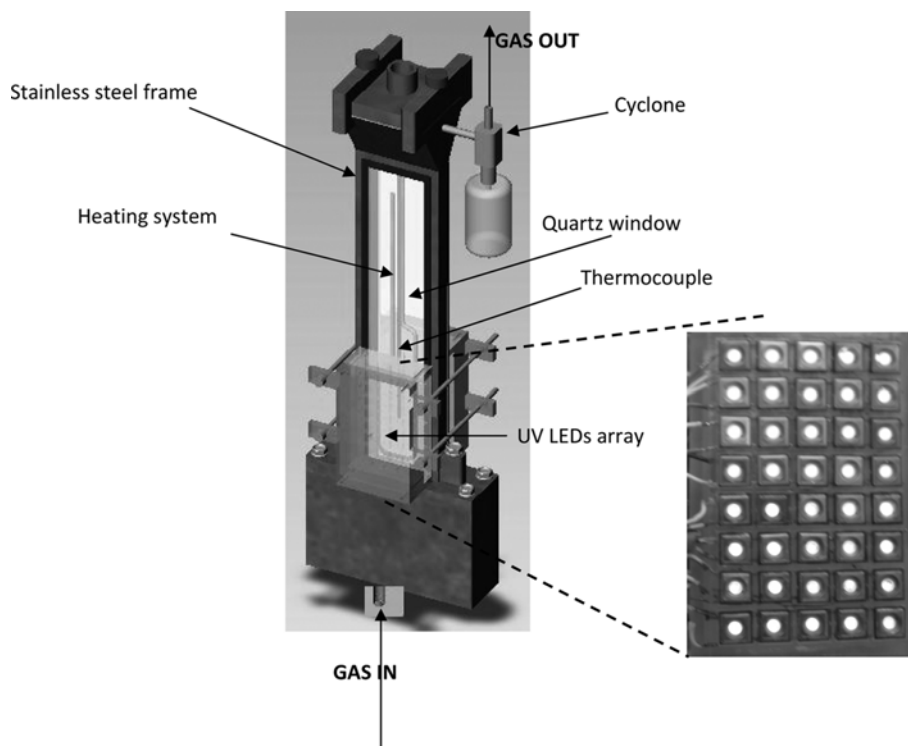


Fig. 1. Schematic picture of the UVA-LEDs photocatalytic fluidized bed reactor [6,10,25-28].

tion [22].

However, in the literature pertaining to influencing factors of the gas phase PCO reactions, the effects of initial concentration of pollutants, relative humidity (RH), light intensity and temperature have been widely investigated for different pollutants [23,24]. In other words, the effects of the mentioned parameters have been mostly reported in terms of pollutants' conversion and, therefore, little attention has been paid to the level of carbon dioxide (CO_2) formed in the reaction, as one of the desired products of a PCO reaction. However, the role of temperature and RH could strongly influence the selectivity to CO_2 in a PCO reaction. Therefore, in the current study, the effect of temperature and RH on the conversion of methyl ethyl ketone (MEK) in parallel with selectivity to CO_2 and carbon monoxide (CO) was investigated in a fluidized bed photo reactor (FBPR). In addition, the dependence of the reaction rate on light intensity was experimentally determined under UV irradiation realized by light emitting diodes (LEDs).

EXPERIMENTAL

1. Catalysts and their Characteristics

P25 and PC500 titania nano-powders were chosen to study the influence of operating parameters on the PCO of MEK. P25 and PC500 samples were obtained from Degussa Evonik and Cristal Global (formerly Millennium Inorganic Chemicals) companies.

The characteristics of photocatalysts, including specific surface area, crystalline structure, crystallite size, band gap energy and hydroxyl content, are reported in our previous work [6]. P25 was composed by a mixture of anatase/rutile (80/20) phases while PC500 was pure anatase. The specific surface area of PC500 was five-fold

higher than that of P25 (240 vs. $47 \text{ m}^2 \text{g}^{-1}$), and the crystallite size of P25 was 17 nm against 7 nm for PC500. The values of band gap energy were 3.2 and 3.3 eV for P25 and PC500, respectively. Based on the band gap values, UV-A LEDs were able to excite photocatalysts.

2. Fluidized Bed Photoreactor and Photocatalytic Tests

The schematic picture of the fluidized bed photoreactor (FBPR) has been illustrated elsewhere [6,10,25-28] and also is depicted in Fig. 1. The reactor was made of two parallel Pyrex glass windows incorporated in a steel frame with dimensions of 23 , 4 and 0.6 cm in height, width and thickness, respectively. A particle disengagement zone ($5 \text{ cm} \times 5 \text{ cm}$) was embedded at the top of the reactor to minimize the elutriation of catalyst particles. Eighty UVA- LEDs, whose emission spectrum is centred at the wavelength of 365 nm , were positioned into two $8 \times 5 \text{ cm}$ arrays and were installed in front of the reactor windows. The temperature of the fluidizing bed was measured and controlled by a proportional-integral-differential (PID) controller, which was connected to a heating system placed inside the reactor.

The concentrations of MEK and water vapor in the air stream were controlled by passing a known flow rate of air through saturators containing pure MEK and distilled water. To control the air flow in the setup, three mass flow controllers (Brooks Instruments) were used. Because of the low amount of MEK typically present in the air stream, the concentration of MEK was $1,000 \text{ ppm}$, while water vapor concentration was varied in the range 0.1 - 1 vol\% . The values of MEK concentration in the feed were verified by thermal catalytic oxidation using $0.3 \text{ wt\% Pt/Al}_2\text{O}_3$ pellets (by Engelhard), heated to 550°C . For photocatalytic tests, 0.14 g of titania powders were physically mixed with 20 g of glass spheres (size between 70

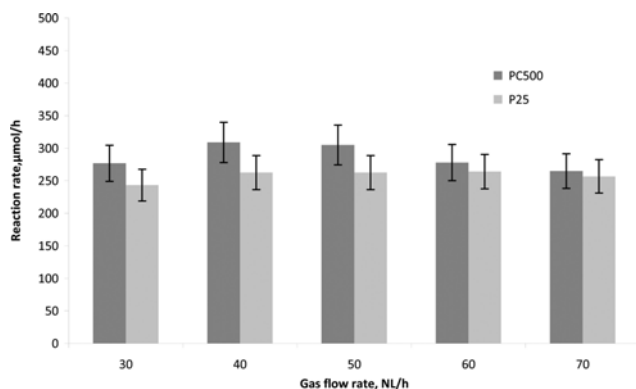


Fig. 2. Influence of flow rate on the oxidation rate of MEK over P25 and PC500 photocatalysts ($C_{MEK}=1,000$ ppm, $C_{H_2O}=0.1$ vol%, $I_0=90$ mW·cm⁻²).

and 110 μm) to improve the quality of fluidization. After the completion of dark adsorption of MEK on photocatalysts surface, LEDs were switched on and MEK concentration was continuously analyzed using an online quadrupole mass detector (Trace MS, ThermoQuest). An online non-dispersive infrared analyzer (Uras 10, Hartmann & Braun) was used to continuously measure the concentrations of CO₂ and CO.

RESULTS AND DISCUSSION

1. Influence of Superficial Gas Velocity (Flow Rate)

Fig. 2 illustrates the influence of gas flow rate on the oxidation rate of MEK in presence of photocatalysts. Since the minimum fluidization conditions (U_{mf}) of catalysts were experimentally reached at 15 NL/h, the flow rates of 30 and 70 NL/h correspond to 2 and 4.6 times of the U_{mf} of catalysts. As shown in Fig. 2, the increase of flow rate beyond the U_{mf} did not noticeably affect the reaction rate, and hence there was not a significant mass transfer limitation in the FBPR.

The superficial gas velocity, and hence the gas flow rate, is an important parameter in FBRs from the viewpoint of the bed hydrodynamics. The increase of the superficial gas velocity beyond the U_{mf} results in the circulation of the bed material, and therefore in the provision of better mass and heat transfer in an FBR [29]. In an FBPR, because of the requirement of the photocatalyst to be activated by receiving photons, the expansion of the bed, furthermore induces an improved UV photon transfer. By contrast, at high value of the superficial gas velocity, the growth of bubbles and their coalescence as well as the shorter residence time, could lead to lower conversions [1,30].

The highest TCE degradation rate in a photocatalytic fluidized bed reactor has been reported at 3 U_{mf} [30], which is close to the designated value in the current study. Thus, the flow rate of 50 NL/h (3.3 U_{mf}) was chosen to study the influence of other operating parameters. Note that the mass of 0.14 g of catalyst was chosen on the basis of previous experiments, carried out to find the optimal mass of photocatalysts, already published elsewhere [6]. Also, the higher specific surface area (SSA) of PC500 does not help to enhance the activity of this catalyst remarkably with respect to P25, as shown

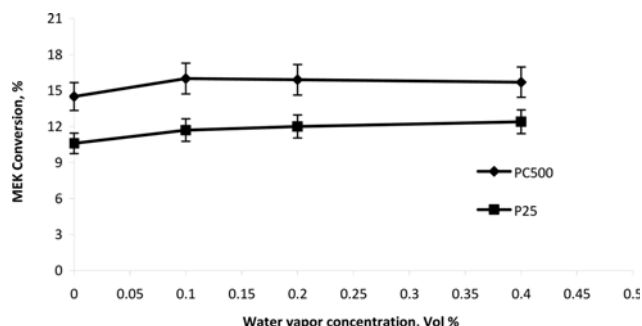


Fig. 3. Photocatalytic conversion of MEK over P25 and PC500 photocatalysts in dry and humidified atmospheres ($C_{MEK}=1,000$ ppm, gas flow rate=50 NL/h, $I_0=90$ mW·cm⁻²).

in our previous work [6]. P25 showed a transient behavior yielding, initially, a higher CO₂ formation rate, while PC500 starts to convert MEK at a slower rate. This difference was attributed to the lifetime of charge carriers of the two tested catalysts, and the better performance of P25 was attributed to a higher ability in the lowering of the recombination rate of charge-carrier [31].

The higher SSA of PC500 is correlated to the presence of surface defects and also of amorphous domains, but this is unfavorable to the charge separation, and so this characteristic led to higher recombination rate of charge carriers [6], lowering the activity expectation on the basis of the evaluation of only SSA.

2. Influence of Water Vapour Content

The role of water vapor and its content in the photocatalytic oxidation of 1,000 ppm MEK over P25 and PC500 photocatalysts is shown in Fig. 3. For both photocatalysts, only a very little change in MEK conversion was observed by increasing water vapor concentration, evidencing that the presence of water molecules in the air stream did not affect the conversion of MEK remarkably. In other words, the PCO of MEK was not hindered in dry condition. The progress of MEK PCO reaction in dry air can be attributed to the pre-adsorbed water molecules on the surface of photocatalysts and also the formation of water molecules, as a final product, during the PCO reaction. The direct oxidation of MEK molecules by the holes (h^+) of valence band is also another possibility for the progress of reaction in the dry atmosphere [32,33].

Although water molecules act as a source of reactive species, such as hydroxyl radicals, their presence in the air stream did not enhance the PCO of MEK. The change of conversion was less than 5% between the two catalysts.

Next, we studied the role of temperature in the PCO of MEK to investigate its impact on the reaction at fixed and different humidity levels.

3. Influence of Temperature

The influence of temperature on MEK conversion as well as the selectivity to CO and CO₂ is shown in Fig. 4. The temperature did not determine a significant improvement both on the conversion of MEK and on the selectivity to CO and CO₂ in the range of 40–60 °C. However, the activity of PC500 was somewhat higher than P25 at the temperatures beyond 60 °C.

As the temperature increased from 60 to 120 °C, both the conversion of MEK and selectivity to CO increased, while the selectiv-

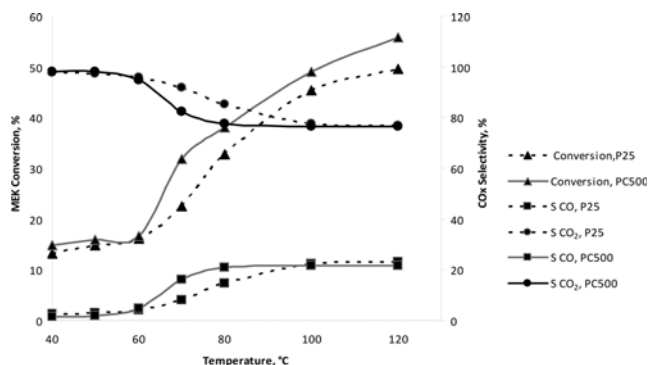


Fig. 4. The influence of temperature on conversion of MEK and selectivity to CO and CO₂ ($C_{MEK}=1,000$ ppm, gas flow rate=50 NL/h, $C_{H_2O}=0.1$ vol%, $I_0=45$ mW·cm⁻²).

ity to CO₂ decreased. This behavior can be explained considering that, at low temperature, CO interacts strongly with TiO₂ anatase surface, and so it can be converted into CO₂ by the hydroxyl radicals, as happens in the thermal radical combustion reaction. At higher temperature, CO desorbs more easily from the catalyst surface and only a fraction can be converted to CO₂, which is the probably reason for its evidence in gas-phase [34]. The obtained results underline that the elevated temperature would be useful for a PCO reaction if the level of CO could be reduced. Otherwise, the remarkable formation of CO could be accounted as a major drawback.

Photocatalytic oxidation is a photon-dependent reaction and the activity of a photocatalyst at room temperature is regarded as a main advantage. Therefore, the exposing of the photocatalyst at higher temperature to enhance the conversion of chemicals might be considered unfavorable from the energy standpoint. Another issue in the use of temperature, as an enhancer, is its double role in the PCO reaction. Some studies have reported that after a given temperature the reaction could be hindered because of the weak adsorption of reactants on the surface of the photocatalyst [35,36]. Besides the limitations related to the use of temperature in a PCO reaction, the formation of significant CO amounts, as indicated in the cur-

rent study, could remain the use of temperature in a PCO reaction as a challenge.

It seems that the formation of CO in a heated photoreactor happens over the bare TiO₂. Doping of titania with transition metals, such as platinum, has increased the selectivity to CO₂ at higher temperatures in PCO of cyclohexane [4]. Consistent with the result of the current study, the selectivity to CO₂ decreased with increase of temperature. Over Pt/TiO₂, selectivity to CO₂ was equal to 100%. Sano et al. reported complete degradation of toluene and acetaldehydes without formation of CO over Pt-loaded TiO₂ at 40-190 °C [37]. In the PCO of TCE over Pt/TiO₂, Sánchez et al. [38] did not report the formation of CO in a heated reactor. It could be concluded that when higher temperature than ambient one is used to enhance the photocatalytic performance, a modified photocatalyst is required to avoid the formation of CO.

Although doping of a semiconductor with noble metals could be regarded as a method to lessen the concentration of CO in a PCO reaction, increasing the level of a reactant such as water vapor in the air stream might reduce the concentration of CO. Therefore, we performed the PCO of MEK with heated reactor under dry and humidified condition to evidence the simultaneous influence of humidity and temperature.

4. Simultaneous Influence of Humidity and Temperature

Fig. 5 illustrates the simultaneous influence of humidity and temperature in the range 60-100 °C on the PCO of MEK over P25 photocatalyst. From the experimental data, it is clear that the increase of temperature, in both dry and humidified conditions, improves the conversion of MEK. Interestingly, the increase of humidity at 60 and 80 °C led to the decrease of conversion. This phenomenon could be an expression of a competitive adsorption [23]. At 100 °C the MEK conversion did not change significantly, indicating that, at a temperature near to the boiling point of water, the competitive water adsorption with MEK is minimized.

Although the increase of humidity resulted in the decrease of conversion, particularly at lower temperatures, the improvement in the MEK conversion could compensate for the loss of selectivity towards CO₂ at high temperature. However, to better evaluate the

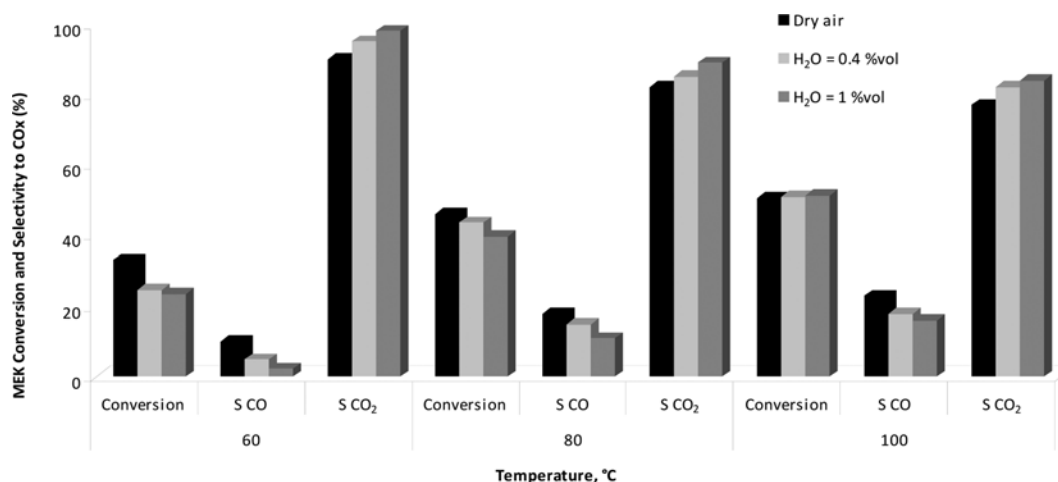


Fig. 5. Simultaneous influence of humidity and temperature on MEK conversion and selectivity (S) to CO₂ and CO over P25 photocatalyst ($C_{MEK}=1,000$ ppm, gas flow rate=50 NL/h, $I_0=45$ mW·cm⁻²).

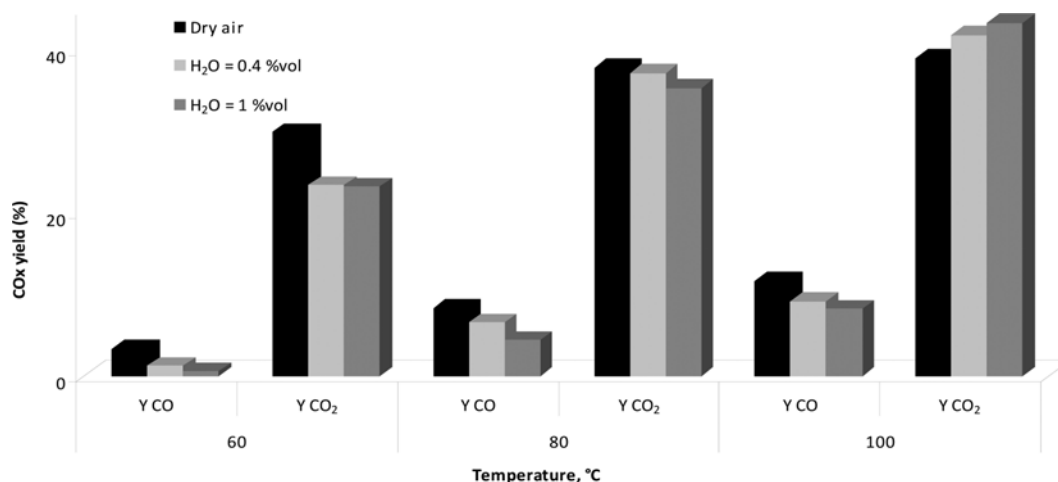


Fig. 6. Simultaneous influence of humidity and temperature on CO₂ and CO yield (Y) over P25 photocatalyst ($C_{MEK}=1,000$ ppm, gas flow rate=50 NL/h, $I_0=45$ mW·cm⁻²).

combined influence of temperature and RH, the obtained yield to CO and CO₂ (Fig. 6) could give a more clear indication with respect to the selection of operating conditions. In summary, the results obtained from these experiments showed that the use of high humidity with high temperature importantly improves the yield to CO₂.

5. Influence of UV Light Intensity

Since light quanta act as a reactant in a PCO reaction [39–41], the dependence of the PCO reaction on light intensity is an important issue. Therefore, to experimentally determine the dependence of MEK PCO rate on light intensity, PC500 and P25 photocatalysts were irradiated under 10–90 mW/cm² of UV-A light.

Fig. 7 shows the results of UV light irradiance on the reaction. As the intensity of light was increased, the rate of MEK oxidation increased over both catalysts, with the better activity of PC500 than P25 particularly at higher light intensities.

To calculate the functional dependence of MEK PCO rate on light intensity, the term I^α , mW/cm², was determined into a modified Langmuir-Hinshelwood (L-H) model (Eq. (1)) [42], and similar to that used by us to model photocatalytic PCO in the liquid phase [9].

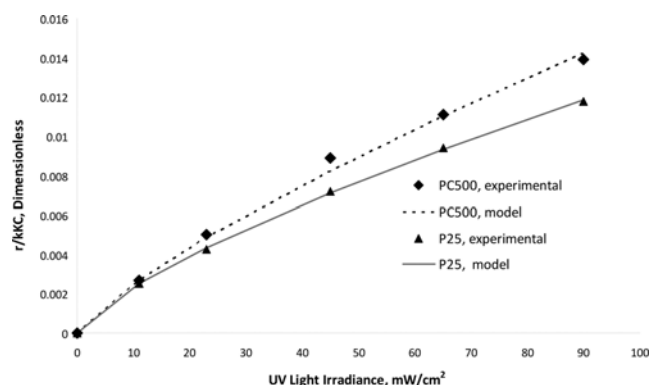


Fig. 7. Behaviour of photocatalytic oxidation rate of MEK over P25 and PC500 photocatalysts as a function of UV light irradiance ($C_{MEK}=1,000$ ppm, gas flow rate=50 NL/h, $C_{H_2O}=0.1$ vol%).

$$r = I^\alpha \frac{kKC}{1 + KC} \quad (1)$$

where:

r =reaction rate, $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$

C =concentration of MEK in the inlet of reactor, $\mu\text{mol}\cdot\text{L}^{-1}$

k =reaction kinetic, $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ (mW cm⁻²) $^\alpha$

K =adsorption constant, L μmol^{-1}

I =light intensity, mW cm⁻²

Considering the term $KC \ll 1$, due to the reaction in the gas phase with relative lower concentration, the pseudo-first-order form of the equation was used (Eq. (2)).

$$r = kKC I^\alpha \quad (2)$$

The constants k and K were calculated from MEK conversions obtained by photocatalytic tests performed with MEK concentration in the range 250–1,000 ppm (10.23–40.9 $\mu\text{mol}\cdot\text{L}^{-1}$) with 0.14 g of photocatalyst (Table 1). To determine the value of α using the least square method, the mean squared residuals of the r/kKC and $r/kKC \cdot (I_i/I_1)^\alpha$ terms were obtained at different light intensities and then were summed. Then, the sum of the squared residuals was minimized to obtain the value of α . The value of r/kKC was calculated with the constants presented in Table 1 and the reaction rate obtained from oxidation of 1,000 ppm MEK at different UV light intensity (Fig. 7). I_i and I_1 are the different light intensities and the first light intensity emitted by LEDs, respectively. After applying the least square method, the value of α was equal to 0.74 and 0.79 for P25 and PC500, respectively (Table 1). The fitting of experimental trends with model curves $r/kKC \cdot (I_i/I_1)^\alpha$ using the obtained α are also shown in Fig. 7 for both photocatalysts.

In the PCO literature, the dependence of reaction rate on light intensity was studied for several pollutants. In the photocatalytic oxidation of TCE, the increase of light intensity from 0.09 to 0.45 mW/cm² increased the reaction rate with $\alpha=0.61$. Jacoby et al. instead reported the linear regime in the oxidation of TCE in irradiances lower than 2 mW/cm² [43]. The linearity between benzene decomposition rate and light intensity was reported by Wang et al.

Table 1. Values of calculated reaction kinetic (k) and adsorption (K) constants with together a values for oxidation of MEK over P25 and PC500 photocatalysts

C, μmol/L	MEK conversion, %		r		k		K		α	
	P25	PC500	P25	PC500	P25	PC500	P25	PC500	P25	PC500
10.23	79	85	2884.91	3104.02						
20.45	47	48	3432.68	3505.71						
30.68	34	36	3724.82	3943.93	5000	5366	0.18	0.16	0.74	0.79
40.9	27	29	3943.93	4236.07						

in irradiances lower than 1.83 mW/cm² [44]. The increase of UV light intensity from 1.83 to 2.75 mW/cm² did not increase the reaction rate linearly. Also, the linear relationships were observed in photocatalytic oxidation of H₂S at 3.3–4.9 mW/cm² [45]. Doucet et al. obtained a constant quantum yield for TCE and methanol oxidation in irradiances lower than 2.1 mW/cm², which implies linear proportionality [46]. They observed square root dependency for benzene degradation.

The effect of photon flux in the kinetic study of TCE, acetone, methanol, and toluene has been reported under germicidal and black light lamps [47]. Under a germicidal lamp (1.12–3.38 mW/cm²) the exponent value, α , ranged from 0.35 to 0.57, whereas under black light (light intensity lower than 1.17 mW/cm²) α increased and reached values in the range 0.89–0.95. Obee and Brown obtained the oxidation dependence of formaldehyde, toluene, and 1,3-butadiene on UV light equal to 0.55 in intensities above one sun equivalent [48]. In another paper [49] similar values, 0.64 and 0.6, have been reported for the oxidation dependence of toluene and formaldehyde, respectively.

With regard to the results of the literature studies obtained with different pollutants, reactors, and concentrations, at relatively high irradiances, the dependence of reaction rate to UV light intensity follows the half-order regime. Since the photon fluxes used in the current study were greater than one sun equivalent, the relative higher values of obtained exponent, 0.73 and 0.79, could be related to the illumination of the flat plate FBPR from both sides as well as the better exposing of catalyst with light in this configuration of the reactor [22]. It could be concluded that in an FBPR the periodic exposition of photocatalysts to the photons, induced by the solid mixing, increases the possibilities of using the sent quanta.

CONCLUSIONS

The photocatalytic oxidation of MEK was studied over two commercial TiO₂ samples in a UV-A-LEDs equipped fluidized bed reactor. The operation of FBPR at superficial gas velocities of 2–4.6 U_{mf} did not significantly change the reaction rate, indicating the absence of mass transfer limitation at 30–70 NL/h flow rates. The result of PCO tests in dry and humidified atmosphere over two structurally different TiO₂, showed that the heterogeneous photocatalytic oxidation of MEK does not highly depend on the presence of water molecules at air stream. The increase of reaction temperature from 60 up to 120 °C determined an increase of MEK conversion as well as selectivity to CO, while the selectivity to CO₂ decreased in this range of temperature, indicating the function of temperature in limit-

ing the competitive water adsorption in the PCO reaction over the tested titanias. During the exposition of photocatalyst at elevated temperature, the increase of humidity could maintain the level of the improved conversion constant, enhancing the yield to CO₂. However, when the water molecules could be adsorbed in a multilayer mode, as it could happen at temperatures lower than that of the boiling point of water, the competition with the MEK for the adsorption was stronger.

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REFERENCES

1. M. Hajaghazadeh, H. Kakooei, A. Motamed Dashliborun, R. Sotudeh-Gharebagh, F. Golbabaie, S. Afshar and A. Rahimi Foroushani, *Fresenius Environ. Bull.*, **22**, 435 (2013).
2. M. Hajaghazadeh, H. Kakooei, A. Motamed Dashliborun, R. Sotudeh-Gharebagh, F. Golbabaie, A. Rahimi Foroushani and S. Afshar, *Fresenius Environ. Bull.*, **22**, 1719 (2013).
3. A. Motamed Dashliborun, R. Sotudeh-Gharebagh, M. Hajaghazadeh, H. Kakooei and S. Afshar, *Chem. Eng. J.*, **226**, 59 (2013).
4. J. J. Murcia, M. C. Hidalgo, J. A. Navío, V. Vaiano, D. Sannino and P. Ciambelli, *Catal. Today*, **209**, 164 (2013).
5. D. Sannino, V. Vaiano, G. Sarno and P. Ciambelli, *Chem. Eng. Transactions*, **32**, 355 (2013).
6. M. Hajaghazadeh, V. Vaiano, D. Sannino, H. Kakooei, R. Sotudeh-Gharebagh and P. Ciambelli, *Catal. Today*, **230**, 79 (2014).
7. V. Vaiano, O. Sacco, D. Sannino and P. Ciambelli, *Chem. Eng. J.*, **261**, 3 (2015).
8. L. Rizzo, D. Sannino, V. Vaiano, O. Sacco, A. Scarpa and D. Pietrogiammi, *Appl. Catal., B*, **144**, 369 (2014).
9. V. Vaiano, O. Sacco, M. Stoller, A. Chianese, P. Ciambelli and D. Sannino, *Int. J. Chem. React. Eng.*, **12**(1), 1 (2014).
10. D. Sannino, V. Vaiano and P. Ciambelli, *Catal. Today*, **205**, 159 (2013).
11. V. Augugliaro, M. Bellardita, V. Loddo, G. Palmisano, L. Palmisano and S. Yurdakal, *J. Photochem. Photobiol., C*, **13**, 224 (2012).
12. G. Palmisano, E. García-López, G. Marci, V. Loddo, S. Yurdakal, V. Augugliaro and L. Palmisano, *Chem. Commun.*, **46**, 7074 (2010).
13. V. Vaiano, O. Sacco, D. Sannino, P. Ciambelli, S. Longo, V. Venditto and G. Guerra, *J. Chem. Technol. Biotechnol.*, **89**, 1175 (2014).

14. V. Vaiano, G. Iervolino, D. Sannino, L. Rizzo, G. Sarno and A. Farina, *Appl. Catal., B*, **160-161**, 247 (2014).
15. M. Kitano, M. Matsuoka, M. Ueshima and M. Anpo, *Appl. Catal., A*, **325**, 1 (2007).
16. U. I. Gaya and A. H. Abdullah, *J. Photochem. Photobiol., C*, **9**, 1 (2008).
17. W. K. Jo and R. J. Tayade, *Ind. Eng. Chem. Res.*, **53**, 2073 (2014).
18. R. J. Tayade, T. S. Natarajan and H. C. Bajaj, *Ind. Eng. Chem. Res.*, **48**, 10262 (2009).
19. T. S. Natarajan, M. Thomas, K. Natarajan, H. C. Bajaj and R. J. Tayade, *Chem. Eng. J.*, **169**, 126 (2011).
20. T. S. Natarajan, K. Natarajan, H. C. Bajaj and R. J. Tayade, *Ind. Eng. Chem. Res.*, **50**, 7753 (2011).
21. Z. Wang, J. Liu, Y. Dai, W. Dong, S. Zhang and J. Chen, *J. Hazard. Mater.*, **215-216**, 25 (2012).
22. D. Sannino, V. Vaiano, P. Ciambelli, P. Eloy and E. M. Gaigneaux, *Appl. Catal., A*, **394**, 71 (2011).
23. J. Mo, Y. Zhang, Q. Xu, J. J. Lamson and R. Zhao, *Atmos. Environ.*, **43**, 2229 (2009).
24. J. Zhao and X. Yang, *Build. Sci.*, **38**, 645 (2003).
25. D. Sannino, V. Vaiano and P. Ciambelli, *Curr. Org. Chem.*, **17**, 2420 (2013).
26. D. Sannino, V. Vaiano and P. Ciambelli, *Res. Chem. Intermed.*, **39**, 4145 (2013).
27. D. Sannino, V. Vaiano, P. Ciambelli, G. Carotenuto, M. Di Serio and E. Santacesaria, *Catal. Today*, **209**, 159 (2013).
28. D. Sannino, V. Vaiano, P. Ciambelli, J. J. Murcia, M. C. Hidalgo and J. A. Navío, *J. Adv. Oxid. Technol.*, **16**, 71 (2013).
29. R. Jafari, R. Sotudeh-Gharebagh and N. Mostoufi, *Chem. Eng. Technol.*, **27**, 123 (2004).
30. T. H. Lim and S. D. Kim, *Chemosphere*, **54**, 305 (2004).
31. S. T. Martin, H. Herrmann, W. Choi and M. R. Hoffmann, *J. Chem. Soc., Faraday Trans.*, **90**, 3315 (1994).
32. C. Raillard, V. Héquet, P. L. Cloirec and J. Legrand, *Appl. Catal., B*, **59**, 213 (2005).
33. G. Vincent, A. Queffelec, P.-M. Marquaire and O. Zahraa, *J. Photochem. Photobiol., A*, **191**, 42 (2007).
34. P. K. Dutta, A. Ginwalla, B. Hogg, B. R. Patton, B. Chwieroth, Z. Liang, P. Gouma, M. Mills and S. Akbar, *J. Phys. Chem. B*, **103**, 4412 (1999).
35. S. Hager and R. Bauer, *Chemosphere*, **38**, 1549 (1999).
36. H. Yu, K. Zhang and C. Rossi, *Indoor Built Environ.*, **16**, 529 (2007).
37. T. Sano, N. Negishi, K. Takeuchi and S. Matsuzawa, *Sol. Energy*, **77**, 543 (2004).
38. B. Sánchez, A. I. Cardona, M. Romero, P. Avila and A. Bahamonde, *Catal. Today*, **54**, 369 (1999).
39. G. Camera-Roda, F. Santarelli and C. A. Martin, *Sol. Energy*, **79**, 343 (2005).
40. V. Palma, D. Sannino, V. Vaiano and P. Ciambelli, *Ind. Eng. Chem. Res.*, **49**, 10279 (2010).
41. A. Vorontsov, D. Kozlov, P. Smirniotis and V. Parmon, *Kinet. Catal.*, **46**, 437 (2005).
42. K. H. Wang, Y. H. Hsieh, C. H. Lin and C. Y. Chang, *Chemosphere*, **39**, 1371 (1999).
43. W. A. Jacoby, D. M. Blake, R. D. Noble and C. A. Koval, *J. Catal.*, **157**, 87 (1995).
44. W. Wang, L.-W. Chiang and Y. Ku, *J. Hazard. Mater.*, **101**, 133 (2003).
45. A. Alonso-Tellez, D. Robert, N. Keller and V. Keller, *Appl. Catal., B*, **115**, 209 (2012).
46. N. Doucet, F. Bocquillon, O. Zahraa and M. Bouchy, *Chemosphere*, **65**, 1188 (2006).
47. S. B. Kim and S. C. Hong, *Appl. Catal., B*, **35**, 305 (2002).
48. T. N. Obee and R. T. Brown, *Environ. Sci. Technol.*, **29**, 1223 (1995).
49. T. N. Obee, *Environ. Sci. Technol.*, **30**, 3578 (1996).