# COMPETITIVE ADSORPTION BEHAVIOUR OF BINARY MIXTURES ON TITANIUM DIOXIDE

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Exploration of the adsorption mechanism for mixtures at photocatalyst surfaces is a prerequisite for a full understanding of photocatalytic oxidation (PCO) technology for treatment of gaseous contaminants in indoor air applications. However, there has been very little work on the competitive adsorption of photocatalysts. In this article, an experimental and analytical study on the co-adsorption of nine binary mixtures on a commercial PCO filter was investigated using a bench-scale single-pass continuous flow system. Adsorption tests were performed with a concentration of 500 ppb for the selected mixtures at various molar ratios. The experiments were performed at 40 % RH, 21 °C, and a gas flow rate of 10 L/min. Quantitative methods were developed to describe inhibitory and facilitatory effects on the adsorption of one component by the other. It was found that for the non-polar mixture of p-xylene and toluene, the polar mixture of MEK and acetone, and the polar/non-polar mixture of MEK and p-xylene, adsorption selectivity varied from 0.83–1.81, 1.80–1.21, and 2.60–1.78, respectively, when mixing ratio of each mixture changed from 1:2.33 to 2.33:1. In addition, a time-dependent co-adsorption model was developed and validated with the experimental results. It was concluded that competitive adsorption performance is dependent upon the composition of the gas mixture, the natures of the adsorbate and substrate, and the initial molar ratio of VOCs.

Keywords: competitive adsorption, binary mixtures, titanium dioxide, inhibitory effect, facilitatory effect

## INTRODUCTION

ith the development of the global economy, building occupants' requirements for a comfortable and healthy working environment result in considerable attention to indoor air quality (IAQ). In past decades, a great deal of research has been conducted to identify and characterize the source and emission of indoor air contaminants.<sup>[1-4]</sup> Besides particulate matter, volatile organic compounds (VOCs) are known to act as the dominant contributor in air contamination due to the high frequency of personal exposure to the wide use of man-made materials. In the heating, ventilating, and air conditioning (HVAC) industry, researchers, building engineers, and designers are striving to provide safe, healthy, productive, and comfortable indoor environments while making efforts to conserve resources and protect the environment. Hence, a variety of technologies associated with the improvement of IAQ have been recommended, including dilution with outdoor air, air filtration and purification, reduction of indoor contaminant level through material selection, and control of indoor pollution sources.<sup>[5,6]</sup>

Carbon filtration, as a rather mature technology, has been demonstrated to be effective in removing gaseous contaminants due to its advantages of being both high in capacity and high in efficiency.<sup>[7–9]</sup> However, the need for a system with low pressuredrops and low energy requirements drives the research and development sector to produce new technologies to overcome the weakness of the adsorption aspect which is faced by this type of filtration.

Photocatalytic oxidation (PCO) is an emerging and advanced oxidizing technology that has great potential for application in the HVAC industry for the elimination of chemical gas pollutants such as VOCs. Not only can this promising technology provide high IAQ, but it also has the potential for saving energy as a result of the reduction of unconditioned outdoor supply air to buildings. A large number of experimental and modelling studies have been devoted to the investigation and exploration of PCO performance of a single compound for indoor air purification.<sup>[10–13]</sup> Indoor air may contain hundreds of chemical gas pollutants at various ppb levels. Each of these simultaneously adsorbed pollutants leads to the necessity to explore the effect of their competition on the catalyst surface for the same active sites and quantify their influence on UV-PCO performance. With regards to competitive PCO behaviour challenged by gas mixtures, there is an insufficient amount of information concerning this topic. To improve the possibility of wide applications of PCO technology in buildings, it is essential to understand the catalyst surface adsorption since it is one of the fundamental processes occurring at a heterogeneous photocatalytic reaction. An accurate description of the competitive adsorption may promote the development of an in-depth understanding of the UV-PCO surface chemistry with mixtures.

In the field of PCO air cleaners, titanium dioxide (TiO<sub>2</sub>) is a widely used photocatalyst due to its favourable characteristics, such as high photocatalytic activity, photostability, and chemical stability. Although TiO<sub>2</sub> is not a powerful adsorbent like activated carbon for trapping multiple gases, the nature of its microporous structure and superhydrophility trait grants TiO<sub>2</sub> the unique characteristic of adsorption. Some recent studies focused on the adsorption dynamics of several compounds on the surface of TiO<sub>2</sub>.<sup>[14–17]</sup> Wang et al. observed competitive adsorption between methanol and water on TiO<sub>2</sub> at the molecular level through in situ use of sum frequency generation (SFG).<sup>[14]</sup> The SFG results

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indicated that methanol is much more strongly adsorbed to the TiO<sub>2</sub> surface than water. Co-adsorption of 2-propanol and toluene on the photocatalytic filter at 0 % and 60 % RH was investigated by Vildozo et al., and results demonstrated that the competition is insignificant at dry conditions, and adsorption of toluene is lower than 2-propanol due to the presence of water vapour.<sup>[16]</sup> A similar conclusion was made by Geng et al.<sup>[17]</sup> They reported that the coadsorption mechanism of methanol-benzene not only is related to the competition adsorption but it is also involved in penetrating the multi- or mono-water layer formed on the catalyst surface. The common limitation of the previous studies is that they reported only qualitative descriptions of competitive adsorption phenomena for a few compounds. Also, the different RH conditions involved in the adsorption tests complicate the process of competitive adsorption since water molecules compete with other VOCs for active sites on TiO<sub>2</sub>. Hence, the water vapour was kept constant in this study to allow for the exploration of the competitive adsorption of selected challenge VOCs at the catalyst surface. The extended Langmuir model is used to describe a competitive adsorption isotherm of two molecules which are both adsorbed molecularly, and compete for the same adsorption sites. The limitations are (1) the model is intended to describe the competitive adsorption in solid phase in equilibrium; (2) the model ignores adsorbate-adsorbate interactions. To overcome these weaknesses, a kinetic model is proposed to describe the competitive behaviour of molecules in both gas and solid phases with time. This modelling also considers the fact of catalyst properties being changed by one component, in turn affecting the adsorption of other components.

The purpose of this study is to quantitatively describe the competitive selection of binary mixtures for adsorption on a commercial TiO<sub>2</sub>-loaded PCO filter in the absence of light sources. In this research, the competitive adsorption performance has been experimentally investigated for four compounds at different binary combinations: toluene, p-xylene, methyl ethyl ketone (MEK), and acetone. These compounds are representative of the contaminants found in indoor air, as well as possessing various physical and chemical properties, including polarity, solubility, molecular weight, and molecular structure, which can be utilized to fully study the competition effect. The possible by-products generated from UV-PCO systems using the selected VOCs usually contain carcinogenic compounds, like formaldehyde and acetaldehyde.<sup>[10]</sup> The knowledge obtained from this project helps to design a PCO reactor with desirable adsorption selectivity in order to minimize generation of these toxic by-products. In addition, a mathematical co-adsorption model is developed to simulate the competitive behaviour. Quantitative descriptions of interactions of two components during the co-adsorption process are also provided in order to assist in the acquisition of further knowledge associated with the physical forces and chemical bonds on the catalyst surface. Moreover, rationalizations of the tested results in terms of adsorbate nature and surface chemistry are presented. The outcomes of this study can be applied and extended to adsorption selectivity and catalytic selectivity of UV-PCO systems.

## EXPERIMENTAL

#### Materials

A commercial PCO filter (Quartzel<sup>®</sup> PCO, Saint-Gobain Quartz) was used in this study, which was made up of long, continuous amorphous silica fibres coated with a layer of TiO<sub>2</sub>. Table 1 gives some technical data, including BET surface area, thickness, pore

Table 1. Technical data of a PCO filter				
Parameter	PCO filter			
Fibre diameter	90 µm			
Areal weight	100 g/m <sup>2</sup>			
Specific surface area (BET)	100–120 m <sup>2</sup> /g			
Thickness	15–20 mm (0.6–0.8 inch)			
Pressure drop	100 Pa at 2 m/s			
	(0.4 inch WG at 400 fpm)			
BJH desorption average pore diameter	3.6 nm			

diameter, etc., of the PCO filter. The morphological aspect of the PCO filter surfaces was characterized via scanning electron microscopy (SEM, Hitachi S-4700 Model) and energy dispersive spectroscopy (EDS, INCA system, Oxford Instruments); see Figure 1. The EDS result of elemental composition demonstrates that the mass fractions and atomic percentages of O, Si, and Ti are 36.26, 32.37, and 31.37 %, and 54.92, 26.48, and 18.60 %, respectively. Other characterization, such as the nitrogen adsorption–desorption isotherm and the pore size distribution, can be found in the previous publication.<sup>[18]</sup>

Four reagent grade chemicals were selected as model VOC air contaminants, which include toluene (99.9%), p-xylene (99.9%), MEK (99.9%), and acetone (99.5%) from Fisher Scientific Inc. (Canada), the physical characteristics of which are given as Supporting Material. The inlet concentrations and injection rates for nine binary mixtures are illustrated in Table 2. Ultra-high purity (99.999%) nitrogen and helium from Praxair Canada Inc. were employed as carrier gases for automated thermal desorption coupled to gas chromatography-mass spectrometry analysis (ATD–GC–MS, Perkin Elmer, USA). The liquid in the humidity generation system was deionized water filtered with a







Figure 1. SEM image and EDS spectrum of a PCO filter.

Table 2. Inlet VOC mixture and concentration						
	Mixture A		Mixture B		Mixture C	
VOCs	Mix ratio (ppb)	Injection rate ( $\mu$ L/min)	Mix ratio (ppb)	Injection rate ( $\mu$ L/min)	Mix ratio (ppb)	Injection rate ( $\mu$ L/min)
p-xylene	$150\pm3$	0.008	$350\pm7$	0.018	$250\pm5$	0.013
Toluene	$350\pm7$	0.016	$150\pm3$	0.007	$250\pm5$	0.011
	Mixture D		Mixture E		Mixture F	
Compound	Mix ratio (ppb)	Injection rate ( $\mu$ L/min)	Mix ratio (ppb)	Injection rate ( $\mu$ L/min)	Mix ratio (ppb)	Injection rate ( $\mu$ L/min)
MEK	$150\pm3$	0.006	$350\pm7$	0.013	$250\pm 5$	0.009
Acetone	$350\pm7$	0.011	$150\pm3$	0.005	$250\pm 5$	0.008
	Mixture G		Mixture H		Mixture I	
Compound	Mix ratio (ppb)	Injection rate ( $\mu$ L/min)	Mix ratio (ppb)	Injection rate ( $\mu$ L/min)	Mix ratio (ppb)	Injection rate ( $\mu$ L/min)
MEK	$150\pm3$	0.006	$350\pm7$	0.013	$250\pm 5$	0.009
p-xylene	$350\pm7$	0.018	$150\pm3$	0.008	$250\pm 5$	0.013

Milli-Q system (Millipore Inc.). In this study, all competitive adsorption tests were conducted with no light illumination.

## Adsorption Apparatus and Procedure

To qualitatively and quantitatively examine competitive adsorption behaviour, a bench-top adsorption test system in accordance with ASHRAE Standard 145.1 was used as shown in Figure 2.<sup>[19]</sup> The laboratory compressed air was used as the carrier gas for the adsorption tests; its flow rate  $(10.12 \pm 0.16 \text{ L/min})$  was controlled by a mass flow meter (Matheson model 8274) and was accurately measured by a calibrated flow meter (DryCal DC-Lite) before and after each run in order to check the consistency of the flow measurement. The experiments were performed at 40 % relative humidity (RH). Before regulating RH, the inlet air was purified by passing it through a granular activated carbon (GAC) filter which removed possible traces of VOCs. The RH of the inlet air was controlled to be  $40.0\% \pm 0.9\%$  by adjusting the proportion of the compressed air into a water bottle filled with distilled water. In addition, the water bottle was placed in a controlled water bath (Thermo Haake) so that its temperature remained constant at 21 °C. A probe (Testo 625) was used to continuously monitor the temperature and RH of the controlled air stream during the test. The selected pure liquid binary VOCs were separately injected using two syringe pumps (KD Scientific) with corresponding injection rates. Then the liquids were vaporized and immediately mixed with the treated air stream, and the gaseous steam was delivered to the adsorption section. A media column made of a highly non-reactive material was filled with three layers of the PCO filter with a diameter of 44.5 mm and a total thickness of 50 mm. New PCO filter material was used in each experiment in order to reduce residual contamination. The weight of the PCO filters was  $0.546 \pm 0.007$  g. The experiments were performed at ambient temperature of  $21.3\pm0.4\,^\circ C$  and a total inlet concentration of 500 ppb with various ratios for binary VOCs ( $150 \pm 3$ ppb,  $250 \pm 5$  ppb,  $350 \pm 7$  ppb). Before performing each adsorption experiment, the air filter was routinely conditioned by pure air overnight with 40 % RH in order to reduce the effect of competitive interaction of water with TiO<sub>2</sub>.

Before starting an adsorption test, a chemically inert polytetrafluoroethylene (PTFE) tube (Figure 2) transporting gaseous



pollutants was first connected to the test system. After the inlet concentrations reached and maintained a steady state for 2 h, "Air Toxic" tubes (Perkin Elmer, USA) were used to collect the upstream samples in accordance with the U.S. EPA Compendium Method TO-17.<sup>[20]</sup> After two samples were taken from upstream, the PTFE tube was replaced by the media column. The downstream samples after the media column were taken by 5 tubes at an interval of 4 min, and then by 4 tubes at an interval of 10 min, and finally by 1 tube at an interval of 30 min. A calibrated gas flow monitor (Definer 220) was deployed to accurately measure the actual sampling rates for each sampling tube. The total competitive adsorption test lasted for 90 min at which adsorption capacities of each component were expected to reach equilibrium state. The media column was replaced by the PTFE tube to collect two upstream samples again in order to check the consistency of inlet concentrations.

Periodically collected samples were analyzed by a GC equipped with an ATD and a MS. A column with an Elite-VMS phase ( $60 \text{ m} \times 0.32 \text{ mm} \times 1.8 \mu\text{m}$ , Perkin Elmer, USA) was used for the separation of the analyzed compounds. The analytes were desorbed from the "Air Toxic" tube at 250 °C for 4 min with a desorb flow rate of 40 mL/min, and then were sent to a focusing trap for second-stage desorption by rapid heating (40 °C/s) from 10 °C to 300 °C. After the desorption process, the analytes were sent into the split injector of the GC (inlet split 34 mL/min and outlet split 34 mL/min). The temperature of valves and transfer line was maintained at 225 °C. The GC oven temperature was balanced at 40 °C followed by a ramp of 12 °C/min to 100 °C and then by a second ramp of 9 °C/min to 180 °C, holding for 1 min. The details of the MS method and its parameters are available as Supporting Material.

#### Adsorption Analysis Method

Using the upstream and downstream air concentration measurements, the adsorbed mass of component i on the PCO filter during the testing period can be obtained:

$$m_i^t = Q \int_0^t (C_i^{up,t} - C_i^{down,t}) dt \tag{1}$$

where  $m_i^t$  is the adsorbed mass (g) of component i during the adsorption time t, which is 90 min for all cases; Q is the airflow rate ( $m^3/min$ ) which is regarded as constant during a test and is calculated as the average airflow rate (measured before and after an adsorption test with a variation of less than 1 %);  $C_i^{up,t}$  and  $C_i^{down,t}$  are the upstream and downstream concentration of component i (g/m<sup>3</sup>) as a function of elapsed time, respectively.  $C_i^{up,t}$  is the average concentration measured before and after an adsorption test. It had a variation of less than 2 %.

The adsorption performance of the mixtures at the catalyst surface can also be evaluated by the percentage of the adsorbed amount of component i,  $\eta_i^t$  (%) as a function of time:

$$\eta_i^t = \frac{C_i^{up,t} - C_i^{down,t}}{C_i^{up,t}} \times 100\%$$
(2)

The adsorption selectivity is defined as the ratio of the percentage of adsorbed mass. The adsorption selectivity is a dimensionless number which takes into account the adsorbed masses as well as the impact of the inlet amount.

$$\alpha_{1/2} = \frac{\overline{o}_{0}^{t} c_{0}^{up,t} dt}{\sqrt{\frac{m_{2}^{t}}{o} \int_{0}^{t} c_{0}^{up,t} dt}} = \frac{\int_{0}^{t} \eta_{1}^{t}}{\sqrt{\int_{0}^{t} \eta_{2}^{t}}}$$
(3)

Co-adsorption usually modifies the adsorption capacity of a pollutant due to the inhibitory or facilitatory effect introduced by the other co-pollutant. In order to quantify the inhibitory effect, an inhibitory factor is developed as an index to evaluate the adsorption capacity difference when the tested VOC exists as a single compound and as a mixture. The definition is defined as follows:

$$\delta_i = \frac{m_{i,theory} - m_{i,actual}}{m_{i,actual}} \tag{4}$$

where  $m_{i,theory}$  is the theoretical adsorbed mass of component i as a single compound, which is calculated on the basis of the linear relationship of a Langmuir adsorption isotherm created by adsorption tests of a single VOC at 500 ppb;  $m_{i,actual}$  is the actual adsorbed mass of component i as a mixture, calculated from a co-adsorption test using Equation (1).

## Modelling

The aim of modelling is to develop a simulation tool that can be used to accurately predict competitive adsorption behaviour for binary mixtures. Earlier, we developed and validated a mathematical model to simulate UV-PCO system performance.<sup>[21]</sup> In the present study, the model is simplified to account only for the sorption dynamics of mixtures (there will not be any UV lights or PCO reaction).

Gas phase:

$$\frac{dC_{i,B}}{dt} = \frac{\varepsilon}{\tau} D_{i,obs} \frac{d^2 C_{i,B}}{dx^2} - u_x \frac{dC_{i,B}}{dx} - k_{i,g} a (C_{i,B} - C_{i,S})$$
(5)

Catalyst phase : 
$$\frac{dC_{i,S}}{dt} = k_{i,g}a(C_{i,B} - C_{i,S})$$
 (6)

Initial and boundary conditions:

$$C_B = C_S = 0 \quad \text{at} \quad t = 0 \tag{7}$$

$$C_{B0} = C_{up} \quad at \quad x = L_0 \tag{8}$$

$$\mathbf{C}_{\mathrm{Bn}} = \mathbf{C}_{\mathrm{dn}} \quad \mathrm{at} \quad \mathbf{x} = \mathbf{L}_1 \tag{9}$$

where  $\varepsilon$  is the porosity of the catalyst,  $\tau$  is the tortuosity of the catalyst,  $D_{i,obs}$  is the observable molecular diffusion coefficient (m<sup>2</sup>/s), u<sub>x</sub> is the air velocity (m/s), 'a' is the geometric surface area of a PCO filter per unit reactor volume (m<sup>-1</sup>), k<sub>g</sub> is the inter-phase mass transfer coefficient (m/s), C<sub>i,B</sub> and C<sub>i,s</sub> are the concentration of component *i* at bulk and sorbed phase, respectively (mg/m<sup>3</sup>), and L<sub>1</sub>-L<sub>0</sub> is the total thickness of three layers of PCO filters (m). A detailed description of the determination of model parameters can be found in Zhong et al.<sup>[21]</sup> It should be noted that the observable diffusion coefficients, D<sub>i,obs</sub> (m<sup>2</sup>/s), of binary mixtures of dilute gases are different from the ones obtained from the Langmuir adsorption isotherm tests using a single VOC. For binary gas mixtures, two kinds of diffusion behaviours are taken into

Table 3. Model parameters					
	Gas 1	350 ppb	250 ppb	150 ppb 350 ppb	
Mixture	Gas 2	150 ppb	250 ppb		
1: p-xylene	1	$D_{obs} = 9.3 \times 10^{-6} \text{ (m}^2/\text{s)}$ $k_a = 0.33 \text{ (m/s)}$	$D_{obs} = 7.3 \times 10^{-6} \text{ (m}^2/\text{s)}$ k <sub>g</sub> = 0.30 (m/s)	$D_{obs} = 6.1 \times 10^{-6} \text{ (m}^2\text{/s)}$ $k_a = 0.27 \text{ (m/s)}$	
2: toluene	2	$D_{obs} = 6.1 \times 10^{-6} (m^2/s)$ $k_g = 0.27 (m/s)$	$D_{obs} = 7.5 \times 10^{-6} (m^2/s)$ $k_g = 0.30 (m/s)$	$D_{obs} = 9.7 \times 10^{-6} \text{ (m}^2/\text{s)}$ $k_g = 0.34 \text{ (m/s)}$	
1: MEK	1	$D_{obs} = 14.0 \times 10^{-6} \text{ (m}^2/\text{s)}$ $k_a = 0.39 \text{ (m/s)}$	$D_{obs} = 11.8 \times 10^{-6} \text{ (m}^2/\text{s)}$ k <sub>a</sub> = 0.37 (m/s)	$\begin{array}{c} D_{\rm obs}\!=\!10.1\!\times\!10^{-6}~(\mathrm{m}^2/\mathrm{s})\\ k_{\rm g}\!=\!0.34~(\mathrm{m}/\mathrm{s}) \end{array}$	
2: acetone	2	$\begin{array}{c} D_{obs} = 10.4 \times 10^{-6} \ (m^2/s) \\ k_g = 0.35 \ (m/s) \end{array}$	$D_{obs} = 12.2 \times 10^{-6} \text{ (m}^2/\text{s)}$ $k_g = 0.37 \text{ (m/s)}$	$D_{obs} = 15.0 \times 10^{-6} \text{ (m}^2/\text{s})$ $k_g = 0.41 \text{ (m/s)}$	
1: MEK	1	$D_{obs} = 11.2 \times 10^{-6} \text{ (m}^2/\text{s)}$ $k_a = 0.36 \text{ (m/s)}$	$D_{obs} = 8.7 \times 10^{-6} \text{ (m}^2/\text{s)}$ k <sub>g</sub> = 0.32 (m/s)	$\begin{array}{c} D_{obs}\!=\!7.1\!\times\!10^{-6}~(m^2/s)\\ k_{\rm g}\!=\!0.29~(m/s) \end{array}$	
2: p-xylene	2		$D_{obs} = 8.2 \times 10^{-6} \text{ (m}^2/\text{s)}$ $k_g = 0.31 \text{ (m/s)}$	$D_{obs} = 10.2 \times 10^{-6} \text{ (m}^2\text{/s)}$ kg = 0.34 (m/s)	
All mixtures			ε=0.65		
			$\tau = 3$ $u_x = 0.107 \text{ (m/s)}$ a = 0.05  (1/m)		

account for computing the diffusion coefficients: one is mutual diffusion,  $D_{12}$ , which can be regarded as diffusion of component 1 at infinite dilution through component 2, or equivalently, diffusion of component 2 at infinite dilution through component 1. Another one is self-diffusion,  $D_{11}$ , which is defined by the diffusion of a component through itself. Wilke and Lee provided a basis for computing the diffusion coefficients for various scenarios including  $D_{11}$  and  $D_{12}$ .<sup>[22]</sup> The observable diffusion of component 1 in the binary mixture is expressed as follows:

$$\frac{1}{D_{1,obs}} = \frac{P_1}{D_{11}} + \frac{P_2}{D_{12}} \tag{10}$$

where  $P_1$  and  $P_2$  are the pressure (atm, kPa  $\times$  101) of gas 1 and gas 2 in the mixture, respectively. This expression indicates diffusion coefficients of binary mixtures are a function of their partial pressure (concentrations) in the mixture. The intra-particle diffusion resistance is negligible in modelling due to the thin  $TiO_2$  layer thickness of 5  $\mu$ m. The mass transfer coefficient,  $k_g$ , is related to the observable diffusion coefficient according to the definition of Sherwood number,  $Sh = k_g D/D_{obs}$  (D is characteristic length of fibrous media, m). When the velocity is taken as a constant for all experiments, the mass transfer coefficient is mainly dependent on the observable molecular diffusion coefficient. In this case, the mass transfer coefficient is closely related to the concentrations since  $D_{obs}$  is a function of the partial concentrations. Table 3 lists values of  $D_{obs}$  and  $k_g$  for different combinations in this study. The value determination for other parameters can be found in Zhong et al.<sup>[21]</sup>

## RESULTS

## Toluene and P-xylene

Figure 3 presents the experimental results and model predictions of co-adsorption for binary mixtures of toluene and p-xylene as a function of time. Prior work shows that toluene and p-xylene are



**Figure 3**. Co-adsorption of toluene and p-xylene at various molar ratios: mixture A (p-xylene/toluene = 1:2.33), mixture B (p-xylene/toluene = 2:33:1), mixture C (p-xylene/toluene = 1:1).



Figure 4. Co-adsorption of MEK and acetone at various molar ratios: mixture D (MEK/acetone = 1:2.33), mixture E (MEK/acetone = 2.33:1), mixture F (MEK/acetone = 1:1).

weakly adsorbed on TiO<sub>2</sub> supported by fibreglass.<sup>[18]</sup> Figure 3 shows that toluene and p-xylene mutually reduced each other's adsorption, and the degree of inhibition was closely related to their molar ratios. To be more specific, for the mixture A with molar ratio of 1:2.33 (p-xylene/toluene), both experimental results and the model's predictions displayed that toluene had better adsorption performance than p-xylene, since the amount of adsorbed toluene was higher than that of adsorbed p-xylene (Figure 3 (mixture A)). P-xylene was preferentially adsorbed on the TiO<sub>2</sub> when the ratio was equal to or greater than 1 (mixtures B and C). The competitive phenomenon in the case of mixture A is somewhat different from the fact that for compounds in the same chemical class, adsorption capacity increases with the increase of molecular weight and boiling point when tested as a single compound.<sup>[18]</sup> Possible reasons will be discussed in the Discussion section. Adsorption equilibrium is defined as the rate of adsorption being equal to the rate of desorption, so that the amount of adsorbed molecules is constant over time. From that moment, the adsorption capacity of TiO<sub>2</sub> is reached so that the output concentration is equal to the inlet concentration. For toluene and p-xylene at three molar ratios, the time to reach 100 % breakthrough was decreased from 90 min for a single VOC to approximately 60 min for binary mixtures (Figure 3).



Figure 5. Co-adsorption of MEK and p-xylene at various molar ratios: mixture G (MEK/p-xylene = 1:2.33), mixture H (MEK/p-xylene = 2:33:1), mixture I (MEK/p-xylene = 1:1).

#### MEK and Acetone

Figure 4 shows the percentage of the amount adsorbed that was predicted by the model versus that obtained from the experiments for the mixtures of MEK and acetone at three molar ratios. This demonstrates that when the molar ratio of MEK to acetone was 1:2.33 (Mixture D), MEK and acetone had slightly facilitatory effects on each other's competitive adsorption, due to the superior adsorption performance of the mixture compared to a single VOC. Moreover, they mutually extended around 10 min to reach the breakthrough on co-adsorption, while when the molar ratio was  $\geq 1$  (Mixtures E and F), these two mixtures had no observable effects on either each other's adsorption capacity or the adsorption equilibrium time in Figure 4. However, if one applies Equations (3, 4) to quantitatively analyze the experimental results, the inhibitory effect can be identified, which will be discussed in the Discussion section.

#### MEK and P-xylene

It has been shown that the adsorption capacity of MEK is much higher than that of p-xylene for a wide range of RH, since MEK, being a polar compound, has a significantly higher adsorption preference.<sup>[18]</sup> Figure 5 presents the adsorption efficiency of model predictions versus experimental results for the mixtures of MEK



(c) MEK, p-xylene, and their binary mixtures

**Figure 6**. Comparison of total adsorbed amount of a single VOC and binary mixtures in the same total concentration of 500 ppb.

and p-xylene at three different initial fractions. Both experimental results and simulation results demonstrate the same trend, that the adsorption capacity of MEK is higher than that of p-xylene for mixtures G, H, and I. From the point of competition, MEK significantly diminished the adsorption of p-xylene on TiO<sub>2</sub>, while p-xylene slightly reduced the adsorption of MEK. P-xylene had a slight inhibitory effect on the adsorption capacity of MEK, and MEK accelerated the adsorption breakthrough of p-xylene. The observed phenomena are similar for the three mixtures despite their different molar ratios.

## DISCUSSION

Test results indicate that the presence of selected pairs of VOC mixtures can affect each other's adsorption behaviour via an interaction of inhibition or facilitation, and the adsorption rate of a VOC can be altered due to competition among other VOCs. In this section, further quantitative descriptions of inhibitory or facilitatory effects as well as theoretical explanations are provided.

<b>Table 4.</b> Inhibitory factor and adsorption selectivity of each mixture pair at various inlet concentrations				
Mixture	Inhibitory factor $\delta_1,  \delta_2/$ Adsorption selectivity $\alpha_{1/2}$	1: 150 ppb 2: 350 ppb	1: 250 ppb 2: 250 ppb	1: 350 ppb 2: 150 ppb
1: p-xylene, 2: toluene	$\delta_1$	162.4%	171.1%	74.8%
	δ2	52.9%	145.9%	121.7%
	$\alpha_{1/2}$	0.83	1.30	1.81
1: MEK, 2: acetone	$\delta_1$	-20.1 %*	14.3%	53.2%
	δ2	-6.3%*	2.6%	21.0%
	$\alpha_{1/2}$	1.80	1.38	1.21
1: MEK,	$\delta_1$	4.0%	36.3%	53.0%
2: p-xylene	δ2	173.2%	189.0%	160.4%
	α <sub>1/2</sub>	2.60	2.22	1.78

\*Positive values indicate inhibitory effect; negative values indicate facilitatory effect. For cases with negative values, the tests were duplicated and results exhibited the repeatability.

## Adsorbate Nature

Adsorption tests of selected VOCs for a single compound were carried out at an inlet concentration of 500 ppb which is equal to the total concentration of pairs of mixtures. Figure 6 presents the comparison of total adsorbed amounts of two single VOCs and their binary mixtures for each combination. It is clearly shown that the adsorption capacities were decreased for the mixtures of p-xylene/toluene and MEK/p-xylene compared with their corresponding single VOC rates, and the adsorption capacities of the mixtures of the mixtures of MEK/acetone were between those of their single VOC.

Zhong et al. reported that the adsorption isotherms of toluene, p-xylene, MEK, and acetone are linear with respect to equilibrium concentrations from 0.5–5 ppm at 10–70 % RH conditions, indicating that the adsorption behaviour follows ideal monolayer adsorption at low ppm concentrations.<sup>[18]</sup> Hence, this conclusion can be applied to predict the theoretical adsorbed masses at inlet concentrations of 150, 250, and 350 ppb, respectively, on the basis of known adsorbed mass from a test with a single VOC of 500 ppb. Then the adsorption selectivity and the inhibitory factor of each competitive adsorption test can be calculated using Equations (3, 4). Table 4 gives the inhibitory factor and adsorption selectivity of each pair of mixtures at different concentrations.

The experiments of co-adsorptions of p-xylene and toluene were conducted in order to evaluate the possible competitive effect on non-polar/non-polar mixture adsorptions. Table 6 shows when the concentration of p-xylene increases from 150 to 350 ppb, the inhibitory effect for p-xylene increases from 52.9 to 121.7 %, while the inhibitory effect for toluene decreases from 162.4 to 74.8 % as the concentration of toluene deceases from 350 to 150 ppb. Similarly, toluene was subjected to the same interfering trend as p-xylene. This table shows that the inhibitory effect increases with the concentration of the co-adsorbate. These observations can be interpreted as follows: for non-polar/non-polar mixture adsorptions, vapour pressure is the main driving force to attract VOC molecules to be adsorbed at the catalyst surface. At low challenge concentrations, surface coverage of a VOC is linearly proportional to its partial pressure. Hence, the higher the vapour pressure of a competitor, the greater the inhibitory effect on the adsorption of a target VOC on the TiO<sub>2</sub> surface. This phenomenon was analogous to the observation by Twesme et al.: they used a tertiary nonpolar mixture (propane, isobutene, and *n*-butane) to carry out UV-PCO tests, and conversion differences were partially attributed to the disparity in vapour pressure.<sup>[23]</sup> As shown in Table 4, adsorption selectivity was favourable to p-xylene when the molar ratio of p-xylene to toluene was equal to or greater than unity.

MEK and acetone are selected as a polar/polar mixture which can be used to examine the weak chemisorption formed by ketones with the surface of TiO<sub>2</sub>. It is interesting to note that the inhibitory factors were negative when the molar ratio of MEK to acetone was 1:2.33, indicating that they mutually increased adsorption of each other. This phenomenon is explained by considering the miscible nature of acetone (see Supporting Material) which rehydroxylated the TiO<sub>2</sub> surface and thereby increased the density of adsorption sites for MEK and acetone. A similar observation was reported by Lichtin et al.<sup>[24]</sup> They observed that methanol increased dark-adsorption of methylene chloride about five-fold over Degussa P-25 TiO<sub>2</sub>. When the acetone concentration decreased to 250 or 150 ppb, the effect of rehydroxylation disappeared, and an inhibitory effect occurred. This observation is attributed to the fact that a concentration increase of MEK is far greater than the increase of active sites induced by acetone. Hence, MEK and acetone competed for the same adsorption sites at molar ratios of 1:1 and 2.33:1. Table 4 also shows that the inhibitory effect of acetone on MEK increased from 14.3 to 53.2 % when the molar ratio of MEK to acetone increased from 1:1 to 2.33:1. An analogous situation occurred for the inhibitory effect of MEK on acetone. Moreover, Table 4 demonstrates that the adsorption selectivity was always favourable to MEK regardless of molar ratios.

MEK and p-xylene is a polar/non-polar mixture which can be utilized to compare the difference of weak chemisorption and physisorption in competitive adsorption. MEK preferentially adsorbs to the active site better than p-xylene due to its larger adsorption coefficient in comparison with p-xylene.<sup>[18]</sup> Table 4 shows that the inhibitory effects of MEK on p-xylene at the molar ratios of 1:2.33, 1:1, and 2.33:1 were 173.2, 189.0, and 160.4 %, respectively, indicating that p-xylene with low affinity was possibly displaced by MEK. In addition, it is interesting to find from Table 4 that very weakly adsorbed p-xylene has the ability to reduce the adsorption of strongly adsorbed MEK. Moreover, the degree of the inhibitory effect of p-xylene on MEK was inversely proportional to the concentration of p-xylene. This effect may be caused by availability of hydroxylated adsorption sites at various molar ratios. When 150 ppb MEK existed in the mixture, the hydroxylated adsorption sites on the TiO<sub>2</sub> surface could be sufficient for MEK adsorption, even though p-xylene at a concentration of 350 ppb was present as an adsorption competitor. It should be noted that the presence of p-xylene more or less dehydroxylated the  ${\rm TiO}_2$  surface, but the measured results indicate chemisorption was more competitive than physisorption. When the concentration of MEK increased, under the assumption of adsorption sites keeping constant at the same test conditions, the competition of p-xylene had a negative effect on MEK adsorption due to the lack of a corresponding increase of required adsorption sites. Hence, when the availability of adsorption sites becomes a dominating factor, a more strongly adsorbed VOC is sensitive to the inhibitory effect caused by a more weakly adsorbed VOC.

#### Surface Chemistry

The adsorption kinetic study of the influence of concentration on the competing compounds enables the determination of possible inhibitory effects. The extended Langmuir isotherm model is used to describe the sorbed-phase concentration of a VOC during a competitive process:<sup>[25]</sup>

$$C_{s,i} = f(C_i) = \frac{C_{s,i}^0 K_i C_i}{1 + \sum_{i=1}^n K_i C_i}$$
(11)

where  $C_{s,i}$  is the sorbed-phase concentration of specie *i*;  $C_{s,i}^0$  is the sorbed-phase concentration corresponding to monolayer coverage of the surface; the terms of K<sub>i</sub> and C<sub>i</sub> are Langmuir's constants and gas phase concentrations of specie i, respectively; and n is the total number of species contained in air. The K<sub>i</sub>C<sub>i</sub> product of all participating species *i* in the denominator can be ignored since the gas stream of binary mixtures is highly diluted and the Langmuir's constants from the earlier work are known (i.e.  $K_{MEK} = 1.67 \times 10^{-2}$  $m^3/g$ ,  $C_{MEK} = 8.42 \times 10^{-4} g/m^3$  (350 ppb),  $K_{MEK} \times C_{MEK} = 1.41$  $\times 10^{-5} << 1$ ).<sup>[18]</sup> The sorbed-phase concentration of specie *i* is mainly dependent on its K<sub>i</sub>C<sub>i</sub>. It is worth mentioning that this expression is applicable when the surface adsorption sites are abundant. Therefore, the method of adsorption kinetics is not suitable to be applied here to discuss the competition effect. Adsorption is a surface-based phenomenon involving physical attraction of the van der Waals forces and/or interactions of the kinds of bonds between molecules and surface atoms. It is necessary to further explore the competitive behaviour from the point of surface chemistry to fundamentally interpret some chemical inferences.

A key issue for the theoretical understanding of the interactions of adsorbed species with the TiO<sub>2</sub> surface is an understanding of the manner in which they bind to the surface. The interactions of aromatics with surfaces tend to be weak due to the nature of  $\pi$ bonding; physisorbed layers are usually found from vibration spectra and the molecule orients with the carbon ring parallel to the surface.<sup>[26]</sup> McCash observed bonding by using UV-photoelectron spectroscopy (UPES) and Auger electron spectroscopy, finding that toluene appears to adsorb non-dissociatively at ambient temperature, while at high temperatures it is dissociated to  $-CH_2$  and  $C_6H_5$ -.<sup>[26]</sup> All experiments in this study were implemented at room temperature, so there was almost no possibility of dissociation. The relationship of a van der Waals force being proportional to the molecular weight of aromatics leads to the favourable adsorption of p-xylene rather than toluene when each gas has the same partial pressure. Due to the weak physical adsorption interactions, the time required to reach saturation is relatively longer for a single aromatic VOC.

With regards to ketones, it is understood that the adsorption takes place via hydrogen bonding of the carbonyl group with the hydroxyl groups of TiO<sub>2</sub>.<sup>[27]</sup> In fact, this bond is attributed to the high electron-donor ability nature of carbonyl groups. Formation of new bonds during chemisorption indicates that ketones are much more strongly adsorbed to the TiO<sub>2</sub> surface than aromatics. In the absence of any VOC exposure, water exists as an adsorption layer close to the TiO<sub>2</sub> surface due to its nature of hydrophilicity.<sup>[28]</sup> As reported by Allegretti et al. using the technique of the scanned-energy mode photoelectron diffraction (PhD), the TiO<sub>2</sub>-water bond length is  $221 \pm 2$  pm, much longer than other chemisorption bonds of formate (208 pm) and hydroxyl (202 pm) found on the surface.<sup>[15]</sup> The solubility of ketones is higher than aromatics (see Supporting Material). Hence, it is reasonable to assume that ketones could easily pass through the water layer and/or compete with water molecules for adsorption sites on the surface by forming a shorter adsorption bond length. Another



**Figure 7**. (a) Co-adsorption selectivity of binary mixtures at different molar ratios; (b) overall model predictions versus experimental results of selectivity.

observed phenomenon is an acceleration of equilibrium time of aromatics in the mixture compared to a single compound. Earlier research reveals that it is possible for an adsorbed molecule to undergo a rearrangement or to fragment on the catalyst surface following adsorption. For example, Wang et al.'s observation of competitive adsorption between methanol and water showed that molecular methoxy produced by dissociative chemisorption of methanol was detected on the TiO<sub>2</sub> surface through a nonlinear spectroscopic technique of sum frequency generation (SFG) when a relatively low amount of water vapour was presented.<sup>[14]</sup> Therefore, among all the above discussed adsorption forces/ bonds, possessing or lack of an electron-donor functional group plays an essential role in determining the competitive performance of an adsorbate on TiO<sub>2</sub>.

## Comparison of Model with Experimental Results

Figures 3–5 present the adsorption efficiency of model predictions versus experimental results. In general, simulation results are in accordance with experimental measurements, particularly for MEK and acetone. It is noted that there is variation between the predictions made by the model and experimental results for aromatics at the early period of co-adsorption, which may be caused by the slightly unbalanced water vapour between the inlet air and the static air around the catalyst. The high affinity to water vapour of  $TiO_2$  has a significant negative effect on the adsorption of aromatics. Vildozo et al. obtained similar results.<sup>[16]</sup> Therefore, a slight difference in water vapour has a negligible negative impact on the adsorption performance of ketones, resulting in great consistency between model predictions and co-adsorption test results.

Figure 7 shows the adsorption selectivity predicted by the adsorption model and experimental data for nine mixtures. Figure 7a demonstrates that model predictions are in line with experimental measurements for binary mixtures at various molar

ratios. The linear regression formula in Figure 7b shows a slope of 1.059, which is very close to unity performed by a perfect model in theory, with an  $R^2$  of 0.945. These results indicate a satisfactory agreement between the model predictions and the experimental results, and thus the validity of the co-adsorption model is verified.

One of the limitations of the proposed method is that it is currently validated only for binary VOCs using experimental data. However, on the basis of flexibility offered by the proposed modelling approach, it is reasonable to predict that the modelling approach can be further applied to tertiary or more mixtures as long as appropriate values of  $k_g$  and  $D_{obs}$  fitted into the corresponding mixtures are determined, which necessitates collecting more test data in the future to prove this prediction.

### CONCLUSIONS

In summary, the competitive adsorption of nine binary mixtures on the  $TiO_2$  surface was investigated experimentally as well as predicted by a validated model. Both facilitation and inhibition effects of one component on the other were observed, indicating that the co-adsorption behaviour on the  $TiO_2$  surface is closely dependent upon the composition of the mixture gas, the natures of the adsorbate and substrate, and the initial VOC molar ratio. The results of analysis from surface chemistry provide important explanations as to the mechanisms by which the competitive adsorption proceeds on the catalyst. The proposed evaluation methods and the validated co-adsorption model qualitatively and quantitatively describe the co-adsorption phenomena, and detailed conclusions can be derived as follows:

- 1) For non-polar binary mixtures, a heavy VOC prefers to be adsorbed at  $TiO_2$  when the component of the mixture is at an identical molar ratio. At other molar ratios,  $TiO_2$  has selective adsorption of a VOC with a high partial gas pressure. Inhibitory effects increase with the concentration of the co-adsorbate when vapour pressure is the main driving force.
- 2) For polar binary mixtures, physisorption and chemisorption are the key adsorption mechanisms, which results in a portion of the VOCs being adsorbed by forming relatively stronger bonds with the hydroxyl groups of TiO<sub>2</sub>. Molecular weight is a dominating parameter so that adsorption selectivity is always favourable to a heavy VOC regardless of molar ratios.
- 3) For non-polar/polar binary mixtures, a non-polar VOC is subject to a strong inhibitory effect from a polar VOC due to the competitive chemisorption over physisorption on the catalyst surface, while a polar VOC also receives a certain negative effect from a non-polar VOC due to the limited availability of hydroxylated adsorption sites. The degree of inhibitory effect is associated with the molar ratio.
- 4) Introduction of a certain amount of a VOC with a miscible nature could be a way to improve the adsorption performance of the other co-adsorbed VOC due to the catalyst surface modification by the rehydroxylation process.

This developed comprehensive knowledge on adsorptive competition is the first step to examining its effect on the UV-PCO performance since adsorption is one of the fundamental processes occurring at a heterogeneous photocatalytic reaction. The outcomes of this study are of paramount importance in the design of advanced photocatalysts with desirable adsorption selectivity, and eventually, for enhancing the photoadsorption selectivity and minimizing the generation of by-products from PCO air cleaners.

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