



## Solar pyrolysis of waste rubber tires using photoactive catalysts

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### ABSTRACT

The solar pyrolysis of waste tire rubber was investigated with the application of heterogeneous photocatalysts including  $\text{TiO}_2$ ,  $\text{Pd/TiO}_2$ ,  $\text{Pt/TiO}_2$ ,  $\text{Pd-Pt/TiO}_2$ , and  $\text{Bi}_2\text{O}_3/\text{SiO}_2/\text{TiO}_2$ . Experiments were performed at temperatures ranging between 550 and 570 °C under solar irradiations of 950–1050  $\text{W/m}^2$ . The gas yield from non-catalytic solar pyrolysis was at 20% while the use of  $\text{TiO}_2$  catalyst increased the gas yield to 27%. Doping of  $\text{TiO}_2$  with noble metals and  $\text{Bi}_2\text{O}_3/\text{SiO}_2$  metal oxides enhanced further the cracking ability of the catalyst.  $\text{Bi}_2\text{O}_3/\text{SiO}_2/\text{TiO}_2$  gave a 32% gas yield. The highest gas yields of 40% and 41% were achieved over  $\text{Pd-Pt/TiO}_2$  and  $\text{Pd/TiO}_2$  catalysts, respectively. Catalyst characterization by BET, SEM, EDX and XRD showed the role of metal doping in altering the morphology of  $\text{TiO}_2$ , resulting in nanocrystallites, larger pore volume and higher surface area. Both, Pd and Bi influenced the photocatalytic properties of  $\text{TiO}_2$  improving cracking activity during pyrolysis of waste rubber.

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### 1. Introduction

Around 1.4 billion new tires are sold across the world annually and just as many fall into the category of end-of-life tires (Taverne, 2011). At present, an estimated 4 billion waste tires are dumped in landfills or stockpiled worldwide (World Business Council for Sustainable Development, 2011). Other estimates show that 3.2 million tons of tires are discarded annually in EU27 countries and Turkey. This represents around 26.5% of the world tire production (17 million tons). Furthermore, the disposal of scrap tires has become a serious problem in Lebanon in recent years. An estimated 2 million tires are disposed of in open dumps annually (Shamseddine, 2015). This global waste management problem has now become a serious threat to the environment (Williams and Besler, 1995).

Waste rubber, however, can be considered as a rich source of fuel and chemicals and this scientific fact instigated researchers to develop successful methods to help solve the waste rubber disposal problem by transforming it into valuable materials. In this context, pyrolysis (Rezaiyan and Cheremisinoff, 2005) can be used to thermally decompose waste rubber. Pyrolysis involves thermal cracking resulting in complex chain reactions that include dehydrogenation, cracking, isomerization, dehydration, aromatization and condensation (Wampler, 2006). As a result, waste can be transformed to higher calorific compounds. The products derived from solid waste pyrolysis can be further refined into volatile fractions

and carbonaceous solids. The volatiles are partially condensed, at ambient temperature, to form high molecular weight compounds, or pyrolysis oil. The non-condensable portion consists of lower molecular weight compounds evolving from the process in the form of pyrolysis gas (Abdul-Raouf et al., 2010; Raj et al., 2013; Barbooti et al., 2004). The residual solid is a char that can be further used as activated carbon or carbon black (Kaminsky and Mennerich, 2001; Mui et al., 2004; Li et al., 2010).

It is essential to highlight differences between pyrolysis and other waste to energy techniques such as incineration. Several findings bring strong evidence supporting pyrolysis as a cleaner technology (Aylon et al., 2005; Galvagno et al., 2002; Aylon et al., 2010). Pyrolysis has the upper hand in environmental awareness due to its lower emissions of toxic gases to the environment.  $\text{NO}_x$ , dioxins and dibenzofurans which are common problems in incineration processes (Sinn et al., 1976; Malkow, 2004; Bennett, 1993) are reduced to very low levels during pyrolysis due to the absence of oxygen and the non-oxidative pyrolysis environment (Elbaba et al., 2010). In addition, pyrolysis enables the exploitation of both solid and liquid portions of the final products in the form of fuel or chemical derivatives (Aylon et al., 2005; Murillo et al., 2006).

Thermal pyrolysis is usually conducted at optimal temperatures to aggravate cracking reactions. It is well understood that waste tire pyrolysis is an endothermic reaction (Martínez et al., 2013). The temperature factor is widely studied in literature by many authors; for instance, De Marco Rodriguez et al., (2001) noticed the formation of sticky-gummy, which consists of NR (natural rubber), SBR (styrene-butadiene rubber), and BR (butadiene rubber) at

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380 °C, 50 °C, and 460 °C, respectively. Waste tire pyrolysis is considered optimal at a temperature of 500–550 °C. under atmospheric pressure (Mastral et al., 2000; de Marco Rodriguez et al., 2001; Aylon et al., 2005; Murillo et al., 2006; Aguado et al., 2005; Gieré et al., 2006; Ucar et al., 2005; Berruoco et al., 2005).

Both thermal and catalytic pyrolysis processes have been investigated using different types of reactors. These include fixed-bed reactors (Berruoco et al., 2005; Cunliffe and Williams, 1998; Williams et al., 1990; Jantaraksa et al., 2015; Zeaiter et al., 2015; Ismail et al., 2017), autoclaves (Murena, 2000; de Marco Rodriguez et al., 2001), fluidized bed reactors (Williams and Brindle, 2002b; Roy et al., 1997; Raj et al., 2013), and plasma reactors (Tang and Huang, 2005). Similarly, different types of catalysts were used; for instance, H-MOR and MCM-41 were reported to decrease the amount of polar aromatics by 30–50% (Düng et al., 2009). Catalytic pyrolysis over Y-ZSM-5 zeolites resulted in around 20% gas yields and 35% oil (Williams and Brindle, 2002a). In general, the type and nature of the active sites of the catalyst had a great impact on the yields of pyrolysis products.

Commonly, for pyrolysis experiments, an energy source of high temperature is needed such as electrical furnaces or fossil-fuel fired units. A more sustainable approach, however, is to adopt solar energy by concentrating solar irradiations (Zeaiter et al., 2015; Luu et al., 2016; Zeng et al., 2016; Li et al., 2016; Sánchez et al., 2018) with the use of photoactive catalysts (Zeng et al., 2017).

Historically, titanium dioxide (TiO<sub>2</sub>) constituted the basis of applied photocatalytic processes. In 1972, Fujishima (1972) used n-type TiO<sub>2</sub> with UV light to perform photocatalytic water splitting for the first time. The performance of TiO<sub>2</sub> is highly dependent on acquiring light waves and therefore, its optical structure is a crucial specification (Liu et al., 2014; Wen et al., 2015).

There are many techniques for enhancing TiO<sub>2</sub>-based photocatalysts (Kim et al., 2005), using nano-sized particles (Maira et al., 2001) and the incorporation of transition (Litter, 1999) or noble metals (Kennedy and Datye, 1998; Vorontsov et al., 1999). It has been announced that metal-TiO<sub>2</sub> composite catalysts have resulted in significant improvements in the photocatalytic oxidation/reduction of various organic compounds (Tada et al., 2004; Sun et al., 2005; Hosseini et al., 2007). For instance, palladium (Pd) noble metal increased the catalytic activity of TiO<sub>2</sub> (Hosseini et al., 2007). Zhong et al. (2009) demonstrated that Pd/TiO<sub>2</sub> achieved 2.32 times higher activity than pure TiO<sub>2</sub> in oxidizing gaseous benzene substrate. This was achieved by suppressing electron recombination due to electron transfer onto metallic particles surface (Einaga et al., 2001). Similarly, Pt doping on TiO<sub>2</sub>, resulted in the formation of adequate electronic conductivity and nanostructured morphology (G. Kennedy et al., 2014; Brijaldo et al., 2014; Chua et al., 2014; Lopez et al., 2014; Ruiz-Camacho et al., 2014; Rautio et al., 2015). Research revealed that the high dispersion of Pt nanoparticles and interaction between Pt and TiO<sub>2</sub> resulted in an enhanced catalytic activity (Rautio et al., 2015). The application of Pt/TiO<sub>2</sub> catalyst, therefore, has been promising in the electrochemical field (Chang et al., 2013; Du et al., 2013). Based on these observations, TiO<sub>2</sub> is thus considered an attractive support for noble bi-metallic doping. The formation of positively charged sites represented by Ti<sup>4+</sup> allows a good interaction between TiO<sub>2</sub> and the noble metals.

In addition to metal doping, enhancement of TiO<sub>2</sub> photo catalytic activity is also achieved by the addition of SiO<sub>2</sub> which enhances surface hydroxyls of TiO<sub>2</sub> (C. Kim et al., 2012; Ren et al., 2013; QIU et al., 2011). Another alternative is preventing the electron-hole recombination via coupling TiO<sub>2</sub> with narrow band gap semi-conductors. Bi<sub>2</sub>O<sub>3</sub> is considered a prominent metal-oxide semi-conductor having an energy gap between 2.1 and 2.8 eV (Zhang et al., 2006). Xu et al. (2008) found that the composite photo catalyst Bi<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> showed a higher photocatalytic

activity than pure TiO<sub>2</sub> in benzene degradation. Moreover, doping of TiO<sub>2</sub>/SiO<sub>2</sub> with Bi<sub>2</sub>O<sub>3</sub> extended the photocatalytic activity of TiO<sub>2</sub>/SiO<sub>2</sub> from the ultraviolet to the visible light region. This improvement in photoactivity was observed in the degradation of benzene compounds using synthesized Bi<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub>/SiO<sub>2</sub> (Ren et al. 2015).

In this work, and for the first time in literature, we investigate the application of TiO<sub>2</sub> as a photo catalyst during the pyrolysis of waste rubber tires. TiO<sub>2</sub>-based heterogeneous catalysts are synthesized with single metal (Pt or Pd), bimetal (Pt-Pd) and Bi<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> oxide doping. The catalysts are then characterized for surface area, pore volume and surface structure before being used in the catalytic solar pyrolysis of waste rubber tires with the aim of achieving high gas yields.

## 2. Experimental

### 2.1. Catalyst preparation

#### - Pd (0.25 wt.%) /TiO<sub>2</sub>

The preparation of Pd (0.25 wt.%) /TiO<sub>2</sub> involved titanium dioxide (pure anatase) and palladium nitrate hydrate Pd (NO<sub>3</sub>)<sub>2</sub>·xH<sub>2</sub>O. All materials were purchased from Sigma Aldrich.

Palladium doped titanium dioxide catalyst was prepared by wet impregnation method. Palladium nitrate (Pd (NO<sub>3</sub>)<sub>2</sub>·xH<sub>2</sub>O) was added to deionized water and stirred well to form palladium nitrate solution. TiO<sub>2</sub> was then impregnated with the palladium nitrate solution. The impregnated sample was heated with stirring to evaporate water. The cake was calcined at 450 °C for 2 h in a furnace.

#### - Pt (0.25 wt.%) /TiO<sub>2</sub>

For the preparation of Pt (0.25 wt.%) /TiO<sub>2</sub>, titanium dioxide pure anatase (Sigma Aldrich) and Potassium Tetra-chloroplatinate K<sub>2</sub>PtCl<sub>4</sub> as a source of platinum noble metal (Sigma Aldrich) were used.

The Pt/TiO<sub>2</sub> catalyst was synthesized by pore impregnation method. Potassium tetra-chloroplatinate K<sub>2</sub>PtCl<sub>4</sub> was added to deionized water in a small beaker and stirred well to have potassium tetra-chloroplatinate solution. Similarly, TiO<sub>2</sub> was dissolved in distilled water. Afterwards, both solutions were mixed together under heated stirring to evaporate water and remove spectator ions. The cake was then calcined at 723 K for 2 h in a furnace.

#### - Pd (0.5 mol %) - Pt (0.5 mol %) /TiO<sub>2</sub>

Potassium tetra-chloroplatinate K<sub>2</sub>PtCl<sub>4</sub> (Sigma Aldrich) and palladium chloride PdCl<sub>2</sub> solution (Sigma Aldrich, form: liquid, 5 wt.% in 10 wt.% HCl) were used as platinum and palladium metal sources, respectively. As for TiO<sub>2</sub>, titanium (IV) iso-propoxide (TIP) (Sigma Aldrich, form; liquid, purity 97%) was used. In addition, ethanol (Sigma Aldrich, form; liquid, purity 96%) was used for the preparation of the iso-propoxide solution in ethanol.

Pt-Pd/TiO<sub>2</sub> catalyst was prepared by sol-gel method. Titanium (IV) Isopropoxide (TIP) was added to ethanol in a beaker while stirring for 5 min at 500 rpm. After that, deionized water of 5.71 ml was added at a rate of 0.5 ml/min to the alkoxide solution in the beaker. At this point, a white thick precipitate was formed, which was then peptized for 2 h to have a clear solution. Specific amount of K<sub>2</sub>PtCl<sub>4</sub> was added to the solution followed by addition of PdCl<sub>2</sub> solution. The mixture was then mixed for 2 h in order to homogenize the solution. It was then placed in a centrifuge operating at 2000 rpm for 5 min. The heavy cake was dried at 70 °C for 48 h before calcining at 450 °C for 3 h.

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