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## Recent advances of titanium dioxide (TiO<sub>2</sub>) for green organic synthesis

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Titanium dioxide (TiO<sub>2</sub>) has become increasingly popular as a catalyst. Although many applications of TiO<sub>2</sub> involve photocatalysis and photoelectrochemical reactions, there are numerous interesting discoveries of TiO<sub>2</sub> for other reactions. This review focuses on the recent development of TiO<sub>2</sub> as a catalyst in green organic synthesis including in hydrodeoxygenation, hydrogenation, esterification/transesterification, the water–gas shift reaction, and visible light-induced organic transformation owing to its strong metal–support interaction (SMSI), high chemical stability, acidity, and high redox reaction at low temperature. The relationship between the catalytic performance and different metal or metal oxide dopants, and different polymorphs of TiO<sub>2</sub> are discussed in detail. It is interesting to note that the reduction temperature and addition of promoters have a significant effect on the catalytic performance of TiO<sub>2</sub>.

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### 1. Introduction

Titanium dioxide is known as titanium(IV) oxide or titania, with the chemical formula TiO<sub>2</sub>. Compared with bulk TiO<sub>2</sub>, TiO<sub>2</sub> nanomaterials have been passionately studied over the past decades due to their potential applications in many areas. TiO<sub>2</sub> is very useful because of its non-toxicity, chemical stability, low cost, and other advantages. TiO<sub>2</sub> has been broadly used in paint as white pigments, cosmetics, food colouring, solar cells, photovoltaic cells, and photo applications. Many niche applications have also been explored especially in biomedical fields such as cancer therapies, orthopaedic surgery, stent placement, bactericides, and protein separation.<sup>1–3</sup> Recently, research related to TiO<sub>2</sub> catalysts in organic synthesis such as in deoxygenation, hydrogenation, the water–gas shift reaction, and CO oxidation has been carried out.<sup>4–7</sup>

Pure TiO<sub>2</sub> is either colourless or white, but it also tends to exist in other colours (yellow, red, brown, black, *etc.*) due to the presence of impurities (*e.g.* iron, niobium, chromium, tantalum, and vanadium). All three polymorphs of TiO<sub>2</sub> have a very high refractive index and are temperately hard and dense. TiO<sub>2</sub> is classified as non-hazardous according to the United Nations (UN); studies have revealed that ingestion of or skin or eye contact with TiO<sub>2</sub> has no significant harmful effects to health.<sup>8</sup> However, inhalation of TiO<sub>2</sub> dust, especially at a nano-

sized scale, can inflame the lungs. An occupational daily exposure limit of 15 mg of TiO<sub>2</sub> dust has been set by the OSHA.<sup>8</sup> Unlike other dust, TiO<sub>2</sub> dust does not cause scarring as it is not chemically irritating to the lungs.

Various excellent reviews have been done on the synthesis methods of TiO<sub>2</sub> and its application in photocatalysis and photoelectrochemistry; typical examples are on solar cells, hydrogen production by water splitting,<sup>9–11</sup> degradation of organic pollutants,<sup>12–15</sup> and reduction of carbon dioxide.<sup>16</sup> However, there are limited reviews on the application of TiO<sub>2</sub> as a support or catalyst for green organic synthesis. Thus, this paper reviews the challenges of TiO<sub>2</sub> as a catalyst support and its application in various organic synthesis with a particular focus on: (1) deoxygenation; (2) hydrogenation; (3) esterification/transesterification; (4) the water–gas shift (WGS) reaction; and (5) visible light-induced organic transformation.

### 2. TiO<sub>2</sub> crystal structure and properties

TiO<sub>2</sub> has three main crystal polymorphs, namely anatase, rutile, and brookite. Each polymorph exhibits different physical properties. Among the three polymorphs, rutile is the most stable phase under ambient conditions while anatase and brookite are metastable at all temperatures and will transform to rutile when they are heated. Some research reported that the stability of various TiO<sub>2</sub> phases was dependant on the particle size. Anatase is the most thermodynamically stable phase when the nanoparticles are smaller than 11 nm. Rutile has been found to be the most stable for nanoparticles greater than 35 nm in size while brookite is the most stable phase for nanoparticles between 11–35 nm in size.<sup>17</sup>

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Table 1 shows the properties of  $\text{TiO}_2$  in the anatase, rutile, and brookite phases. The structure of  $\text{TiO}_2$  is formed by chains of distorted  $\text{TiO}_6$  octahedra where each Ti atom is surrounded by 6 oxygen atoms. The three-dimensional stacking of the octahedra in anatase, rutile, and brookite is shown in Table 1. The unit cell of tetragonal anatase contains four  $\text{TiO}_2$  units (12 atoms), while the unit cell of tetragonal rutile contains two  $\text{TiO}_2$  units (6 atoms), and the unit cell of orthorhombic brookite contains eight  $\text{TiO}_2$  units (24 atoms). Thus, anatase has a smaller cell volume than that of rutile and brookite. Therefore, most practical work has been carried out with anatase or rutile. The existence of either or both of these phases leads to different activities for chemical reactions which is discussed later. Brookite is the least stable phase among the three due to an orthorhombic structure, thus it is difficult to synthesize.<sup>8</sup> This also means that it is rarely used for most applications and is seldom studied.

The  $\text{TiO}_2$  phase is the most critical parameter determining the properties of the materials, therefore, many researchers attempted to understand the phase transformation between anatase, rutile, and brookite. The initial crystalline  $\text{TiO}_2$  phase formed is generally anatase; rutile is obtained through calcination.<sup>23</sup> The transformation of the anatase to rutile phase is reconstructive and irreversible because the transformation involves bonds breaking and reforming.<sup>20</sup> It was reported that the transformation of anatase to rutile occurs at approximately 600 °C when calcined in air.<sup>24–26</sup> Nevertheless, some research reported that the transformation temperature may vary widely from 400 to 1200 °C with different raw materials, synthesis methods, and heat flow conditions.<sup>19,27–30</sup> Brookite was transformed into the rutile phase when heated at about 800 °C. Rutile is the most thermally stable among the three polymorphs with a melting point between 1830 °C and 1850 °C.<sup>8</sup>  $\text{TiO}_2$  is always difficult to dissolve or react when the sample is heated at above 1000 °C for a long period of time.<sup>8</sup> Phase transformation is of considerable interest as the transformation is capable of altering the properties and performance of the catalyst.

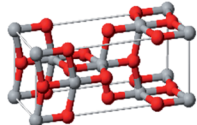
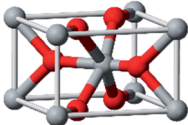
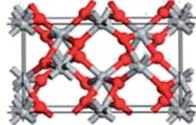
### 3. $\text{TiO}_2$ as catalyst support

Recently, the use of metallic nanoparticles for green and sustainable synthesis has attracted tremendous interest. In particular, the combination of metallic nanoparticles with a catalyst support is essential to enhance the catalytic activity and optimize selectivity in the desired application. Catalyst supports play an important role in improving the stability of the catalyst and reducing the amount of costly metal used.<sup>31</sup> This is due to their unique properties, such as porosity, large surface area, tunable shapes, and high dispersity.<sup>32</sup> Besides, a heterogeneous catalyst support has a significant impact on the catalytic activity and catalyst stability. It exerts a structural and active phase linked effect, which is able to increase the dispersion of metal species and inhibit the aggregation of active metal particles.<sup>33,34</sup> Therefore, the selected heterogeneous catalyst support must retain its specific properties.

According to the literature, catalyst supports can be grouped into four categories including (i) solid acid supports like zeolites,<sup>35</sup> (ii) reducible oxide supports such as titania,<sup>36,37</sup> ceria,<sup>38</sup> and zirconia,<sup>39</sup> (iii) refractory oxide supports like alumina<sup>33</sup> and silica,<sup>38</sup> and (iv) carbon-based supports like mesoporous carbon<sup>40</sup> and carbon nanotubes.<sup>41</sup> Different groups of support revealed different catalytic activity and selectivity towards the chemical reaction.

Among the reducible oxide supports,  $\text{TiO}_2$  is a famous and proven one for contributing to better catalytic activities as it acts as a promoter, a carrier for metals and metal oxides, and an additive or a catalyst.<sup>42,43</sup> The better catalytic activity of  $\text{TiO}_2$  was strongly contributed to by the strong metal-support interaction (SMSI).<sup>44–46</sup> SMSI was first observed by Tauster *et al.*<sup>47</sup> in 1978; he defined the concept of SMSI as the drastic changes in the chemisorption properties of group 8–10 noble metals when supported on  $\text{TiO}_2$ . Prototypical examples of SMSI phenomena were only observed for metallic particles supported on reducible oxides such as  $\text{TiO}_2$ <sup>48,49</sup> and  $\text{CeO}_2$ .<sup>50</sup>  $\text{TiO}_2$  exhibits SMSI after reduction at high temperature in the presence of a hydrogen environment. SMSI is an important and unique effect that

Table 1 Properties of anatase, rutile, and brookite

| Property                            | Anatase   | Rutile  | Brookite  | Ref.      |
|-------------------------------------|---|---|---|-----------|
|                                     | Tetragonal  | Tetragonal  | Orthorhombic  |           |
| Crystal bulk structure              |  |  |  | 18 and 19 |
| Atoms per unit cell (Z)             | 4   | 2   | 8   | 20        |
| Crystal size (nm)                   | <11   | >35   | 11–35   | 17        |
| Lattice parameters (nm)             | $a = b = 0.3785, c = 0.9514$  | $a = b = 0.4594, c = 0.2959$  | $a = c = 0.5436, b = 0.9166$  | 19 and 21 |
| Space group                         | $D_{4h}^{19} - I4_1/amd$  | $D_{4h}^{19} - P4_2/mnm$  | $D_{2h}^{15} - Pbca$  | 18 and 19 |
| Unit cell volume (nm <sup>3</sup> ) | 0.1363  | 0.0624  | NA  | 20        |
| Density (g cm <sup>-3</sup> )       | 3.83  | 4.24  | 4.17  | 22        |
| Band gap (eV)                       | 3.26  | 3.05  | NA  | 19        |
| Hardness (Mohs)                     | 5.5–6   | 6–6.5   | 5.5–6   | 22        |

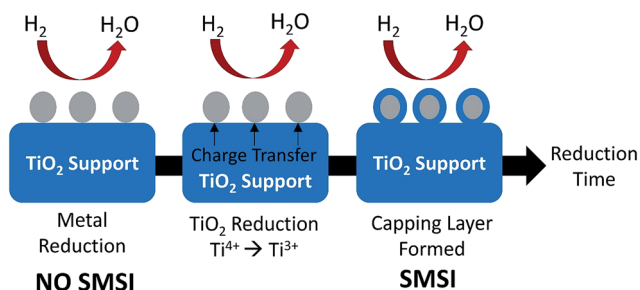


Fig. 1 The SMSI effect occurring during reduction treatment by  $H_2$ . The grey circles represent metallic nanoparticles, while the blue parts represent the  $TiO_2$  support.

occurs due to an electronic or geometrical interaction, and charge transfer between metallic nanoparticles and a support (Fig. 1).<sup>51,52</sup> The metallic nanoparticles are capped with functional groups of the support that migrate to the surface of the metallic nanoparticles during the reduction process.<sup>50</sup> This capping layer can form new active sites and improve the adsorptive and efficiency of the composite.<sup>53,54</sup> The strength of the metal-support interaction can affect the metal particle dispersion on the support, the geometry of adsorption, and electronic structures, and significantly changes the catalytic performance.<sup>55,56</sup> It also plays a dominant role in controlling the size growth of the metal.

Besides the interaction of the metal and support, the size of the active sites is another factor that is pertinent to the efficiency of metal-supported catalysts. The size of the metal particle after heat treatment is highly dependent on the nature of the support. Fang *et al.* reported that gold particles with a mean cluster size of 1.5 nm were dispersed on  $TiO_2$ , carbon, and  $SiO_2$  respectively. After calcination, the size of the gold particles increased significantly on carbon (4 nm) and  $SiO_2$  (5 nm); in sharp contrast, the gold particles on  $TiO_2$  (2 nm) were the smallest.<sup>57</sup> This indicates that  $TiO_2$  effectively prevents the growth and sintering of metal particles.<sup>57</sup> Thus, smaller metal particles can be obtained.

Moreover, the catalytic activity of metal-supported catalysts is attributed to two things: (1) contribution from the metal surface, and (2) other derives from the active sites, where the spill-over hydrogen could react with the adsorbed molecules.<sup>58</sup>  $TiO_2$  acts as a reservoir of H atoms where H atoms may migrate from one reactant to another reactant. The hydrogen molecules adsorbed and dissociated on the metal surface then migrate to

the  $TiO_2$  where they are trapped at surface defects. This migration will provide an active species for reaction. Then  $H^+$  on  $TiO_2$  can be exchanged with  $H_2$  easily in the presence of the metal phase.<sup>59</sup> Fig. 2 demonstrates the route for hydrogen spill-over on acid sites.<sup>59</sup> The hydrogen spill-over can greatly enhance reduction and the hydrogenation capability of  $TiO_2$ . Therefore,  $TiO_2$  as a catalyst support not only acts as a platform for the dispersion of active species but also as an active site that impacts the catalytic performance.<sup>59</sup>

$TiO_2$  is well-known as a weak acid support, mainly with Lewis acid properties, in which Bronsted acidity is not observed.<sup>60</sup> Lewis acid sites tend to attract the oxygen ion pair of the target molecules, therefore, this leads to higher selectivity for the hydrogenated product. Some studies showed that a weak acid support with Lewis acid sites from  $TiO_2$  was able to reduce coke formation or cracked products.<sup>58</sup> It is well-known that coking on a catalyst surface caused by a polymerization reaction is one of the major challenges for the catalytic reaction, as coking significantly reduces the active sites by competition with the reactant. Therefore, catalyst deactivation can be minimized by using a  $TiO_2$ -supported catalyst.

In addition, much research has shown that a variety of metal and non-metal dopants were capable of increasing the surface area and thermal stability of  $TiO_2$  through structural modifications and grain growth inhibition.<sup>44,61–64</sup> It is important to select the appropriate synthetic routes to produce  $TiO_2$  with a higher surface area and more ideal porosity. Three-dimensional mesoporous  $TiO_2$  with a narrow pore size distribution and large surface area is able to increase the degree of dispersion and homogeneity of immobilized catalysts.<sup>65</sup> Olsen *et al.*<sup>61</sup> reported that mesoporous  $TiO_2$  synthesized by modification with aluminium was thermally stable up to 400 °C with a surface area of 479  $m^2 g^{-1}$ . This is apparently the highest thermal stability with a large surface area. It is believed that modifying the  $TiO_2$  catalyst support definitely enhances the catalytic stability and activity of the catalyst.

## 4. Application of $TiO_2$ catalyst for green organic synthesis

### 4.1 Deoxygenation

Deoxygenation involves the removal of oxygenated compounds from a molecule in the form of water,  $CO_2$ , or CO. Deoxygenation can be accomplished with or without the presence of hydrogen during the reaction. Various possible mechanisms for deoxygenation (Table 2) include: (1) decarboxylation that removes carboxyl groups to yield paraffins and  $CO_2$ ; (2) decarbonylation that yields olefins, CO, and water; (3) hydrodeoxygenation that involves C–O bond cleavage under hydrogen and yields hydrocarbons and water, and for fatty acids, it involves reducing the oxidation state of the carbon atom of the carboxylic groups using  $H_2$ ; and (4) hydrogenolysis that involves cleavage of the carbon–carbon or carbon–heteroatom bond when hydrogen is added.<sup>66,67</sup> High oxygenated compounds confer undesirable properties to bio-oil because they contribute to the high corrosiveness, low thermal stability, low volatility,

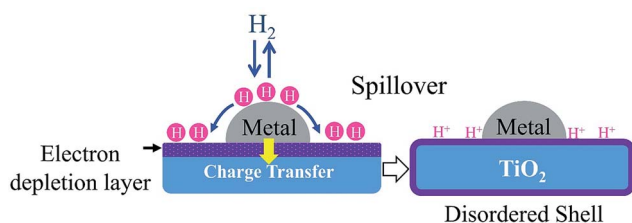


Fig. 2 An example of hydrogen spill-over involved in hydrogenation of metal  $TiO_2$ .

Table 2 Overview of possible deoxygenation reaction pathways

| No. | Liquid phase       | Precursor | End products            |
|-----|--------------------|-----------|-------------------------|
| 1   | Decarboxylation    |           | + CO <sub>2</sub>       |
| 2   | Decarbonylation    |           | + CO + H <sub>2</sub> O |
| 3   | Hydrodeoxygenation |           | + 2 H <sub>2</sub> O    |
| 4   | Hydrogenolysis     |           |                         |

and low energy content.<sup>68</sup> Hence, oxygen removal is the most important process in the production of sustainable and high quality fuel components that are suitable to use with existing technology.

Table 3 shows an overview of the relevant literature for the deoxygenation of vegetable oil-based feedstocks and model compounds under different reaction conditions and the selectivity.

Deoxygenation based on TiO<sub>2</sub> as a catalyst or catalyst support was usually pressurized with hydrogen. The presence of hydrogen was able to enhance the catalyst stability and avoid the formation of unsaturated hydrocarbon products.<sup>35,70</sup> Accumulation of unsaturated hydrocarbon products and partially oxidized intermediates leading to coking occurs on the catalyst surface, thereby causing blockage to the active sites and hindering the catalyst.<sup>58,70</sup> A weak acid support with Lewis acid sites such as TiO<sub>2</sub> showed a low yield of coke or crack products.<sup>58</sup> Coking is a major challenge for the deoxygenation reaction. It correlates with the structure of the catalyst as polymerization reactions are the major reactions

leading to coking occurring on the surface of the catalyst.<sup>73</sup> Therefore, this significantly eliminates the active sites. By using TiO<sub>2</sub> as a catalyst or catalyst support, less coke is formed during the reaction, hence it is able to reduce catalyst deactivation.

TiO<sub>2</sub> is a promising catalyst to catalyze the transformation of guaiacol through demethylation (Table 3, no. 1). The selectivity of the reaction was 50% catechol and 35% phenol, and hydrogenation was the main pathway observed. This contribution is attributed to the Lewis acid property of TiO<sub>2</sub>.<sup>74</sup> When TiO<sub>2</sub> was used as a support for the CoMoS catalyst, it has been clearly observed that CoMoS greatly enhanced the conversion rate and favoured selectivity to hydrodeoxygenation, in which phenol, benzene, and cyclohexane were the major products (Table 3, no. 2). The higher tendency towards hydrodeoxygenation is plausible due to a larger active phase cluster size that weakens the active phase support interaction.<sup>70</sup> The hydrodeoxygenation reaction by TiO<sub>2</sub>-supported catalysts proceeds *via* two paths. Firstly, the phenol was directly deoxygenated to aromatic compounds as the primary product. Secondly, the ring was hydrogenated and then deoxygenated to a naphthenic product.<sup>75</sup> It was believed that adsorption of oxygenated compounds onto TiO<sub>2</sub> plays an important role in the transformation of phenolic compounds: a  $\sigma$ -bonding adsorption through the oxygen atom would give C–O hydrogenolysis while  $\pi$ -bonding of the aromatic ring would allow hydrogenation.<sup>75</sup> The performance of TiO<sub>2</sub> as a catalyst and catalyst support has been compared and it appeared that TiO<sub>2</sub> as a catalyst support gave a very efficient conversion of guaiacol into deoxygenated hydrocarbons with a totally different selectivity. This demonstrated that the selectivity of TiO<sub>2</sub> can be tuned by incorporation of a suitable active metal.

Several reports (Table 3, no. 2 and 3) showed that a metal sulphide catalyst such as nickel molybdenum (NiMo) and cobalt molybdenum (CoMo) supported on TiO<sub>2</sub> showed high selectivity towards hydrodeoxygenation. Compared with sulphided CoMoS supported on Al<sub>2</sub>O<sub>3</sub>, the CoMoS did not facilitate the

Table 3 Overview of literature concerning deoxygenation based on TiO<sub>2</sub> as the catalyst support<sup>a</sup>

| No. | Catalyst               | Metal (w/w)     | Reactant         | <i>t</i> (h) | <i>T</i> (°C) | Reaction conditions  | BET (m <sup>2</sup> g <sup>-1</sup> ) | Phase          | Conv. (%) | Selectivity   | Ref. |
|-----|------------------------|-----------------|------------------|--------------|---------------|--|---------------------------------------|----------------|-----------|---|------|
| 1   | TiO <sub>2</sub>       | NA              | Guaiacol         | 12           | 300           | PT = 15% H <sub>2</sub> S/H <sub>2</sub> /400 °C/4 h, P <sub>H<sub>2</sub></sub> = 4.0 MPa | 120                                   | A <sup>b</sup> | 25        | 50% catechol, 35% phenol  | 69   |
| 2   | CoMoS/TiO <sub>2</sub> | 7.4% Mo         | Guaiacol         | 12           | 300           | PT = 15% H <sub>2</sub> S/H <sub>2</sub> /400 °C/4 h, P <sub>H<sub>2</sub></sub> = 4.0 MPa | 112                                   | A <sup>b</sup> | 100       | 60% phenol, 20% benzene, cyclohexane & cyclohexene                                | 69   |
| 3   | NiMoS/TiO <sub>2</sub> | 3.3% Ni, 15% Mo | Rapeseed oil     | 4            | 300           | P <sub>H<sub>2</sub></sub> = 3.5 MPa   | 117                                   | A <sup>b</sup> | 100       | 56% C <sub>18</sub> , 5% C <sub>17</sub>  | 70   |
| 4   | Ru/TiO <sub>2</sub>    | 5% Ru           | Pyrolysis oil    | 4            | 350           | P <sub>H<sub>2</sub></sub> = 20 MPa  | 55                                    | A : R          | 100       | 67% oil   | 71   |
| 5   | Ru/TiO <sub>2</sub>    | 1% Ru           | Ethyl stearate   | 17           | 200           | P <sub>H<sub>2</sub></sub> = 3.0 MPa, 5 mL hexane  | NA                                    | A              | 99.3      | 91% C <sub>17</sub> , 8.9% C <sub>18</sub> , 0.1% stearyl alcohol                 | 72   |
| 6   | Ru/TiO <sub>2</sub>    | 4% Ru           | Phenol           | 1            | 300           | PT = N <sub>2</sub> /H <sub>2</sub> /400 °C/4 h, P <sub>H<sub>2</sub></sub> = 4.5 MPa      | 33                                    | 3 : 1 A : R    | 12        | 12% cyclohexanone, 2% cyclohexenol, 85% benzene, 1% cyclohexane, 0.6% cyclohexene | 52   |
| 7   | Pt/TiO <sub>2</sub>    | 1% Pt           | <i>m</i> -Cresol | 1            | 300           | PT = H <sub>2</sub> /300 °C/1 h, P <sub>H<sub>2</sub></sub> = 0.1 MPa                      | NA                                    | A <sup>b</sup> | 17        | 88% toluene   | 68   |

<sup>a</sup> Abbreviation: NA (not available in the reference); *t* (time); *T* (temperature); Conv. (conversion); PT (pre-treatment); *P* (pressure); A (anatase); R (rutile). <sup>b</sup> Phase was estimated using the calcination temperature.



hydrodeoxygenation process and favoured direct cleavage of the aromatic carbon–heteroatom bond.<sup>74,76</sup> This has confirmed that the selectivity of the catalyst could be fine-tuned by selection and modification of the support materials. For instance, Kubička *et al.*<sup>70</sup> found that deoxygenation of rapeseed oil *via* NiMoS/TiO<sub>2</sub> yielded *n*-octadecane (C<sub>18</sub>) as the main product and a minor share of *n*-heptadecane (C<sub>17</sub>) (Table 3, no. 3). The C<sub>18</sub>/C<sub>17</sub> ratio for the deoxygenation of rapeseed oil achieved a value as high as ten. This has proven that the NiMoS/TiO<sub>2</sub> catalyst exhibited high selectivity towards hydrodeoxygenation.

A metal sulphide catalyst supported on TiO<sub>2</sub> in principle tackles two main reaction pathways, namely hydrodeoxygenation and hydrogenation. Generally, diesel fuel components are obtained selectively through hydrodeoxygenation *via* this catalyst, with the only by-products being water, carbon oxides, and propane.<sup>66</sup> Due to the excellent performance, the catalysts are well-known and widely used in the industry. However, there are several disadvantages to this approach. The metal sulphide catalyst showed no activity for deoxygenation in hydrogen-free conditions, therefore, high hydrogen consumption is needed. In addition, an external sulfur source is needed to keep the sulfided catalyst in an active state and there is possible leaching of sulfur species in the final product. Hence, the most significant challenges from using metal sulphide catalysts, both from an environmental as well as an economical point of view, are the high hydrogen and sulfur consumption.

Ruthenium (Ru) is the common noble metal used in deoxygenation (Table 3, no. 4–6). For example, hydrodeoxygenation of pyrolysis oil with a Ru/TiO<sub>2</sub> catalyst (Table 3, no. 4) achieved 100% conversion and 67% liquid product with a low oxygen content (about 9%).<sup>71</sup> He *et al.*<sup>72</sup> showed that the Ru/TiO<sub>2</sub> catalyst successfully deoxygenated ethyl stearate to octadecane and heptadecane. Ethyl stearate was first hydrogenated to stearyl alcohol and then deoxygenated to octadecane and heptadecane. The most fascinating finding is that the selectivity towards heptadecane and octadecane is 91% and 8.9%, respectively. The total conversion of ethyl stearate is as high as 99.3% at 200 °C (Table 3, no. 5). On the other hand, Ru/TiO<sub>2</sub> tended to follow the hydrogenolysis and hydrogenation pathway as shown in Table 3, no. 6. In the hydrogenolysis of phenol, the feedstock was reduced to benzene (about 85%). Meanwhile, the hydrogenation pathway firstly hydrogenated phenol to produce cyclohexenol. Cyclohexenol is an unstable product that rapidly tautomerizes to form cyclohexanone and is further converted to cyclohexanol in the presence of hydrogen. Cyclohexanol is then dehydrated to form cyclohexene and further hydrogenated to cyclohexane. The Ru/TiO<sub>2</sub> catalyst shows outstanding activity and high selectivity toward direct hydrodeoxygenation. The superior performance can be explained by the synergistic action between small Ru particles and the TiO<sub>2</sub> support. The role of TiO<sub>2</sub> is explained by a spill-over mechanism in which small Ru particles facilitate hydrogen dissociation to create more active sites.<sup>77</sup> The active sites are around the perimeter of the metal particles at the Ru/TiO<sub>2</sub> interface, and also on the TiO<sub>2</sub> support due to oxygen vacancies created from the spill-over mechanism.<sup>77</sup> Spill-over hydrogen created in the periphery of Ru diffuses to the support in which Ti<sup>4+</sup> was reduced to Ti<sup>3+</sup> Lewis acid sites.<sup>72</sup> Then Ti<sup>3+</sup> interacted strongly with the carboxylic

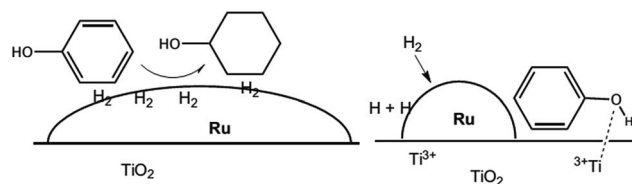


Fig. 3 Illustration of large Ru particles on a TiO<sub>2</sub> support interacting with the aromatic ring and facilitating hydrogenation (left), while small Ru particles create a bifunctional catalyst with the phenyl ring and promote hydrodeoxygenation (right) (adapted from ref. 49).

group or phenol hydroxyl group (Fig. 3),<sup>52</sup> resulting in weakening the C=O bond and promoting hydrodeoxygenation. Therefore, it was believed that Ru/TiO<sub>2</sub> could be a prominent catalyst in hydrodeoxygenation.

Deoxygenation reactions in liquid phase based on various metals such as Ru, Pt, NiMo, and CoMo supported on TiO<sub>2</sub> usually were studied at a temperatures ranging between 300 and 350 °C. Interestingly, the Ru/TiO<sub>2</sub> catalyst showed a very high activity at a very low temperature of 200 °C, and the most attractive result is that the hydrocarbons C<sub>17</sub> and C<sub>18</sub> are produced *via* deoxygenation (Table 3, no. 5). These results are very striking in the upgrading of bio-oil due to both the low reaction temperature and high conversion rate and selectivity by using Ru/TiO<sub>2</sub> as a catalyst.

In a separate study, Nie *et al.*<sup>68</sup> reported that the selectivity of the catalyst to each of the possible pathways can be controlled by the selection of the metal and support. When using a noble metal such as platinum (Pt) supported on TiO<sub>2</sub>, hydrodeoxygenation becomes dominant. In the hydrodeoxygenation of *m*-cresol over Pt/TiO<sub>2</sub>, toluene is the main deoxygenation product (88%) (Table 3, no. 7). This can be explained by SMSI and stabilization of the carbonyl group at interfacial Pt–TiO<sub>x</sub> sites which are oxophilic. The oxophilic sites increase the rate of C=O hydrogenation of *m*-cresol, and form an *m*-cresol tautomer (3-methyl-3,5-cyclohexadienone) as an intermediate which is further hydrogenated to a very reactive unsaturated alcohol (3-methyl-3,5-cyclohexadienol), and the alcohol is then dehydrated to toluene.<sup>68</sup> It demonstrated that noble metal supports on TiO<sub>2</sub> catalyst are promising for hydrodeoxygenation.

The TiO<sub>2</sub> used for most of the hydrodeoxygenation studies was reported with a pure anatase crystalline structure. However, Wildschut *et al.*<sup>71</sup> and Newman *et al.*<sup>52</sup> reported that hydrodeoxygenation using P25 TiO<sub>2</sub>, a mixture of 75% anatase and 25% rutile, demonstrated good catalytic activity (Table 3, no. 4 and 6). This finding is in agreement with the result of Carballo *et al.*<sup>78</sup> that Ru supported on P25 has a significantly better dispersion than that supported on pure anatase TiO<sub>2</sub>. The better metal dispersion is due to the rutile phase of P25 having a similar crystal structure to that of Ru.<sup>79</sup> In addition, the rutile phase has a higher surface free energy than that of the anatase phase, and defect sites are likely to form on the surface of the rutile phase. The presence of defect sites on the rutile surface provides anchorage sites for the metal particles thereby inhibiting the metal particle size growth by coalescence or migration.<sup>77,80</sup> Based on reduction kinetics of Ru supported on anatase and rutile, rutile was 2.5 times faster than anatase.<sup>79</sup> According to Bickley *et al.*, some cases have shown that

small rutile crystallites are interwoven with the anatase crystallite and in some cases, the rutile phase forms a surface layer onto the anatase crystallites. The intimate contact of these two phases will enhance their interaction and further stabilize the metal particles.<sup>80</sup> It was in accordance with the finding of Xaba and de Villiers, where the trend in sintering of metal on the phases of TiO<sub>2</sub> is anatase > rutile > P25.<sup>81</sup> This finding suggested that TiO<sub>2</sub> with a combination of the anatase and rutile crystalline structures has better performance in hydrodeoxygenation.

## 4.2 Hydrogenation

Hydrogenation is the reaction where hydrogen addition occurs without the cleavage of bonds, as depicted in Fig. 4. The process is commonly used to reduce or saturate organic compounds under a hydrogen atmosphere. It is an essential process in the biofuel industry as biomass-derived compounds need to be hydrogenated or hydrodeoxygenated to produce biofuels and chemicals. Metal supported on TiO<sub>2</sub> showed a high selectivity for hydrogenated products due to the Lewis acid properties.<sup>60</sup> In addition, they have a very low yield of coked or cracked products.<sup>58</sup> Hence, more studies have been focused on TiO<sub>2</sub>-supported catalysts in hydrogenation.

Table 4 shows an overview of the relevant literature for the hydrogenation of various model compounds under a hydrogen

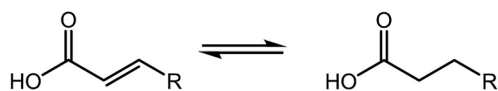


Fig. 4 Hydrogenation reaction of a carboxylic acid.

atmosphere. It was shown that anatase, rutile, and a mixed phase of TiO<sub>2</sub> have revealed good activity when combined with different metals and then reacted with different feedstocks.

The catalytic activity of different metals supported on TiO<sub>2</sub> yielded different hydrogenation efficiency and product selectivity. As shown in Table 4, noble metals such as palladium (Pd), platinum (Pt), and iridium (Ir) have attracted much attention due to the difference in the catalytic activity and selectivity of hydrogenation. For instance, Pd/TiO<sub>2</sub> showed a high activity (72.4%) for alkene production from alkadienes *via* hydrogenation (Table 4, no. 3), while other reports showed that Pt/TiO<sub>2</sub> also achieved outstanding catalytic activity in hydrogenation reactions, which is 100% conversion (Table 4, no. 6–8). Manyar *et al.*<sup>42</sup> revealed a facile hydrogenation of carboxylic acids using Pt/TiO<sub>2</sub>, with 100% conversion and high alcohol selectivity of 93% and 7% of linear alkanes under a low temperature and hydrogen pressure. The enhanced hydrogenation activity could be explained by the SMSI that occurs between noble metals and reducible oxides such as TiO<sub>2</sub>. The oxygen vacancies on TiO<sub>2</sub> that are created through the hydrogen spill-over interact with the carbonyl oxygen of the acid (Fig. 5). The interaction weakens C=O and promotes hydrogenation and C=O bond cleavage.<sup>42</sup> Therefore, this finding confirmed that SMSI between noble metals and TiO<sub>2</sub> is the key factor affecting the hydrogenation activity and catalyst selectivity.

Nickel (Ni) is another metal catalyst for hydrogenation study (Table 4, no. 9–12) due to its cost effectiveness compared to noble metals and ease of separation from homogeneous media by a magnetic field.<sup>87</sup> Saadi *et al.*<sup>38</sup> demonstrated the highest conversion and selectivity for benzaldehyde to 64% toluene and

Table 4 Overview of literature concerning the hydrogenation reaction catalyzed by TiO<sub>2</sub>-based catalysts<sup>a</sup>

| No. | Catalyst              | Metal (w/w)    | Reactant                                       | <i>t</i> (h) | <i>T</i> (°C) | Reaction conditions  | Phase       | Conv. (%) | Selectivity  | Ref. |
|-----|-----------------------|----------------|--|--------------|---------------|--|-------------|-----------|--|------|
| 1   | Pd/TiO <sub>2</sub>   | 1% Pd          | Acetylene in ethylene                          | 1            | 40            | PT = H <sub>2</sub> , 300 °C/1 h, <i>P</i> <sub>H<sub>2</sub></sub> = 0.1 MPa                    | 3 : 1 A : R | 54        | 1% ethylene  | 82   |
| 2   | Pd/TiO <sub>2</sub>   | 1% Pd          | Acetylene in ethylene                          | 1            | 40            | PT = H <sub>2</sub> , 500 °C/1 h, <i>P</i> <sub>H<sub>2</sub></sub> = 0.1 MPa                    | 3 : 1 A : R | 56        | 25% ethylene   | 82   |
| 3   | Pd/TiO <sub>2</sub>   | 0.075% Pd      | Alkadienes (C <sub>10</sub> –C <sub>13</sub> ) | 1            | 100           | PT = H <sub>2</sub> , 200 °C/1 h, <i>P</i> <sub>H<sub>2</sub></sub> = 1.4 MPa                    | A           | 72.6      | 72.4% alkenes  | 83   |
| 4   | Pd/TiO <sub>2</sub>   | 0.075% Pd      | Alkadienes (C <sub>10</sub> –C <sub>13</sub> ) | 1            | 100           | PT = H <sub>2</sub> , 200 °C/1 h, <i>P</i> <sub>H<sub>2</sub></sub> = 1.4 MPa                    | R           | 62.6      | 34.7% alkenes  | 83   |
| 5   | Pd/TiO <sub>2</sub>   | 0.075% Pd      | Alkadienes (C <sub>10</sub> –C <sub>13</sub> ) | 1            | 100           | PT = H <sub>2</sub> , 450 °C/1 h, <i>P</i> <sub>H<sub>2</sub></sub> = 1.4 MPa                    | R           | 69.5      | 86.4% alkenes  | 83   |
| 6   | Pt/TiO <sub>2</sub>   | 4% Pt          | Stearic acid                                   | 20           | 130           | PT = H <sub>2</sub> , 120 °C/1 h, <i>P</i> <sub>H<sub>2</sub></sub> = 2.0 MPa                    | A           | 100       | 93% stearyl alcohol, 7% C <sub>n</sub> + C <sub>n-1</sub>                                      | 42   |
| 7   | PtRe/TiO <sub>2</sub> | 4% Pt, 4% Re   | Stearic acid                                   | 4            | 130           | PT = H <sub>2</sub> , 120 °C/1 h, <i>P</i> <sub>H<sub>2</sub></sub> = 2.0 MPa                    | A           | 100       | 70% stearyl alcohol, 30% C <sub>n</sub> + C <sub>n-1</sub>                                     | 42   |
| 8   | PtIr/TiO <sub>2</sub> | 0.5% Pt, 1% Ir | Cyclohexene                                    | 1            | 100           | PT = H <sub>2</sub> /N <sub>2</sub> , 400 °C/1 h, <i>P</i> <sub>H<sub>2</sub></sub> = 0.1 MPa    | A           | 100       | 100% cyclohexane   | 84   |
| 9   | Ni/TiO <sub>2</sub>   | 10% Ni         | Benzaldehyde                                   | 6            | 140           | PT = H <sub>2</sub> , 350 °C/16 h, <i>P</i> <sub>H<sub>2</sub></sub> = 0.1 MPa                   | R           | 100       | 5% benzyl alcohol, 64% toluene, 31% benzene  | 38   |
| 10  | Ni/TiO <sub>2</sub>   | 15% Ni         | Acetophenone                                   | 1            | 140           | PT = H <sub>2</sub> , 450 °C/4 h, <i>P</i> <sub>H<sub>2</sub></sub> = 3.9 MPa                    | R           | 96.7      | 100% phenylethanol   | 85   |
| 11  | Ni/TiO <sub>2</sub>   | 8% Ni          | Ethanol  | 8            | 500           | PT = H <sub>2</sub> /N <sub>2</sub> , 500 °C/1 h, <i>P</i> <sub>N<sub>2</sub>/He</sub> = 0.1 MPa | A           | 80        | 0.21 mol min <sup>-1</sup> of H <sub>2</sub> , 19% CH <sub>3</sub> CHO, 6% CH <sub>4</sub>     | 86   |
| 12  | Ni/TiO <sub>2</sub>   | 8% Ni          | Ethanol  | 8            | 500           | PT = H <sub>2</sub> /N <sub>2</sub> , 800 °C/1 h, <i>P</i> <sub>N<sub>2</sub>/He</sub> = 0.1 MPa | R           | 86        | 0.44 mol min <sup>-1</sup> of H <sub>2</sub> , 5.9% CH <sub>3</sub> CHO, 13.1% CH <sub>4</sub> | 86   |

<sup>a</sup> Abbreviation: NA (not available in the reference); *t* (time); *T* (temperature); Conv. (conversion); PT (pre-treatment); *P* (pressure); A (anatase); R (rutile).

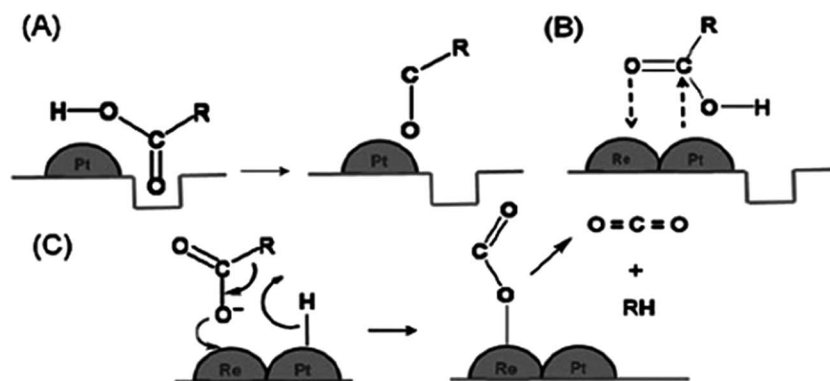


Fig. 5 Hydrogenation of carboxylic acid ensuing through (A) the interaction of the oxygen atom of the carbonyl group with the oxygen vacancies created by hydrogen spill-over by Pt metal, (B) the interaction of the oxygen atom of the carbonyl group with Re on the surface of the PtRe/ $\text{TiO}_2$  bimetallic catalyst, and (C) the decarboxylation of carboxylic acid on the surface of Re on the surface of the PtRe/ $\text{TiO}_2$  bimetallic catalyst (adapted from ref. 40).

31% benzene (Table 4, no. 9). This suggested that Ni/ $\text{TiO}_2$  preferentially hydrogenates the  $\text{C}=\text{O}$  double bond to form benzyl alcohol and toluene (about 69% for both hydrogenated products). While the  $\text{C}-\text{C}$  exocyclic bond of benzaldehyde undergoes hydrogenolysis to form benzene. This observed selectivity was explained by the existence of SMSI between Ni and  $\text{TiO}_2$ , and the existence of SMSI promotes dispersion of Ni.<sup>88</sup> Moreover, strong reducibility and surface acid-base properties of  $\text{TiO}_2$  increase the hydrogenation selectivity.<sup>38,43</sup> Thus, the Ni/ $\text{TiO}_2$  catalyst is a potential non-noble metal catalyst for hydrogenation and hydrogenolysis.

As compared to the hydrogenation with monometallic Pt/ $\text{TiO}_2$  to that with bimetallic PtRe/ $\text{TiO}_2$ , the addition of rhenium (Re) increased the rate of hydrogenation and thus significantly increased the selectivity towards linear alkanes by 23%. Surprisingly, the reaction duration with PtRe/ $\text{TiO}_2$  to completion was 5 times faster than that with monometallic Pt/ $\text{TiO}_2$ . The presence of Re increased oxyphilicity because the Re interacts with the lone pair electrons of the carbonyl group oxygen (Table 4, no. 7). The interaction of the substrate with Re on the catalyst surface favours the formation of alkanes.<sup>42</sup> Other studies reported that bimetallic PtIr/ $\text{TiO}_2$  showed a higher hydrogenation ability than Pt/ $\text{TiO}_2$  did. It can be explained by the high dispersion of Pt or Ir on  $\text{TiO}_2$  and the mean size of PtIr is 2.1 nm smaller than Pt alone. It was found that Ir particles strongly interacted with  $\text{TiO}_2$  and acted as nucleation sites for Pt atom assembly.<sup>84</sup> Therefore, the bimetallic catalyst could be an alternative to a monometallic catalyst for more active hydrogenation and can shorten the reaction duration.

Interestingly, the reduction temperature of the catalyst also plays an important role in stabilizing the catalyst to achieve a higher hydrogenation rate. As discussed above, the hydrogenation reaction on the  $\text{TiO}_2$ -supported catalyst depends on the strong metal-support interaction (SMSI). It was believed that the reduction temperature affects the SMSI of  $\text{TiO}_2$ -supported catalysts. This was confirmed by Kang *et al.*<sup>82</sup> where Pd interacted strongly with  $\text{TiO}_2$  particularly after reduction at high temperatures due to SMSI. By comparing Pd/ $\text{TiO}_2$  reduced at 300 °C and 500 °C (Table 4, no. 1 and 2), it was found that Pd/ $\text{TiO}_2$  reduced at 500 °C induced SMSI and revealed higher conversion and

selectivity of hydrogenation from acetylene to ethylene. Li *et al.*<sup>83</sup> also reported that SMSI corresponding to noble metals supported on  $\text{TiO}_2$  was only observed when the catalyst was reduced at a temperature above 300 °C. In addition, this finding was further proven by Wildschut *et al.*<sup>71</sup> where SMSI exists in between Pd and anatase  $\text{TiO}_2$  at a low reduction temperature (Table 4, no. 3). However, SMSI for Pd supported on rutile  $\text{TiO}_2$  was only observed when the catalyst was reduced at a higher temperature because rutile is thermodynamically and structurally more stable than anatase. Pd/rutile  $\text{TiO}_2$  reduced at 200 °C does not induce SMSI and hence the conversion and selectivity are low. The elevation of the reduction temperature from 200 °C to 450 °C leads to the presence of SMSI between Pd and  $\text{Ti}^{3+}$  in rutile  $\text{TiO}_2$ . The presence of SMSI has enhanced the conversion of alkadienes and selectivity of hydrogenation by 52%. Therefore, it is important to reduce the catalyst at high temperature prior to reaction to induce the SMSI phenomenon for improving selectivity.

Furthermore, some research showed that  $\text{TiO}_2$  in different polymorphs exhibits different physicochemical properties which influenced the catalytic activities. Hydrogenation of acetophenone with Ni/rutile  $\text{TiO}_2$  exhibits prominent activity (96.7% conversion and 100% selectivity) as compared to that of Ni/anatase  $\text{TiO}_2$  (Table 4, no. 10). In separate studies, Nichele *et al.*<sup>86</sup> highlighted that Ni/rutile  $\text{TiO}_2$  demonstrated high ethanol conversion (86%) as compared to that of Ni/anatase  $\text{TiO}_2$  (80%). The higher activity of Ni/rutile  $\text{TiO}_2$  is essentially attributed to SMSI between Ni and rutile, arising from the higher surface enthalpy of rutile than that of anatase.<sup>85</sup> This has prevented the aggregation of Ni particles leading to the higher dispersion of Ni on the surface of rutile  $\text{TiO}_2$  which led to a higher activity.<sup>85,88,89</sup> Besides, electron density on Ni is altered due to electron transfer between Ni and rutile. The interaction between Ni and  $\text{Ti}^{3+}$  may generate a negative charge on Ni atoms that enhances the activity of the Ni/rutile  $\text{TiO}_2$  catalyst for the hydrogenation.<sup>52</sup> Thereby, it is affirmed that rutile  $\text{TiO}_2$  is more active as compared to anatase  $\text{TiO}_2$  in hydrogenation.

In addition, the hydrogenation activity also depends on the morphology of the catalyst support and particle size distribution.<sup>84</sup> Bimetallic PtIr/ $\text{TiO}_2$  nanotubes (Table 4, no. 8) exhibited

excellent hydrogenation of cyclohexene to cyclohexane with 100% conversion and the unique properties of  $\text{TiO}_2$  nanotubes have enhanced the hydrogenation process. For example, the Pd/ $\text{TiO}_2$  nanotubes and Pt/ $\text{TiO}_2$  nanotubes showed a better response and high selectivity towards double bond hydrogenation.<sup>51,90</sup>  $\text{TiO}_2$  nanotubes are regarded as an outstanding catalyst support because they exhibit a large internal and external surface, along with available surface in the vertex and in the interlayer. In line with this, the nanotubes have a bigger specific surface area (SSA) for the high population of exposed Ti-OH. The SSA of  $\text{TiO}_2$  nanotubes is almost twice the size of  $\text{TiO}_2$  nanoparticles.<sup>90,91</sup> This is also suggested by the fact that the surface area and the number of adsorption sites have increased extensively. Hence, it is believed that  $\text{TiO}_2$  nanotubes have better adsorption and performance in hydrogenation.

### 4.3 Esterification and transesterification

Esterification is a reaction between alcohol with acid to produce ester and water, while transesterification is the reaction of an ester with alcohol to replace the alkoxy group (Fig. 6). Catalysts with basicity perform better in transesterification than an acid catalyst does. Transesterification of triglycerides with short chain alcohol is the most common method to produce biodiesel. It is relatively simple and has easy operation, but the product as the transportation fuel suffers from engine compatibility issues due to the incomplete removal of oxygenates.<sup>92</sup> Meanwhile, esterification is a chemical process to convert

platform molecules into renewable base chemicals (alkyl ester) in the presence of an acid catalyst.<sup>93,94</sup> Both esterification and transesterification are an important technology in the chemical and fuel industries.

Acid-modified metal oxides such as sulfated  $\text{TiO}_2$  ( $\text{TiO}_2\text{-SO}_4$ ), sulfated zirconium dioxide ( $\text{ZrO}_2\text{-SO}_4$ ), and sulfated iron oxide ( $\text{Fe}_2\text{O}_3\text{-SO}_4$ ) have been studied as potential catalysts for the last two decades in different types of reactions. Lin *et al.*<sup>95</sup> reported that  $\text{TiO}_2\text{-SO}_4$  catalyzed the esterification reaction between acetic acid and cyclohexanol well (Table 5, no. 1), whereas  $\text{TiO}_2$  alone was not reactive towards the esterification reaction. In another study, it was shown that the esterification of levulinic acid to ethyl levulinate using  $\text{TiO}_2\text{-SO}_4$  achieved as high as 83.2% conversion (Table 5, no. 2). Besides, transesterification of soybean oil and castor oil using  $\text{TiO}_2\text{-SO}_4$  was also reported; the catalyst exhibited high transesterification conversion of 40% and 25%, respectively (Table 5, no. 4 and 5). Sulfate on  $\text{TiO}_2$  plays an important role in esterification/transesterification by offering active acid sites. The sulfate linked to  $\text{TiO}_2$  on the chelate form and induced Bronsted acid sites (Fig. 7). The existence of strong Bronsted acid sites on  $\text{TiO}_2\text{-SO}_4$  promotes the esterification/transesterification reaction.<sup>97,99</sup> This clearly showed that the acid sites comprised of Lewis and Bronsted sites are crucial for the esterification/transesterification reaction.

Additionally, modification of a  $\text{TiO}_2$  support with a metal oxide such as  $\text{ZrO}_2$  is capable of enhancing the esterification

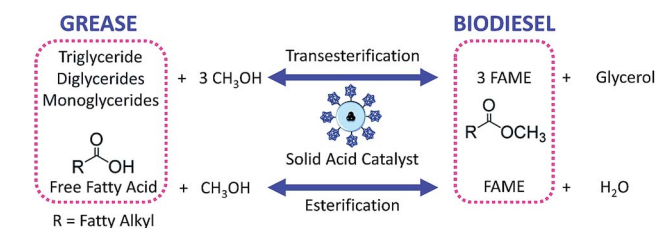


Fig. 6 Esterification of fatty acids and transesterification of triglyceride to produce biodiesel.

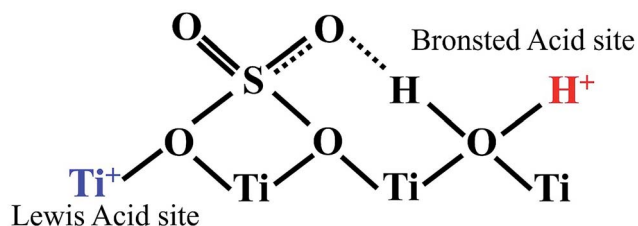


Fig. 7 Illustrative structure indicates the presence of both Bronsted and Lewis acid sites on the surface of  $\text{TiO}_2\text{-SO}_4$ .

Table 5 Overview of literature concerning the esterification and transesterification based on  $\text{TiO}_2$  as a catalyst support<sup>a</sup>

| No. | Catalyst                                | Metal (w/w)                   | Reactant                               | <i>t</i> (h) | <i>T</i> (°C) | Reaction conditions | $\text{TiO}_2$ morphology | Phase | Conversion/selectivity           | Ref. |
|-----|---|-------------------------------|--|--------------|---------------|---------------------|---------------------------|-------|----------------------------------|------|
| 1   | $\text{TiO}_2\text{-SO}_4$              | NA                            | Acetic acid                            | 10           | 100           | NA                  | Nanotubes                 | A     | 55%                              | 95   |
| 2   | $\text{TiO}_2\text{-SO}_4$              | NA                            | Levulinic acid                         | 3            | 105           | NA                  | Nanorods                  | A     | 83.2% ethyl levulinate           | 96   |
| 3   | $\text{ZrO}_2/\text{TiO}_2\text{-SO}_4$ | 20% $\text{ZrO}_2$            | Levulinic acid                         | 3            | 105           | NA                  | Nanorods                  | A     | 90.4% ethyl levulinate           | 96   |
| 4   | $\text{TiO}_2\text{-SO}_4$              | 17% $\text{H}_2\text{SO}_4^b$ | Soybean oil                            | 1            | 120           | $P = 0.5$ MPa       | Mesoporous                | A     | 40% FAMES                        | 97   |
| 5   | $\text{TiO}_2\text{-SO}_4$              | 17% $\text{H}_2\text{SO}_4^b$ | Castor oil                             | 1            | 120           | $P = 0.5$ MPa       | Mesoporous                | A     | 25% FAMES                        | 97   |
| 6   | $\text{Au}/\text{TiO}_2$                | 1% Au                         | 5-hydromethylfurfural (HMF) + methanol | 3            | 130           | $P = 0.3$ MPa       | NA                        | NA    | 98% 2,5-furandimethylcarboxylate | 98   |
| 7   | $\text{Au}/\text{TiO}_2$                | 1% Au                         | 5-hydromethylfurfural (HMF) + methanol | 3            | r.t.          | $P = 0.3$ MPa       | NA                        | NA    | No conversion                    | 98   |

<sup>a</sup> Abbreviation: NA (not available in the reference); *t* (time); *T* (temperature); Conv. (conversion); *P* (pressure); A (anatase); R (rutile). <sup>b</sup> Estimated value based on mol ratio.



reaction.  $\text{TiO}_2\text{-SO}_4$  and zirconia-modified  $\text{TiO}_2\text{-SO}_4$  ( $\text{ZrO}_2/\text{TiO}_2\text{-SO}_4$ ) was used for esterification of levulinic acid (Table 5, no. 2 and 3). It was observed that  $\text{ZrO}_2/\text{TiO}_2\text{-SO}_4$  enhanced the esterification of levulinic acid to ethyl levulinate by 30.4% as compared to that of unmodified  $\text{TiO}_2$ . The reaction reached equilibrium for  $\text{ZrO}_2/\text{TiO}_2\text{-SO}_4$  with a levulinic acid conversion of 90.4% in 3.5 hours, while in the case of the reaction catalyzed by  $\text{TiO}_2\text{-SO}_4$ , the conversion is 7.2% lower than with  $\text{ZrO}_2/\text{TiO}_2\text{-SO}_4$ .<sup>96</sup> The author claimed that  $\text{ZrO}_2$  was highly dispersed on the surface of  $\text{TiO}_2$  using powder X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). It was assumed that introduction of  $\text{ZrO}_2$  to  $\text{TiO}_2\text{-SO}_4$  increased the adsorption of sulfate on the surface of  $\text{TiO}_2$  and acted as active sites for esterification.<sup>96</sup> This clearly showed that  $\text{TiO}_2$  with modification exhibited an increased reaction for esterification and achieved equilibrium in a shorter reaction time.

Gold (Au) is another excellent catalyst for oxidative esterification. For instance, Taarning *et al.*<sup>98</sup> demonstrated esterification of a primary alcohol in hydromethylfurfural (HMF) with  $\text{Au}/\text{TiO}_2$  at 130 °C for 3 hours. Furan-2,5-dimethylcarboxylate (FDMC) is formed directly with an excellent yield of approximately 98% (Table 5, no. 6). Besides, oxidation of HMF with  $\text{Au}/\text{TiO}_2$  at room temperature (22 °C) under oxygen atmosphere produced 90% of 5-hydroxymethylfuroate (HMMF) within 5 hours. Highly dispersed Au on a  $\text{TiO}_2$  support has been shown to be efficient for esterification and oxidation of HMF with remarkable selectivity.<sup>98</sup> Thereby,  $\text{Au}/\text{TiO}_2$  offers an alternative to other oxidation catalysts for esterification and transesterification.

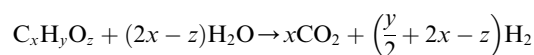
The morphological properties of a catalyst such as SSA, the mean pore size, and pore distribution are crucial parameters that influence the conversion and selectivity of esterification and transesterification. The specific morphology of the catalysts included nanorods, nanotubes, mesoporous materials, nanoparticles, *etc.* Several studies discussed the outstanding performance of nanotubes in esterification and transesterification (Table 5, no. 1–3). Nanotubes have larger internal and external surfaces, which reveal better adsorption sites. Moreover, mesoporous  $\text{TiO}_2$  with a bigger SSA and mean pore size featured transesterification with a higher yield (Table 5, no. 4 and 5). Therefore, it is of utmost importance to select a synthesis method with a specific morphology to obtain optimal catalytic performance.

#### 4.4 Water–gas shift reaction

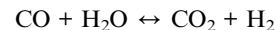
The water–gas shift (WGS) reaction is the main reaction used for the production of hydrogen by converting carbon monoxide in the presence of water. It is always used in conjunction with the steam reformation of methane or other hydrocarbons to produce hydrogen gas.<sup>100,101</sup> The WGS reaction is also one of the important reactions used in the Fischer–Tropsch and methanation reaction to balance the hydrogen to carbon monoxide ratio. Recently, the interest for the WGS reaction as an integral component of fuel processing for hydrogen in fuel cell applications has grown significantly. With the high demand for clean

fuel and hydrogen fuel cells, the development of WGS catalysts is one of the current research interests.

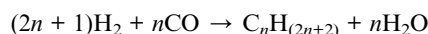
##### (1) Steam reforming



##### (2) Water–gas shift reaction



##### (3) Fischer–Tropsch reaction



##### (4) Methanation reaction



The WGS reaction normally involves both an active metallic phase and support. A redox process is one of the mechanisms proposed, whereby CO adsorbed on the metal and is oxidized by the catalyst support.<sup>101</sup> The other WGS mechanism involves formates or carbonates on the catalyst surface as intermediates that decompose into hydrogen and carbonate, prior to  $\text{CO}_2$  liberation. Formates or carbonates are produced from the CO reaction with active hydroxyl from supports.<sup>34,105</sup> Hence, it is clear that the catalyst support plays an important role in determining the WGS reaction owing to its role in dispersing metal on the support and the potential to reversibly exchange oxygen ions during the redox reaction.

The redox process of the WGS reaction primarily depends on the surface properties of the  $\text{TiO}_2$  support. Noble metals supported on  $\text{TiO}_2$  have been reported as promising low temperature WGS catalysts due to a high redox capability, resulting in the creation of oxygen vacancies (defects) through reduction of the cation charge ( $\text{Ti}^{x+}$ ,  $x < 4$ ) with CO.<sup>34,106</sup> The oxygen vacancies could dissociate  $\text{H}_2\text{O}$  to  $\text{H}_2$ , regenerate surface oxygen sites, and form hydroxyl groups.<sup>107</sup> As mentioned earlier, the surface properties of  $\text{TiO}_2$  are modifiable by combination with other transition metals or rare earth oxides. Panagiotopoulou *et al.*<sup>103</sup> found that the conversion of CO at low temperature (<300 °C) was notably improved when Pt was dispersed on  $\text{TiO}_2$ . The turnover frequency of CO increases exponentially when the primary crystallite size of  $\text{TiO}_2$  decreases, and this is accompanied by a considerable reduction of the apparent activation energy of the reaction.<sup>103</sup> The noble metal catalysts highly dispersed on  $\text{TiO}_2$  are promising candidates for use in low temperature WGS reactors for fuel cell applications.

A noble metal such as platinum (Pt), rhodium (Rh), ruthenium (Ru), and palladium (Pd) supported on  $\text{TiO}_2$  is very effective for the WGS reaction (Table 6, no. 1–10). Among the various noble metals supported on  $\text{TiO}_2$ , the CO conversion and turnover frequency (TOF) for the WGS reaction follow the order  $\text{Pt} > \text{Rh} > \text{Ru} > \text{Pd}$  (Table 6, no. 2–5). Pt is about 20 times more

Table 6 Overview of literature concerning the water–gas shift (WGS) reaction catalyzed by a TiO<sub>2</sub>-based catalyst<sup>a</sup>

| No. | Catalyst              | Metal (w/w)      | <i>t</i> (h) | <i>T</i> (°C) | Reaction conditions  | BET (m <sup>2</sup> g <sup>−1</sup> ) | Phase       | Conv. (%) | TOF (s <sup>−1</sup> ) | Ref. |
|-----|-----------------------|------------------|--------------|---------------|--|---------------------------------------|-------------|-----------|------------------------|------|
| 1   | Ru/TiO <sub>2</sub>   | 2% Ru            | 0.03         | 700           | 24 MPa   | 49                                    | NA          | 82        | NA                     | 102  |
| 2   | Pd/TiO <sub>2</sub>   | 0.5% Pd          | 1            | 250           | PT = 300 °C/2 h/H <sub>2</sub> , <i>P</i> <sub>H<sub>2</sub></sub> = 0.1 MPa, 200 cm <sup>3</sup> min <sup>−1</sup>                                    | 39                                    | 3 : 1 A : R | 2         | 0.027                  | 103  |
| 3   | Ru/TiO <sub>2</sub>   | 0.5% Ru          | 1            | 250           | PT = 300 °C/2 h/H <sub>2</sub> , <i>P</i> <sub>H<sub>2</sub></sub> = 0.1 MPa, 200 cm <sup>3</sup> min <sup>−1</sup>                                    | 39                                    | 3 : 1 A : R | 6         | 0.07                   | 103  |
| 4   | Rh/TiO <sub>2</sub>   | 0.5% Rh          | 1            | 250           | PT = 300 °C/2 h/H <sub>2</sub> , <i>P</i> <sub>H<sub>2</sub></sub> = 0.1 MPa, 200 cm <sup>3</sup> min <sup>−1</sup>                                    | 39                                    | 3 : 1 A : R | 8         | 0.16                   | 103  |
| 5   | Pt/TiO <sub>2</sub>   | 0.5% Pt          | 1            | 250           | PT = 300 °C/2 h/H <sub>2</sub> , <i>P</i> <sub>H<sub>2</sub></sub> = 0.1 MPa, 200 cm <sup>3</sup> min <sup>−1</sup>                                    | 39                                    | 3 : 1 A : R | 22        | 0.46                   | 103  |
| 6   | Pt/TiO <sub>2</sub>   | 0.5% Pt          | 1            | 250           | PT = 300 °C/2 h/H <sub>2</sub> , <i>P</i> <sub>H<sub>2</sub></sub> = 0.1 MPa, 200 cm <sup>3</sup> min <sup>−1</sup>                                    | 71                                    | A           | 34        | 7                      | 103  |
| 7   | Pt/TiO <sub>2</sub>   | 3% Pt            | 1            | 250           | PT = 500 °C/2 h/H <sub>2</sub> , <i>P</i> <sub>H<sub>2</sub></sub> = 0.1 MPa, 9500 L h <sup>−1</sup> kg <sub>cat</sub> <sup>−1</sup>                   | 74                                    | A           | 33        | 82.4 × 10 <sup>2</sup> | 104  |
| 8   | Pt/TiO <sub>2</sub>   | 3% Pt            | 1            | 250           | PT = 500 °C/2 h/H <sub>2</sub> , <i>P</i> <sub>H<sub>2</sub></sub> = 0.1 MPa, 9500 L h <sup>−1</sup> kg <sub>cat</sub> <sup>−1</sup>                   | 44                                    | R           | 52.3      | 84.9 × 10 <sup>2</sup> | 104  |
| 9   | Pt/TiO <sub>2</sub>   | 0.5% Pt          | 1            | 300           | PT = 300 °C/1 h/H <sub>2</sub> /He, <i>P</i> <sub>H<sub>2</sub></sub> = 0.1 MPa, 41 000 L h <sup>−1</sup> kg <sub>cat</sub> <sup>−1</sup>              | NA                                    | 3 : 1 A : R | 60        | 10                     | 100  |
| 10  | PtCe/TiO <sub>2</sub> | 6.6% Ce, 0.5% Pt | 1            | 300           | PT = 275 °C/2 h/H <sub>2</sub> /N <sub>2</sub> , <i>P</i> <sub>H<sub>2</sub></sub> = 0.1 MPa, 21 200 L h <sup>−1</sup> kg <sub>cat</sub> <sup>−1</sup> | 62                                    | NA          | 90        | NA                     | 105  |

<sup>a</sup> Abbreviation: NA (not available); *t* (time); *T* (temperature); Conv. (conversion); TOF (turnover frequency); PT (pre-treatment); *P* (pressure); A (anatase); R (rutile).

active than Pd. Pt/TiO<sub>2</sub> was one of the most studied WGS catalysts due to the outstanding performance in hydrogen selectivity (Table 6, no. 5–10) and high redox properties.<sup>34,106</sup> Pt/TiO<sub>2</sub> is able to pass through both the classical redox route and the associative formate route for the WGS reaction. Thereby, Pt/TiO<sub>2</sub> is an auspicious catalyst support for the WGS reaction at low temperature.

As discussed in other chemical reactions (Sections 4.1 to 4.3), TiO<sub>2</sub> in different polymorphs has a different effect on the catalytic activity, and the WGS reaction is no exception. Anatase and Degussa P25 (a mixture of 75% anatase and 25% rutile) are common TiO<sub>2</sub> polymorphs used for the study of the WGS reaction. Iida *et al.*<sup>104</sup> observed that the Pt/rutile TiO<sub>2</sub> catalyst (Table 6, no. 8) has a relatively high activity for the WGS reaction at low temperature. Pt/rutile TiO<sub>2</sub> achieved 52.3% conversion which is 19.3% higher than that for Pt/anatase TiO<sub>2</sub> (Table 6, no. 7). The superior catalytic activity was mainly attributed to the SMSI between Pt and TiO<sub>2</sub>. Besides, it was also mentioned that Pt/rutile TiO<sub>2</sub> had a larger dispersion than Pt/anatase TiO<sub>2</sub>. A linear relationship was shown between the catalytic activity, SMSI, and Pt dispersion. This is in accordance with the previous report which stated that rutile revealed a greater catalytic activity than anatase due to better dispersion on rutile.<sup>78,104</sup> The better dispersion can be explained by a high degree of lattice matching, ensuring better interaction between Pt and TiO<sub>2</sub>, preventing the agglomeration of Pt particles during the calcination.<sup>108</sup> This shows that the efficiency of the catalyst also depends significantly on the crystal structure of the support.

The Pt/TiO<sub>2</sub> catalysts are promising candidates for the WGS reaction. A report showed cerium (Ce)-modified TiO<sub>2</sub> as a new support of Pt for the WGS reaction. Ce is a particularly interesting substance to be mixed with TiO<sub>2</sub> substrates because Ce

ions have useful surface properties for the WGS reaction. The addition of Ce to Pt/TiO<sub>2</sub> increased the hydroxyl concentration on the TiO<sub>2</sub> surface, and consequently induced a higher activity (approximately 90%) at the low temperature WGS reaction (Table 6, no. 10). The addition of Ce affects the redox properties of TiO<sub>2</sub> because Ce was well dispersed and interacted with Ti atoms. Besides, Ti<sup>4+</sup> ions can be replaced by Ce<sup>4+</sup> ions to improve the thermal stability and redox properties of TiO<sub>2</sub>.<sup>105</sup> The bimetallic PtCe/TiO<sub>2</sub> was found to be highly active and stable in the WGS reaction, which indicated that it is a promising formulation as a WGS catalyst.

#### 4.5 Visible light-induced organic transformation

Heterogeneous visible light photocatalysts have gained much attention recently in organic synthesis due to their simple chemical work-up and easy recovery. Solar energy is comprised of three main components, *i.e.* ultraviolet ( $\lambda$  = 200–400 nm), visible light ( $\lambda$  = 400–800 nm), and infrared ( $\lambda$  > 800 nm).<sup>109</sup> Visible light is abundant in nature compared to ultraviolet and infrared, however it cannot be adsorbed directly by the reactant molecules to drive the reaction.<sup>110</sup> Hence, visible light photocatalysts are needed as a bridging media for the energy transfer between the substrates and visible light. In the past decades, TiO<sub>2</sub>, a semiconductor with a relatively large band gap (3.2 eV), has been known to be an excellent photocatalyst under irradiation of ultraviolet light.<sup>111,112</sup> The most recent research found that TiO<sub>2</sub> also performed well as a photocatalyst under visible light irradiation.<sup>113,114</sup>

Higashimoto *et al.* first reported the selective photocatalytic oxidation of benzyl alcohol to aldehydes under visible light irradiation; the conversion rate and selectivity to aldehydes was as high as 99% on TiO<sub>2</sub> in the presence of O<sub>2</sub> (Table 7, no. 1).<sup>115</sup>

Table 7 Overview of literature concerning the visible light-induced organic transformation catalyzed by TiO<sub>2</sub>-based catalysts<sup>a</sup>

| No. | Catalyst                           | Reactant        | <i>t</i> (h) | <i>T</i> (°C) | Reaction conditions | Oxidant              | Phase | BET | Conv. (%) | Selectivity      | Ref. |
|-----|------------------------------------|-----------------|--------------|---------------|---------------------|----------------------|-------|-----|-----------|------------------|------|
| 1   | TiO <sub>2</sub>                   | Benzyl alcohol  | 4            | r.t.          | Visible light       | O <sub>2</sub>       | A     | NA  | 99        | 99% benzaldehyde | 115  |
| 2   | Rh <sup>3+</sup> /TiO <sub>2</sub> | Benzyl alcohol  | 30           | r.t.          | Visible light       | O <sub>2</sub>       | A : R | 98  | 100       | 97% benzaldehyde | 116  |
| 3   | TiO <sub>2</sub>                   | Benzylic amines | 4            | r.t.          | Visible light       | 1 atm air            | A     | 135 | 54        | 98% imine        | 113  |
| 4   | TiO <sub>2</sub>                   | Benzylic amines | 4            | r.t.          | Visible light       | 2 atm O <sub>2</sub> | A     | 135 | 76        | 98% imine        | 113  |
| 5   | TiO <sub>2</sub>                   | Benzylic amines | 4            | r.t.          | Visible light       | 1 atm air            | A : R | 54  | 35        | 98% imine        | 113  |

<sup>a</sup> Abbreviation: NA (not available); *t* (time); *T* (temperature); r.t. (room temperature); Conv. (conversion); A (anatase); R (rutile).

Modified TiO<sub>2</sub> with rhodium ions (Rh<sup>3+</sup>) also catalyzes the oxidation of benzyl alcohol in the presence of visible light and O<sub>2</sub> (Table 7, no. 2). Benzaldehyde was obtained in a high yield (97%) with 100% conversion of benzyl alcohol. The visible light response is derived from the surface complexes formed when the alcohol was absorbed by the hydroxyl groups on the surface of TiO<sub>2</sub>.<sup>116</sup> This research indicated the direct correlation between benzaldehyde formation and specific surface area, and the conversion rate increased with an increase in the surface area, showing that the surface area of the TiO<sub>2</sub> supports was a decisive factor controlling the conversion rate.<sup>116</sup>

Oxidation of amines by TiO<sub>2</sub> under visible light irradiation showed that with 1 atm of air as oxidant, the reaction proceeded smoothly with a conversion rate of 54% to produce the imine with 98% selectivity (Table 7, no. 3). When 2 atm of pure dioxygen was used as the oxidant, the conversion rate increased to 76% without having any influence on the selectivity (Table 7, no. 4). Hence, the purity of the oxidant affects the conversion rate of the photo-oxidation reaction. Nevertheless, atmospheric dioxygen is the most abundant oxidant, and a reaction carried out under air is greener. In addition, the surface area is also one of the important factors that affects the photocatalytic activity. Degussa P25 TiO<sub>2</sub> (85% anatase and 15% rutile) usually has the highest activity for the reaction under ultraviolet irradiation.<sup>112,113</sup> However, in the reaction under visible light irradiation, it is interesting to find out that Degussa P25 has a lower conversion rate as compared to anatase TiO<sub>2</sub> (Table 7, no. 3 and 5). The conversion rate is correlated to the surface area of the catalyst where anatase TiO<sub>2</sub> has a larger surface area than that of Degussa P25. The results showed that the formation of surface complexes is the key point for the

photocatalysis reaction to proceed under visible light irradiation. The surface complexes are formed by the interaction between the substrate and the active species (metal active sites<sup>113</sup> or surface hydroxyl<sup>114,115</sup>). The substrate which has a higher energy level than the valance band of TiO<sub>2</sub> acts as a donor. This is the reason that TiO<sub>2</sub> could respond to visible light activation and promote electron transfer to the conduction band of TiO<sub>2</sub>.<sup>110</sup> The principle of photocatalysis for TiO<sub>2</sub> in visible light is depicted in Fig. 8.

## 5. Conclusions

TiO<sub>2</sub> is a promising reducible oxide catalyst for green organic synthesis such as in deoxygenation, hydrogenation, esterification, transesterification, the WGS reaction, visible light-induced organic transformation *etc.* This catalyst can be modified by a variety of metal or non-metal dopants to increase the textural properties and thermal stability of TiO<sub>2</sub>, thereby enhancing the catalytic stability and activity. The redox and surface properties of TiO<sub>2</sub> are strongly affected by interaction with the metal/metal oxide dopant. This metal-support interaction induced the SMSI effect during the reduction treatment by H<sub>2</sub> and thus contributed to the high catalytic activity towards green organic synthesis.

The catalytic activities of the TiO<sub>2</sub>-based catalyst are mainly influenced by the active metal dopant, where each metal has its own activity and selectivity profile for different organic synthesis reactions. Noble metals (Pt, Ru, Pd, Rh, Au) supported on TiO<sub>2</sub> showed superior performance and high selectivity toward hydrodeoxygenation and hydrogenation. Among the noble metals, Ru/TiO<sub>2</sub> showed a very high activity even at a very low temperature. As for the WGS reaction, the reaction activity follows the order of Pt > Rh > Ru > Pd. Ni/TiO<sub>2</sub> is another potential non-noble catalyst extensively used in hydrogenation due to the high reactivity and cost effectiveness. The high performance of the TiO<sub>2</sub>-supported catalysts strongly relies on a higher dispersion and stabilization of small metallic particles on the TiO<sub>2</sub> support. This is because of the synergistic effect between the bifunctional system that is generated.

The TiO<sub>2</sub> polymorphs (anatase, rutile, and brookite) with different physicochemical properties are another key factor to influence the reactivity of organic synthesis. The existence of either one of the TiO<sub>2</sub> polymorphs affects the performance and the TiO<sub>2</sub> catalytic activity. Rutile has better lattice matching and interaction with Pt, Ru, and Ni if compared to the anatase phase, thereby the rutile phase TiO<sub>2</sub> reveals a greater catalytic activity. Besides, the morphology of the TiO<sub>2</sub> catalyst influences

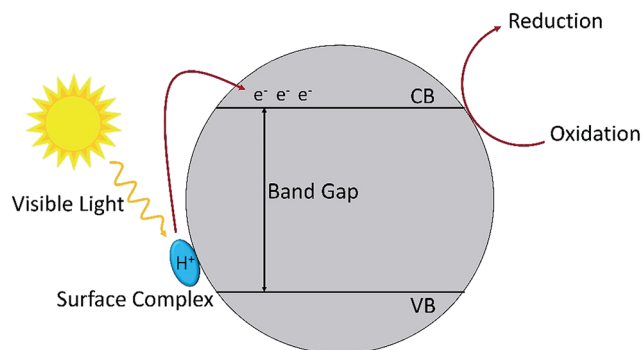


Fig. 8 The mechanism for surface complex excitation by visible light to produce an oxidized substrate and to transfer an electron in the conduction band.

the conversion and product selectivity of the organic synthesis. In addition, a different type of acid site and acid density also contributed to the performance of the catalyst in the reaction. Hence, it is important to choose a synthesis method with a specific morphology to obtain a good catalytic performance.

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