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# 1. Introduction

The palladium (Pd) catalyzed Heck reaction is one of the most important C-C coupling reactions with a remarkably wide scope in organic synthesis.<sup>1-3</sup> The C-C bond formation between aryl halide and olefins provides the simplest and efficient route for the regioselective attachment of side chains to aromatic rings using a variety of homogeneous and heterogeneous catalysts. A wide variety of Pd catalysts have been reported to promote the vinylation of aryl halides, of which many follow the "classical" Pd(0)/Pd(II) mechanism, i.e. that includes oxidative addition, migratory insertion,  $\beta$ -hydride elimination and reductive elimination.<sup>4-7</sup> Of the homogeneous and heterogeneous catalysts, due to beneficial advantages like recyclability, easy separation, and use of a small amount in the reaction, heterogeneous catalysts have received more and more attention.8-10 In this context, many reports are available on the Heck reaction in which Pd was supported on various metal oxides, silica, carbon, zeolite, graphene oxide etc.<sup>11-13</sup> and out of these, Pd-incorporated mesoporous materials enhance the catalytic activity and recyclability in the reactions.<sup>11</sup>

As per one of green chemistry's principles stating that "the energy requirements of chemical processes should be recognized for their environmental and economical impacts and should be minimized",<sup>14</sup> it would be a significant breakthrough if we could enhance the catalytic activity of Pd at ambient temperature and pressure using sunlight as the

# Time-dependent stereoselective Heck reaction using mesoporous Pd/TiO<sub>2</sub> nanoparticles catalyst under sunlight<sup>†</sup>

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Pd(0)-doped mesoporous TiO<sub>2</sub> nanoparticles (Pd/TiO<sub>2</sub>) have been synthesized using an EISA method. The catalytic activity of Pd/TiO<sub>2</sub> nanoparticles (NPs) is significantly enhanced under solar light irradiation for the Heck reaction. The Heck coupling product gives a considerable amount of *Z*-isomer, due to photochemical isomerization of the initially formed *E*-isomer, providing a facility for the time-dependent selectivity of *E*/*Z*-isomers under sunlight at ambient conditions.

cheaper, abundant and greener energy source. Very early on, the use of solar energy for organic chemical reactions was reported and was limited to photochemical and photothermal reactions.<sup>15–17</sup> Besides these, in recent years there have been many reports that summarize the sunlight-mediated reactions carried out in organic synthesis using photoactive catalyst materials. However, the focus of research has been mostly directed towards the chemistry of reaction in which molecules undergo the desired bond modifications by absorbing light.<sup>18–21</sup>

The effectiveness of a catalyst towards selectivity and efficiency has been increased by carrying out the Heck reactions under irradiation of UV-visible or sunlight.<sup>22-25</sup> Fredricks et al. reported the acceleration of the Heck reaction using UV-vis irradiation over Pd(OAc)<sub>2</sub> and heterogeneous catalyst Pd/Al<sub>2</sub>O<sub>3</sub>.<sup>22,23</sup> Very recently, Waghmode et al. showed stereoselectivity towards the trans-isomer in the Heck reaction using a PdCl<sub>2</sub>/TiO<sub>2</sub> catalyst after 5 h of UV-vis radiation.<sup>25</sup> Chaudhary and Bedekar<sup>24</sup> reported the Mizoroki-Heck reaction over Pd(OAc)<sub>2</sub> and phosphine free naphthol-based ligand under sunlight and obtained ~65% Z-isomer after 9 days of irradiation. Except for these reports the stereoselectivity of Heck coupling products has been strictly restricted to the trans- or E-isomer as the major or only product. It has now become a challenge to form a particular isomer of interest and control the cis- and trans-isomer ratio. To overcome this challenge their interconversions has been carried out either by using thermal-chemical interconversion or by photochemical means.<sup>26-29</sup> For the selective formation of the Z-isomer, special conditions for the Heck reaction have also been reported by some groups, which involved the design of ligands or other parameters or the use of bioactive materials.<sup>30–32</sup> Therefore, it is desirable to have a new catalyst structure which could be designed in such a way that the vast potential of sunlight can be exploited instead of energy-consuming heat as the source to drive the reactions, with good efficiency and

Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar, 388 120Gujarat, India. E-mail: soni\_b21@yahoo.co.in; Tel: +91 2692 226856 ext. 216 † Electronic supplementary information (ESI) available: SEM, TEM, EDS and FTIR data of Pd/TiO<sub>2</sub> catalyst is shown. The characterization of coupling products by GC–MS and <sup>1</sup>H and <sup>13</sup>C NMR spectra is shown. See DOI: 10.1039/ c3cy00602f

stereoselectivity. With this goal in mind, we have incorporated Pd into mesoporous  $TiO_2$  nanoparticles to catalyze various Heck reactions under sunlight. The idea behind selecting the titania support is the peculiar properties of its anatase phase which exhibits strong photocatalytic activity under sunlight and its potential use for environmental and biological remediation purposes.<sup>33–35</sup>

# 2. Results and discussion

The ordered mesoporous Pd/TiO<sub>2</sub> nanoparticles (NPs) were synthesized based on our earlier report using an Evaporation Induced Self Assembly (EISA) route.<sup>36</sup> In a departure from this procedure,  $Pd(OAc)_2$  was introduced in an initial sol for uniform distribution of Pd in the titania matrix. As the P123 [(PEO)<sub>20</sub>-(PPO)<sub>70</sub>-(PEO)<sub>20</sub>] block copolymer contains polyethylene oxide (PEO) units, which have the capability to reduce metal salts<sup>37-40</sup> to nanoparticles, Pd<sup>2+</sup> ions were reduced to  $Pd^{0}$  (Pd black) *in situ*. During the solvent evaporation, ~50% RH was maintained to obtain mesophase formation and at the end of two days a sticky material was obtained. In order to obtain photoactive mesoporous crystalline anatase TiO<sub>2</sub> the obtained material was calcined at 450 °C for 30 min at a heating rate of 2 °C min<sup>-1</sup>. After calcination the resultant material obtained was a free-flowing powder mesoporous in nature, which was subjected for structural and morphological characterization. The powder diffraction pattern (Fig. 1) of the Pd/TiO<sub>2</sub> NPs is analyzed, and from the Bragg reflections the anatase phase of titania was clearly identified, but no specific peaks were obtained for the Pd NPs. This might be due either to a low % Pd in the titania matrix or to merging of the characteristic peaks of Pd(0) nanoparticles which appear at ~39° (1 1 1) and ~47° (2 0 0) with the anatase titania peaks.40 The average particle size calculated using the Scherrer equation is 13.8 nm.

TEM analysis (Fig. 2) confirmed the generation of uniform spherical nanoparticles with an average diameter of  $\sim$ 15 nm and, as observed, the black dots with diameters of 6–7 nm



Fig. 2 TEM micrographs and DLS study (inset) or particle size distribution of Pd-doped titania mesoporous materials.

were of palladium NPs distributed uniformly on the titania surface. The particle size obtained from DLS measurements (inset of Fig. 2) is in the range of 12–15 nm. A similar kind of observation can be predicted from SEM measurement (Fig. 3) which shows the particle size in the range of 12–15 nm with a regular particle shape. The obtained particle sizes from TEM and DLS measurements are compatible with that acquired from XRD analysis. Energy dispersive spectroscopy (EDS) analysis (ESI,† S3) reveals the presence of 1.23 wt% of Pd along with Ti (47.71 wt%) and O (51.06 wt%), which proves the presence of Pd in the composites as well as in aggregates.

In order to obtain information regarding the surface area and porosity of the Pd/TiO<sub>2</sub> NPs, nitrogen adsorption–desorption isotherm measurements were carried out (Fig. 4). The result shows a type-IV isotherm with a large hysteresis indicating a 3D intersection network of porous structure and that capillary condensation of N<sub>2</sub> is occurring during the adsorption process. The specific surface area for Pd/TiO<sub>2</sub> was calculated according



Fig. 1 X-Ray diffraction analysis of Pd-doped titania mesoporous materials.



Fig. 3 SEM micrographs of Pd-doped titania mesoporous materials.

to the BET equation and was 107.27 m<sup>2</sup> g<sup>-1</sup> and the total pore volume was 0.0312 cm<sup>3</sup> g<sup>-1</sup> which corresponds to an average pore diameter (4V/A by BET) of 2.8 nm. The pore size distribution derived from the isotherm data using the Barrett–Joyner–Halenda (BJH) model was quite broad, with a maximum at 3.15 nm. The above measurements show that Pd/TiO<sub>2</sub> NPs are porous and have a large surface area; therefore, they can be a good candidate as a catalyst for numerous reactions.

The photocatalytic activity of the mesoporous Pd/TiO<sub>2</sub> catalyst was evaluated under sunlight for the Heck reaction of iodobenzene with styrene using Et<sub>3</sub>N as base and DMF (dimethylformamide) as solvent. The reaction was exposed to sunlight with a maximum light power ~30 mW cm<sup>-2</sup> for 6-7 days and the product formation was checked on each day with the help of GC-MS. In order to confirm whether the reaction is photochemical or thermal, the reaction was carried without irradiation of sunlight (by covering the flask with black paper) keeping the other reaction parameters constant (Scheme 1). All the reactions were performed three times maintaining the same reaction conditions (sunlight intensity may vary a little in the range of 30 mW cm<sup>-2</sup> ± 5 mW cm<sup>-2</sup>) to check the reproducibility of the reaction, and the results for coupling yield obtained were approximately the same obtained in the first run.

The result clearly shows that the present reaction is a photo-induced reaction as in the presence of sunlight the coupling product was found in 91% yield whereas in the absence of sunlight the reaction progress was very slow, giving 33% yield (Table 1, entry 1). The effect of  $TiO_2$  and  $Pd(OAc)_2$  as an individual catalyst for the same reaction under sunlight was also carried out and the result shows formation of the coupling product in low yield (Table 1, entry 2 and 3). This proves a synergistic effect of Pd and  $TiO_2$  (Pd/TiO<sub>2</sub>) NPs for the enhancement of coupling yields in heterogeneous fashion under sunlight which is also supported



Fig. 4  $N_2$  adsorption-desorption isotherms of Pd/TiO<sub>2</sub> and (b) the corresponding pore size distribution derived from the adsorption isotherm.



Scheme 1 Heck reaction compared under sunlight with open and black-coated flask.

Table 1 Test experiments for optimization of the Heck coupling reactions of iodobenzene and styrene<sup>a</sup>

Entry	Catalyst	%Yield under light <sup>b</sup>	%Yield under dark <sup><math>b</math></sup>
1	Pd/TiO <sub>2</sub>	91	33
2	TiO <sub>2</sub>	25	16
3	$Pd(OAc)_2$	43	28
4	Pd/TiO <sub>2</sub>	$42^c$	$< 10^d$

<sup>*a*</sup> Reaction conditions: aryl halides (1.28 mmol), alkenes (1.66 mmol), triethylamine (2.56 mmol), dodecane (40 mg, as internal standard), Pd/TiO<sub>2</sub> (0.5 wt% of Pd) and DMF (5 ml), for 3 days under sunlight. <sup>*b*</sup> % yields are the isolated yield and based on average results (reaction carried out thrice for reproducibility check). <sup>*c*</sup> Flask coated with black paper. <sup>*d*</sup> 7 days of reaction.

by the Pd leaching test. When the day temperature is at its highest in the afternoon, the Pd/TiO2 catalyst was separated from the reaction mixture and the reaction was allowed to proceed under similar conditions. We found that no further reaction was observed as no coupling product formation was observed (GC-MS), showing no evidence of Pd leaching into the products which was also confirmed by ICP-OES test (which showed 0.667 ppm of Pd in the reaction mass), providing evidence of TiO<sub>2</sub> acting as a good scaffold for Pd catalyst precursors. The ultimate conclusion that the reaction proceeds in a heterogeneous fashion is also supported by a plausible mechanism. The mechanism can be explained as follows: upon sunlight irradiation, electrons from titania are excited from the valence band into the unoccupied conduction band and positive holes in the valence band. These electrons from the conduction band can easily transfer to the Pd surface generating electron heterogeneity at the Pd/TiO<sub>2</sub> surface. Thus, it is reasonable to expect that under sunlight the Pd sites with the energetic electrons at the Pd/TiO2 surface will exhibit superior catalytic activity to that of palladium salt or TiO<sub>2</sub> alone. The most interesting thing to note here is the stereoselectivity of the reaction which shows formation of Z-stilbene in a major amount compared to E-stilbene which is contrary to the usual selectivity of the reaction. The formation of Z-stilbene might be due to photoisomerization which is studied by optimization of the same model reaction again over a period of time in the presence of sunlight. The catalytic photoisomerization of cis-/trans-stilbene and derivatives has previously been very well studied which makes our interpretation even stronger.24,26-29 It is very well reported that the photochemical isomerization of arylethenes (stilbene derivatives) usually takes place in the

excited state through rotation around the C=C double bond. For instance, highly branched stilbene dendrimers with molecular weights of over 6000 underwent E-Z isomerization in less than 10 ns, the lifetime of the excited singlet state.<sup>41,42</sup> Analysis of first two days' results shows formation of both the isomers in moderate yield with the E-isomer in excess (Fig. 5). With increasing the time of sunlight exposure by three days, formation of the Z-isomer eventually increased which is, as said earlier, due to photochemical isomerization of stilbene-like compounds when exposed to light. After that a sudden fall in percentage vield of the E-isomer and increase in the Z-isomer was obtained, which decreases a little on day 4. A reverse trend again was observed on day 5 as the ratio of the E-isomer increases and Z-isomer decreases. A maximum of 72% coupling yield was obtained at day 3 for the Z-isomer and 63% yield of the E-isomer on day 5. The possible mechanism for the photoisomerization can be explained by the double-bond-shift of stilbene over Pd/TiO<sub>2</sub> (Fig. 6) which follows the same mechanistic pathway earlier reported by Hashimoto et al. for the photoisomerization of 1-butene over Pd-loaded TiO2.43

As the reaction occurs on the surface of the Pd/TiO<sub>2</sub>, stilbene produced will be adsorbed on the surface and lead to the formation of stilbene carbenium ion by abstraction of hydride. The photogenerated electrons from the titania surface transform to Pd particles under the irradiation of sunlight followed by addition of hydride to the stilbene carbenium ion. These photogenerated electrons and holes finally recombine after addition of hydride to the stilbene carbenium ion, resulting in the formation of the stilbene isomer.<sup>33</sup> The formation of *E*- and *Z*-isomers using Pd/TiO<sub>2</sub> is very selective and proceeds in a controlled manner under sunlight. Depending upon the requirement, one can have time-dependent selection of the desired isomeric product. With these results in hand, we carried out the Heck coupling reaction of various substrates by photocatalysis (Table 2). A variety of aryl halides reacts with various alkenes such as acrylates and styrene, to give the required products with good to excellent yields. Interestingly, the ability of Pd/TiO<sub>2</sub> to promote coupling reactions of different alkenes with a variety of



Fig. 5 Formation of E/Z isomers with the exposure of sunlight.



Fig. 6 Possible mechanism for E/Z photoisomerization in the presence of Pd/TiO<sub>2</sub>.

 Table 2
 The Heck coupling reactions of aryl halides with alkenes<sup>a</sup>

R1-	X + R2	Pd/TiO <sub>2</sub> (0.5wt? DMF, Et <sub>3</sub> N, Sunlight	$\frac{6}{3 \text{ days}} R_1$	Cis-/Trans-
No.	R <sub>1</sub>	$R_2$	Х	Yield <sup>b</sup> $(E/Z)^c$
1	-H	$-C_6H_5$	Ι	94 (22:78)
2	-OCH <sub>3</sub>	$-C_6H_5$	Ι	90 (25:75)
3	-COOH	$-C_6H_5$	Ι	92 (18:82)
4	-H	$-C_6H_5$	Br	80 (20:80)
5	-COOH	$-C_6H_5$	Br	77 (24:76)
6	-H	$-CO_2C_4H_9-t$	Br	76 (21:79)
7	-H	$-CO_2C_4H_9-t$	Ι	90 (30:70)
8	-COOH	$-CO_2C_4H_9-t$	Ι	89 (21:79)
9	$-OCH_3$	$-\mathrm{CO}_{2}\mathrm{C}_{4}\mathrm{H}_{9}$ - $t$	Ι	85 (27:73)

<sup>*a*</sup> Reaction conditions – aryl halides (1.28 mmol), alkenes (1.66 mmol), triethylamine (2.56 mmol), dodecane (40 mg, as internal standard), Pd/TiO<sub>2</sub> (0.5 wt% of Pd) and DMF (5 ml) under sunlight for 3 days. <sup>*b*</sup> Isolated yields. <sup>*c*</sup> Isomer ratio determined by NMR.

activated and non-activated aryl iodides is satisfactory. Aryl iodides possessing either an electron-withdrawing (-COOH) or electron-releasing (-OCH<sub>3</sub>) substituent on the benzene ring efficiently cross-coupled with styrene and acrylates, regardless of the substituent position to afford the products in good to excellent yields. The reactivity of iodides is higher than bromo-derivatives because of their role of photochemical cleavage of the Ar-I bond for the S<sub>RN</sub>1-type substitution reaction assisted by sunlight. Apparently Pd/TiO<sub>2</sub> results in a much higher catalytic activity which can be observed from the high turnover frequency (TOF =  $2.89 \text{ h}^{-1}$ ) of the catalyst (ESI,† Table S1). The stilbene or cinnamate derivatives formed were found to have a considerable amount of the Z-isomer in most of the cases. This method thus proves to be a versatile one for the synthesis of olefins with Z-stereochemistry.

As the catalyst is heterogeneous in nature, it can easily be recovered after work up. The recovered Pd/TiO<sub>2</sub> was washed with diethyl ether and dried under vacuum at 80 °C and further used for the next run. The time profile for the model reaction using recovered catalyst does not vary much in days. Pd/TiO<sub>2</sub> was effectively used for 3 runs showing the same trend (*i.e.* formation of the *Z*-isomer) with a little loss in catalytic activity. The recovered Pd/TiO<sub>2</sub> was characterized by FTIR and the Pd content was measured using EDS analysis which shows 1.19 wt% of Pd, signifying that no major loss of Pd occurs during the reaction.

# 3. Conclusions

In the study, palladium metal-doped titanium dioxide (Pd/TiO<sub>2</sub>) has been successfully prepared in a stable form and tested as a heterogeneous photocatalyst for the Heck reaction. The synthesized Pd/TiO<sub>2</sub> was characterized by XRD, BET, SEM-EDS, TEM, and DLS techniques. From these various analyses the particle size obtained for the Pd/TiO<sub>2</sub> mesoporous nanomaterials is in the range of 12–15 nm. Mesoporous Pd/TiO<sub>2</sub> exhibited high activity and stereoselectivity for the Heck reaction, showing photoisomerization under sunlight owing to the synergistic effect of Pd and TiO<sub>2</sub> both. The synthetic reaction conditions here are environmentally benign, providing a facility for the time-dependent selectivity of E/Z-isomer under sunlight at ambient conditions with good recyclability.

### 4. Experimental section

#### 4.1 Materials and method

The block co-polymer surfactant (P123, PEO-PPO-PEO MW-5750 g mol<sup>-1</sup>), Ti(OC(CH<sub>3</sub>)<sub>3</sub>)<sub>4</sub>, Pd(OAc)<sub>2</sub> and the starting substrates for the Heck coupling were purchased from Sigma-Aldrich, India. HCl and ethanol used were of analytical grade laboratory reagent. The synthesized Pd-doped nanoparticles were characterized for their structure and texture by XRD, BET, TEM, SEM, EDS and DLS. The XRD measurements were performed using a Rigaku D/max 2500 X-ray Diffractometer. Diffraction patterns were recorded with Cu K $\alpha$  radiation (40 kV, 30 mA) over a 2 $\theta$  range of 3–80 °C at a scan rate of 2° min<sup>-1</sup>. The BET surface area, average pore volume, and average pore diameter were measured by physisorption of N2. The isotherms were elaborated according to the BET (Brunauer, Emmett and Teller) method for surface area calculation, and pore size distribution curves derived from the desorption branches for the porous materials with BJH (Barrett-Joyner-Halenda) methods using a Micromeritics Gemini 2375 Surface area analyzer. The TEM measurements were conducted by using a Philips Tecnai 20 (Holland) transmission electron microscope at an acceleration voltage of 200 kV with a W emitter and LaB6 electron source. A single drop of the sample was deposited on a carbon-coated copper grid and dried at room temperature under atmospheric pressure. The SEM observations were carried out using a JSM-7600F Field Emission Gun-Scanning Electron Microscope (FEG-SEM) at an acceleration voltage of 0.1 to 30 kV. The DLS measurements were carried out using a Malvern instrument, Zetasizer ZS-90 (for nanosizer) Particle size analyzer. The ICP analysis was carried out using an Atomic Emission Spectrometer Perkin Elmer Optima 3300 RL with SCD detector; detection limit: up to ppb level. The IR measurements of Pd/TiO<sub>2</sub> were carried out using an ABB FTIR spectrophotometer (Canada). All the coupling reactions were performed in a container to maintain a constant temperature and kept above a mirror to utilize the reflected sunrays. Reactions were monitored by thin layer chromatography using 0.25 mm E. Merck silica gel-coated glass plates (60F-254) with UV light to visualize the course of reaction and GC-MS (GC-Mass Spectrometer, Perkin Elmer, Auto system XL, GC+). The coupling products were analyzed by <sup>1</sup>H and <sup>13</sup>C NMR (400 MHz Bruker Scientific, Switzerland) spectroscopic techniques.

#### 4.2 Synthesis of Pd/TiO<sub>2</sub> catalyst

Ordered mesoporous Pd/TiO2 materials were synthesized through a simple Evaporation Induced Self Assembly process in the presence of triblock polymer P123 as structure directing agent. To homogeneously distribute Pd nanoparticles into the titania framework, we utilized a multicomponent assembly approach where the surfactant, titania and Pd were assembled in a one-step process. In particular, HCl (37%) (6.4 g, 63 mmol) was added dropwise to Ti(iPrO)<sub>4</sub> (10.24 g, 35 mmol) in an ice-bath at 0 °C under stirring and after completion of addition the reaction mass was allowed to stir further for 3 h at room temperature. On the other hand, the calculated amount of Pd(OAc)2 (30 mg, 0.133 mmol) was added to P123 ethanolic solution (2 g P123 in 25 g ethanol) and stirred vigorously. The dispersion formed was added to the Ti/HCl mixture and further stirred for 3 h for complete homogenization before it was then transferred into a Petri dish for ageing. Ethanol was subsequently evaporated at room temperature at a relative humidity of 60% which was maintained for 24 h. This was subsequently dried and kept in an oven at 60 °C and for an additional 24 h for ageing. The as-made mesostructured hybrids were calcined at 450 °C in air for 30 min at a heating rate of 2 °C min<sup>-1</sup> to remove surfactant and to obtain highly ordered mesostructured Pd/TiO<sub>2</sub>.

#### 4.3 General procedure for the Heck reactions

Aryl halides (1.28 mmol), alkenes (1.66 mmol), triethylamine (2.56 mmol), dodecane (40 mg, as internal standard), Pd/TiO<sub>2</sub> (0.5 wt% of Pd) and DMF (5 ml) were taken in an Erlenmeyer flask. The mixture was kept under sunlight for 3-7 days. After completion of the reaction (confirmed by TLC analysis and GC-MS analysis), the mixture was filtered through a short pad of Celite to remove the catalyst. To the filtrate, diethyl ether and water were added and the layers were separated. The aqueous layer was extracted twice with diethyl ether and the combined organic layers were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated in vacuo to get the desired product. All the coupling products have been previously reported and their identities were confirmed by comparison of their <sup>1</sup>H, <sup>13</sup>C NMR and GC-MS spectral data with the values of authentic samples/earlier reports. (Note: Complete care has been taken to maintain the light intensity (maximum to minimum) between 25 and 30 mW cm<sup>-2</sup> for the reaction carried out during inter-intra days.) The filtered

off solid catalyst was washed with acetone and dried under vacuum after each cycle, and then reused for the next reaction.

#### 4.4 Determination of Pd content in solution (Pd leaching test)

For the determination of the Pd content in solution, the mixture containing the solid catalyst was allowed to stand for half a day allowing it to reach the temperature maximum of the day after which 5 mL of the reaction mixture was hot filtered into a 10-mL round-bottom flask. After careful evaporation of the liquids, the sample was treated with sulfuric acid and nitric acid, diluted, filtered, and analyzed by flame AAS. For better accuracy, multiple analyses were carried out for each sample.

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# Notes and references

- 1 R. F. Heck and J. P. Nolly, J. Org. Chem., 1972, 37, 2320-2322.
- 2 M. Shibasaki, E. M. Vogl and T. Ohshima, *Adv. Synth. Catal.*, 2004, **346**, 1533–1552.
- 3 C. J. Seechurn, M. O. Kitching, T. J. Colacot and V. Snieckus, *Angew. Chem., Int. Ed.*, 2012, 51, 5062–5085.
- 4 G. T. Crisp, Chem. Soc. Rev., 1998, 27, 427-436.
- 5 L. Xua and Z. Lin, Chem. Soc. Rev., 2010, 39, 1692-1705.
- 6 V. Farina, Adv. Synth. Catal., 2004, 346, 1553-1582.
- 7 C. C. J. Seechurn, M. O. Kitching, T. J. Colacot and V. Snieckus, Angew. Chem., Int. Ed., 2012, 51, 5062–5085.
- 8 F. Y. Zhao, B. M. Bhanage, M. Shirai and M. Arai, J. Mol. Catal. A: Chem., 1999, 142, 383–388.
- 9 M. T. Reetz and J. G. de Vries, Chem. Commun., 2004, 1559–1563.
- 10 D. J. Hamilton, Science, 2003, 299, 1702-1706.
- 11 V. Polshettiwar, C. Len and A. Fihri, *Coord. Chem. Rev.*, 2009, 253, 2599–2626.
- 12 L. Yin and J. Liebscher, Chem. Rev., 2007, 107, 133-173.
- 13 N. T. S. Phan, M. Van Der Sluys and C. W. Jones, Adv. Synth. Catal., 2006, 348, 609–679 and reference cited therein.
- 14 P. T. Anastas and J. C. Warner, in *Green Chemistry : Theory* and *Practice*, Oxford University Press, New York, 1998, p. 30.
- 15 E. Paterno, *Gazz. Chim. Ital.*, 1909, 39, 237–250; its English translation: M. D'Auria ed. Emanuele Paterno, *Synthesis in organic chemistry by means of light*, Societa Chimica, Italia, Rome, 2009.
- 16 G. Ciamician, Science, 1912, 36, 385-394.
- 17 G. Ciamician and P. Silber, Chem. Ber., 1908, 41, 1928-1935.

- 18 J. M. R. Narayanam and C. R. J. Stephenson, *Chem. Soc. Rev.*, 2011, 40, 102–113.
- 19 J. Du and T. P. Yoon, J. Am. Chem. Soc., 2009, 131, 14604-14606.
- 20 M. A. Ischay, Z. Lu and T. P. Yoon, J. Am. Chem. Soc., 2010, 132, 8572–8574.
- 21 T. Wu, L.-H. Weng and G.-X. Jin, *Chem. Commun.*, 2012, 48, 4435–4437 and references cited therein for recent light-induced reactions.
- 22 M. A. Fredricks and K. Kohler, Catal. Lett., 2009, 133, 23-26.
- 23 M. A. Fredricks, M. Drees and K. Kohler, *ChemCatChem*, 2010, 2, 1467–1476.
- 24 A. R. Chaudhary and A. V. Bedekar, *Tetrahedron Lett.*, 2012, 53, 6100–6103.
- 25 S. B. Waghmode, S. S. Arbuj and B. N. Wani, *New J. Chem.*, 2013, 37, 2911–2916.
- 26 M. Sumitani and K. Yoshihara, Bull. Chem. Soc. Jpn., 1982, 55, 85–89.
- 27 J. Quenneville and T. J. Martinez, J. Phys. Chem. A, 2003, 107, 829–837.
- 28 D. Tsvelikhovsky, D. Pessing, D. Avnir and J. Blum, Adv. Synth. Catal., 2008, 350, 2856–2858.
- 29 K. Ohara, Y. Inokuma and M. Fujita, *Angew. Chem., Int. Ed.*, 2010, 49, 5507–5509.
- 30 M. Inoue, T. Takahashi, H. Furuyama and M. Hirama, *Synlett*, 2006, **18**, 3037–3040.
- 31 D. Meltzer, D. Avnir, M. Fanun, V. Gutkin, I. Popov, R. Schomaker, M. Schwarze and J. Blum, *J. Mol. Catal. A: Chem.*, 2011, 335, 8–13.
- 32 D. Simoni, F. P. Invidiata, M. Eleopra, P. Marchetti, R. Rondanin, R. Baruchello, G. Grisolia, A. Tripathi, G. E. Kellogg, D. Durrant and R. M. Lee, *Bioorg. Med. Chem.*, 2009, 17, 512–522.
- 33 A. L. Linsebigler, G. Lu and J. T. Yates Jr., Chem. Rev., 1995, 95, 735-758.
- 34 X. Chen and S. S. Mao, Chem. Rev., 2007, 107, 2891-2959.
- 35 S. S. Soni, G. S. Dave, M. J. Henderson and A. Gibaud, *Thin Solid Films*, 2013, 531, 559–565 and references cited therein.
- 36 S. S. Soni, M. J. Henderson, J.-F. Bardeau and A. Gibaud, *Adv. Mater.*, 2008, 20, 1493–1498.
- 37 T. Sakai and P. Alexandridis, Langmuir, 2005, 21, 8019-8025.
- 38 D. Ray, V. K. Aswal and J. Kohlbrecher, *Langmuir*, 2001, 27, 4048–4056.
- 39 S. S. Soni, R. L. Vekariya and V. K. Aswal, RSC Adv., 2013, 3, 8398–8406.
- 40 Y. Piao, Y. Jang, M. Shokouhimehr, I. S. Lee and T. Hyeon, *Small*, 2007, 3, 255–260.
- 41 K. Ferre-Filmon, L. Delaude, A. Demonceau and A. F. Noels, *Coord. Chem. Rev.*, 2004, 248, 2323–2336.
- 42 C. Dugave and L. Demange, *Chem. Rev.*, 2003, **103**, 2475–2532.
- 43 K. Hashimoto, Y. Masuda and H. Kominami, *ACS Catal.*, 2013, 3, 1349–1355.

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