

Study of TiO₂ nanoparticle phase alteration and its catalytic effect on the chemoselective *N*-sulphonylation of amines and urazoles

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Abstract. Anatase and rutile are the two major crystalline phases of TiO₂. Heat treatment can change crystal structure and physical properties of TiO₂ nanoparticles. The effect of particles size on anatase–rutile phase transformation has been studied for the *N*-sulphonylation of amines and urazoles both under the conventional and ultrasound irradiation conditions. The main advantages allocated to this method are chemoselectivity, reduced reaction times, high yield, non-solvent green conditions and easy procedure. The catalyst can be easily recovered simply by filtration and reused with no significant loss in its reactivity.

Keywords. Amine; urazole; sulphonamide; phase transformation; TiO₂P25-900; ultrasound irradiation; solvent-free.

1. Introduction

Sulphonylation of amines has emerged as an important reaction in synthetic organic chemistry.¹ Sulphonamide derivatives belong to the most important class of drug molecules. A wide range of biological activities displayed by sulphonamides include many drugs in clinical medicine as antibacterial, diuretics, anticonvulsants, hypoglycaemic and HIV protease inhibitors.^{2a} In addition, the sulphonamide moiety has been used to protect nitrogen in amines.^{2b–c} Another important feature of sulphonamides is their ability to act as inhibitors of dihydropteroate synthetase.³

Several methods have been reviewed in literature for the synthesis of sulphonamides.^{4–7} The most used method for the synthesis of sulphonamides involves the reaction of sulphonyl chlorides with excess ammonia.^{4a} However, some of these procedures suffer from certain disadvantages such as environmentally unpleasant use of huge organic solvents, high temperature and/or long reaction times, and low yield of the products, especially for less reactive anilines. For sterically hindered primary amines carrying electron-withdrawing substituent, bis-sulphonylation is a common side reaction, which necessitates a later mono desulphonylation step.⁵ Indium metal has been used for the catalytic sulphonylation of amines and alcohols; however, it

requires a longer reaction time and stringent reaction conditions.⁶

Meshram and Patil⁷ have recently reported the CuO-catalysed *N*-sulphonylation of amines in CH₃CN at room temperature. Although *O*- or *N*-sulphonylation reactions were successful under these conditions, no chemoselectivity was observed. Also, in this method, a tedious chromatographic separation is necessary to obtain pure products. Therefore, development of more convenient synthetic approaches to sulphonamides still appears as challenging in research.

In recent years, there has been a tremendous upsurge of interest in various chemical transformations performed under heterogeneous catalysis. Moreover, by using inexpensive and non-corrosive heterogeneous catalysts, chemical transformations occur, especially for industrial processes, with higher efficiency and purity of the products, and easier work-up, that create economical and ecological advantages.^{8,9} Among heterogeneous catalysts, nano-crystalline metal oxides have attracted much attention due to their unusual magnetic, physical and surface chemical and catalytic properties. These materials present numerous surface sites with enhanced surface reactivity such as crystal corners, edges or ion vacancies.¹⁰

As an efficient and versatile catalyst, nano-structured TiO₂ has been the focus of considerable research interests in recent years. Its small size and large specific surface area allow for certain unique and unusual physico-chemical properties.¹¹ Titanium dioxide is a

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prominent material for various kinds of industrial applications related to catalysis, for e.g., in the selective reduction of nitrogen oxides (NO_x) in stationary sources, photocatalysis for pollutant elimination or organic synthesis, photovoltaic devices, sensors, and paints.^{11c-e} TiO₂ include three crystalline phases namely, anatase, rutile and brookite.^{12a-c} Among the three well-known crystalline types, anatase TiO₂ attracts considerable interest due to its excellent photocatalytic behaviour.^{12b}

On the other hand, ultrasound in so-called 'sonochemistry' is a versatile and challenging technique that has progressively been used in organic synthesis over the last few decades.¹³ In an irradiated liquid, collapse of bubbles caused by cavitations produces intense local heating and high pressures with very short lifetimes. Bubble collapse in liquids produces enormous amounts of energy from the conversion of kinetic energy of the liquid motion into heating the contents of the bubble. Compression of the bubbles during cavitations is more rapid than thermal transport, which generates a short-lived localized hot spot. The hot spot has an equivalent temperature of roughly 5000°C, a pressure of about 2000 atmospheres, a lifetime considerably less than a microsecond and heating and cooling rates above 10 billion°C per second.^{13c-e} A large number of organic reactions can be carried out in higher yields, shorter reaction times and milder conditions under ultrasonication. Compared with traditional methods, ultrasonication is a more convenient and easily controlled technique.¹³

The aim of this study is to investigate the effects of phase transformation and crystallite sizes of nano-TiO₂ on the synthesis of sulphonamides. Herein, we report a new, simple and effective procedure for the green synthesis of sulphonamides. In this approach, the TiO₂P25-900 type of catalyst has been explored as an efficient and recyclable heterogeneous catalyst to affect the sulphonylation of amines and urazoles with sulphonyl chlorides both under conventional and ultrasound irradiation conditions at room temperature (scheme 1). TiO₂P25-900 appears as an eco-friendly catalyst which can be safely handled and disposed without posing any environmental problem.

2. Experimental

2.1 General

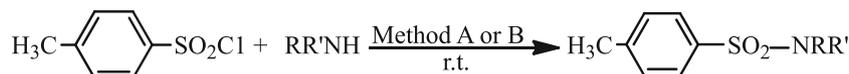
All reagents were purchased from Merck and Aldrich chemical companies and used without further purification. Products were characterized by Fourier Transform Infrared (FT-IR), ¹H Nuclear Magnetic Resonance (NMR) and melting points. The NMR spectra were recorded on a Bruker Avance DRX 90 MHz instrument in CDCl₃. Chemical shifts (δ) are reported in ppm relative to the Tetramethylsilane (TMS) as internal standard and *J* values are given in Hz. FT-IR (KBr) spectra were recorded on a Perkin-Elmer 781 spectrophotometer. Ultrasonication was performed in a PARSONIC 2600s ultrasound with a frequency of 28 kHz and an output power of 50 W (built-in heating, 20–70°C thermostatically adjustable). Melting points were taken in open capillary tubes with a BUCHI 510 melting point apparatus and were uncorrected. TLC was performed on silica gel polygram SIL G/UV 254 plates.

2.2 Preparation of TiO₂P25-*T*

Nano-TiO₂ was purchased as a commercial product in powder form (Degussa Co. P25) with a particle size of about 30 nm.^{12c} TiO₂P25-900 was prepared according to literature. TiO₂ was heated in a furnace in the range of 400–900°C for 2 h and then was cooled slowly.^{12c} The obtained samples were named as TiO₂P25-*T*, where *T* is treatment temperature. Phase transformation from anatase to rutile was studied using X-ray Powder Diffraction (XRD) and the change in particle size was investigated by Transmission Electron Microscopy (TEM).^{12c}

2.3 General experimental procedure for *N*-sulphonylation of amines or urazoles

Method A: To a mixture of amine or urazoles (1.0 mmol) and 4-toluenesulphonyl chloride (1.0 mmol) was added TiO₂P25-900 (0.07 g). The resulting mixture was stirred at room temperature for an appropriate



Method A: TiO₂P25-900, solvent-free

Method B: TiO₂P25-900, EtOH solvent, ultrasound irradiation

Scheme 1. *N*-sulphonylation of amines and urazoles using TiO₂P25-900.

Table 1. Sulfonylation of amines and urazoles under conventional or ultrasound irradiation conditions at room temperature.^a

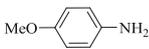
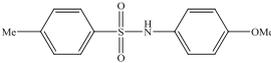
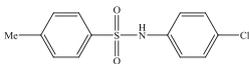
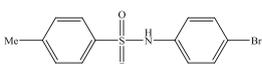
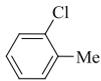
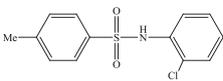
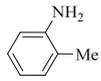
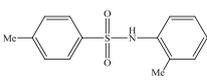
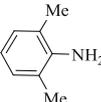
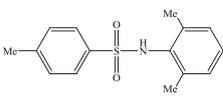
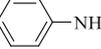
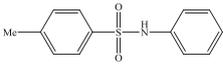
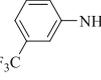
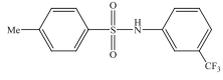
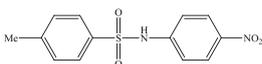
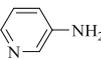
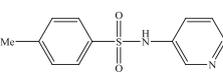
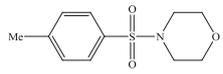
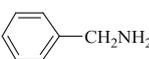
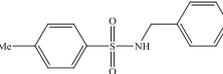
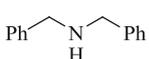
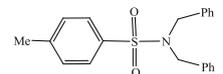
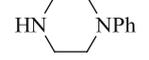
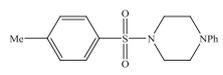
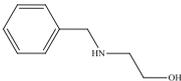
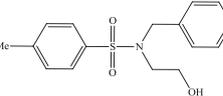
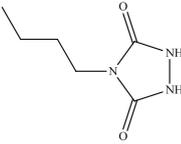
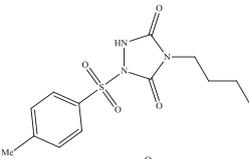
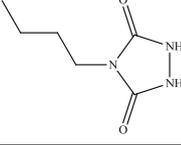
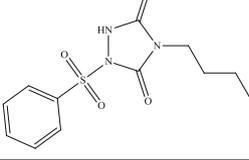
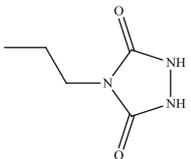
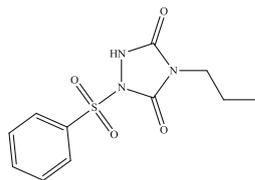
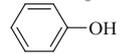
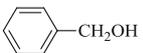
Entry	Substrate	Product	Time (min)	Yield (%) ^b	Ref.
1			3 ^c , 2 ^d	93 ^c , 96 ^d	7
2			4 ^c , 2 ^d	96 ^c , 98 ^d	7,14,15
3			18 ^c , 10 ^d	94 ^c , 96 ^d	7,14
4			15 ^c , 8 ^d	94 ^c , 98 ^d	14
5			35 ^c , 18 ^d	95 ^c , 98 ^d	15
6			15 ^c , 5 ^d	94 ^c , 97 ^d	16
7			15 ^c , 5 ^d	97 ^c , 98 ^d	15,17
8			8 ^c , 3 ^d	93 ^c , 98 ^d	18
9			90 ^c , 40 ^d	92 ^c , 96 ^d	15
10			8 ^c , 3 ^d	94 ^c , 96 ^d	19
11			2 ^c	48 ^c	7
12			20 ^c , 10 ^d	94 ^c , 98 ^d	15
13			30 ^c , 15 ^d	94 ^c , 96 ^d	20
14			7 ^c , 3 ^d	96 ^c , 98 ^d	14
15			150 ^d	93 ^d	ChemSpider ID: 692706
16			50 ^c , 35 ^d	94 ^c , 97 ^d	21
17			50 ^c , 35 ^d	92 ^c , 96 ^d	21

Table 1. (Continued).

Entry	Substrate	Product	Time (min)	Yield (%) ^b	Ref.
18			30 ^c , 35 ^d	91 ^c , 96 ^d	21
19		No reaction	24 h	–	–
20		No reaction	24 h	–	–

^aConditions: amine (1.0 mmol), TsCl (1.0 mmol), room temperature

^bIsolated yield

^cMethod A: TiO₂P25-900 (0.07 g), solvent-free

^dMethod B: TiO₂P25-900 (0.07 g), EtOH (4 mL), ultrasound irradiation

time (table 1). After completion of the reaction as monitored by TLC analysis, EtOAc (10 mL) was added to the reaction mixture followed by centrifugation to separate the catalyst. Then, the organic layer was evaporated under reduced pressure to obtain pure products. All the products are known and the spectral data and melting points were identical to those reported in literature (table 1).^{7,14–21}

Method B: To a mixture of amine or urazoles (1.0 mmol) and 4-toluenesulphonyl chloride (1.0 mmol) in EtOH (4 mL) was added TiO₂P25-900 (0.07 g). Then, the resulting mixture was sonicated at room temperature for appropriate time (table 1). After completion of the reaction, as monitored by TLC analysis, the reaction mixture was filtered and the filtrate was evaporated under reduced pressure to leave the pure products (table 1). All the products are known compounds and the spectral data and melting points were identical to those reported in literature.^{7,14–21}

3. Results and discussion

Crystal structure and physical properties of TiO₂ nano-particles change during heat treatment process. The phase of nano-particles including the reference P25 and the heat-treated samples were characterized by XRD analysis.^{12c} TiO₂ nano-particle, made by Degussa Company, is a combination of anatase and rutile phases. The reported average size of its particles is 30 nm and the phase ratio of anatase to rutile is 80–20. These data are in good agreement with XRD analysis.

As previously reported,^{12c} the TiO₂-Degussa was heated in a furnace at different temperatures ranging

from 400° to 900°C for 2 h. The crystalline pattern of TiO₂ has two characteristic peaks appearing at $2\theta = 25.28^\circ$ and $2\theta = 27.4^\circ$ angles that correspond to anatase (1 0 1) and rutile (1 1 0) crystal phases, respectively. Clearly, heating the TiO₂-Degussa nano-particles up to 600°C did not bring about any phase transition. However, by heating these nano-particles in the range of 700–900°C, the anatase phase percentage decreases, while the rutile phase percentage increases. The XRD pattern shows that, at 900°C, the TiO₂ phase is entirely rutile. As clear from TEM images, heating the TiO₂P25 from room temperature to 900°C results in increase of its size from 30 to 300 nm. Hence, heating TiO₂ nano-particles at different temperatures causes both phase transition and size growth.^{12c}

As mentioned above, phase transformation of TiO₂ nano-particles occurs at temperatures higher than 600°C. Thus, we were prompted to study the behaviour of different phases of TiO₂ nano-particles from room temperature to 900°C in *N*-sulphonylation of amines.

Initially, we chose to study the reaction between aniline and 4-toluenesulphonyl chloride as the model reaction. No reaction was observed when a mixture of aniline (1 mmol) and 4-toluenesulphonyl chloride (1 mmol) was stirred for 4 h under catalyst-free condition at room temperature (entry 9). However, addition of a catalytic amount of TiO₂ to this mixture has shown considerable improvement in the rate and the yield of the reaction. To evaluate the efficiency of various types of TiO₂ in the *N*-sulphonylation reaction, the activity of different catalytic systems was investigated in the model reaction. As shown in table 2, TiO₂P25-900 (pure rutile phase) appeared to be a better catalyst in the synthesis of sulphonamides. The effect of catalyst loading on the model *N*-sulphonylation reaction

Table 2. Effect of catalyst loading on the sulphonylation of aniline under solvent-free conditions at room temperature.^a

Entry	TiO ₂ type (g)	Time (min)	Yield (%) ^b
1	TiO ₂ Degussa P25 (0.07)	40	80
2	TiO ₂ P25-700 (0.07)	37	82
3	TiO ₂ P25-800 (0.07)	30	84
4	TiO ₂ P25-900 (0.03)	45	83
5	TiO ₂ P25-900 (0.04)	42	85
6	TiO ₂ P25-900 (0.05)	35	90
7	TiO ₂ P25-900 (0.07)	20	97
8	TiO ₂ P25-900 (0.08)	20	97
9	No catalyst	4 h	0

^aConditions: amine (1.0 mmol), TsCl (1.0 mmol), room temperature

^bIsolated yield

was also investigated by varying the amount of the TiO₂P25-900 (table 2). As seen in table 2, with increase in amount of catalyst from 0.03 to 0.07 g, reaction time was reduced from 49 to 20 min and yield was improved accordingly from 83% to 97%. No significant improvement in the yield was observed on using higher amounts of the catalyst (entry 8).

Under optimum conditions (0.07 g catalyst, solvent-free, room temperature), we examined the scope of this reaction with a series of amines (method A). According to the results summarized in table 1, all the primary and secondary amines reacted smoothly to afford the corresponding sulphonamides in good to excellent yields although relatively longer reaction times are required for secondary amines. Accordingly, when a mixture of benzylamine and dibenzylamine in equimolar amounts was treated with 4-toluenesulphonyl chloride under optimized conditions, only benzylamine was converted with excellent chemoselectivity while dibenzylamine remained almost intact (scheme 2). Similarly, anilines substituted either with electron-donating or electron-withdrawing groups react efficiently to produce the respective *N*-sulphonamides in excellent yields. As seen in table 1, morpholine and *N*-phenylpiperazine were also conveniently converted to their corresponding sulphonamides in excellent yields (entries 11 and 14).

Interestingly, it was observed that the *N*-sulphonylation of urazoles proceeds in high yields and only mono-sulphonylated products were produced (table 1, entries 16–18).

As we explained earlier, heating nano-TiO₂-Degussa can result in increase of the rutile phase to anatase phase ratio and complete change of anatase phase into rutile phase occurs at 1000°C. Such a phase transfer causes enhancement of physical adsorptivity of nano-TiO₂-900 since its active sites are increased as a result of phase change. This can also explain the improved capability of nano-TiO₂-Degussa in its rutile phase for strongly adsorbing amine substrates such as urazoles. This can be understood as a combination of lower inductive withdrawal by nitrogen and stronger electron release from it. The reason why this catalyst exhibits no catalytic effect towards alcohols (entries 19, 20), can be attributed to its insufficient adsorption power towards alcohols combined with higher inductive withdrawal and weaker electron release by oxygen which make alcohols weaker nucleophiles for adsorption by this catalyst.

Previously reported method employing CuO nanoparticles as catalyst in *N*-sulphonylation of amines,⁷ suffers from drawbacks including use of MeCN as a relatively volatile and non-green solvent, harsh reaction conditions, long reaction times and non-chemoselective. Also, this method was found not applicable for the *N*-sulphonylation of hindered amines such as dibenzylamine and no chemoselectivity was exhibited. In contrast, as seen in the table 1, the present method proved suitable for *N*-sulphonylation of hindered amines, e.g., dibenzylamine (entry 13), and provided high chemoselectivity in *N*-sulphonylation of amines in the presence of other functional groups such as hydroxyl group (entry 15).

Superiority of TiO₂P25-900 as a catalyst to other previously reported catalysts such as CuO, ZnO, SiO₂ and CsF–Celite was substantiated in sulphonylation of various amines (table 3). Results summarized in table 3 indicate that all the reactions catalysed by TiO₂P25-900 proceeded with higher yields and lower reaction times compared with reactions catalysed by other previously reported methods.

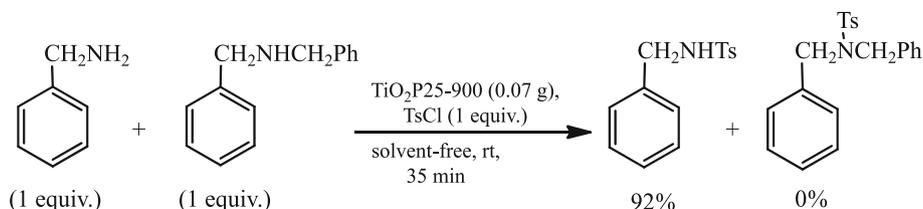
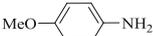
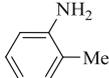
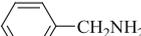
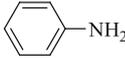
**Scheme 2.** Chemoselective *N*-sulphonylation of amines.

Table 3. Comparison of different methods in *N*-sulphonylation of amines with present methods A and B.

Entry	Substrate	Method	Conditions	Time	Yield(%)	Ref.
1		CuO	CH ₃ CN, rt	60 min	92	7
		CuO	CH ₃ CN, reflux	30 min	90	7
		CuO	CH ₂ Cl ₂ , reflux	120 min	85	7
		ZnO	CH ₃ CN, reflux	120 min	85	7
		Silica gel	CH ₃ CN, reflux	480 min	30	7
		Silica gel	Solvent-free, rt	10 min	97	15
		TiO ₂ P25-900	Method A	3 min	93	Present
2		TiO ₂ P25-900	Method B	2 min	96	Present
		CuO	CH ₃ CN, rt	4 h	82	7
		Silica gel	Solvent-free, rt	40 min	95	15
		TiO ₂ P25-900	Method A	35 min	95	Present
3		TiO ₂ P25-900	Method B	18 min	98	Present
		CuO	CH ₃ CN, rt	1.5 h	84	7
		Catalyst-free	H ₂ O, rt	2 h	98	14
		Silica gel	Solvent-free, rt	30 min	96	15
		TiO ₂ P25-900	Method A	4 min	96	Present
4		TiO ₂ P25-900	Method B	2 min	98	Present
		CuO	CH ₃ CN, rt	1.5 h	86	7
		Catalyst-free	H ₂ O, rt	25 min	95	14
		TiO ₂ P25-900	Method A	18 min	94	Present
5		TiO ₂ P25-900	Method B	10 min	96	Present
		Catalyst-free	H ₂ O, rt	25 min	89	14
		Silica gel	Solvent-free, rt	60 min	96	15
		TiO ₂ P25-900	Method A	20 min	94	Present
6		TiO ₂ P25-900	Method B	10 min	98	Present
		CuO	CH ₃ CN, rt	1.5 h	92	7
		Catalyst-free	H ₂ O, rt	30 min	92	14
		TCT, ^b NEt ₃ ^{c,d}	Acetone, reflux	10 min	80	3b
7		TiO ₂ P25-900	Method A	2 min	98	Present
		Catalyst-free	H ₂ O, rt	30 min	90	14
		TiO ₂ P25-900	Method A	7 min	96	Present
		TiO ₂ P25-900	Method B	3 min	98	Present
8		CuO	CH ₃ CN, rt	2 h	88	7
		Catalyst-free	H ₂ O, rt	25 min	95	14
		Silica gel	Solvent-free, rt	40 min	95	15
		CsF–Celite	Solvent-free, 80°C	30 min	93	17
		TiO ₂ P25-900	Method A	15 min	97	Present
		TiO ₂ P25-900	Method B	5 min	98	Present
9		CuO	CH ₃ CN, rt	4 h	85	7
		Silica gel	Solvent-free, rt	5 h	96	15
		CsF–Celite	Solvent-free, 80°C	3 h	60	17
		TiO ₂ P25-900	Method A	90 min	92	Present
		TiO ₂ P25-900	Method B	40 min	96	Present

Moreover, recyclability of nano-TiO₂P25-900 catalyst was examined using the reaction of 4-toluenesulphonyl chloride with 4-chloroaniline (table 1, entry 2). It was noticed that this catalyst could be easily recovered simply by filtration and reused for five consecutive fresh runs without pre-activation and with no significant drop in its catalytic activity. As seen in figure 1, a slight decrease in yield was observed after the fifth run.

To the best of our knowledge, there are no previous examples of the synthesis of sulphonamides using

TiO₂ as a heterogeneous catalyst under ultrasound irradiation. This success encouraged us to extend our preliminary observation to a diverse series of amines and urazoles preferably under ultrasound irradiation conditions in EtOH in the presence of TiO₂P25-900 at room temperature (method B), since better results are obtained under such conditions. The prominent effect of ultrasound irradiation technique in improving reaction yield as well as reaction rate has already been discussed.

The products were characterized on the basis of their spectral (IR, NMR) and melting points and

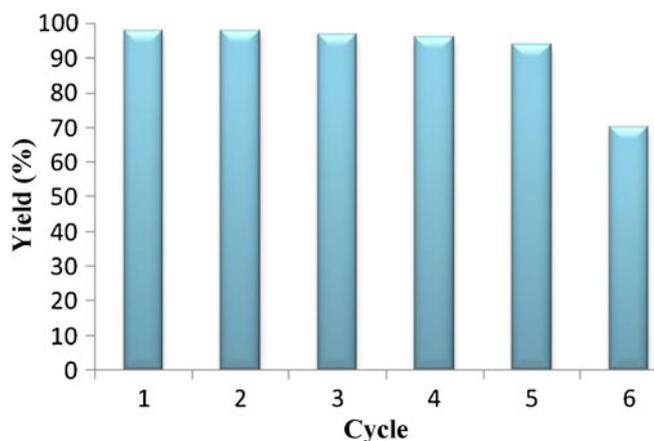


Figure 1. Recyclability of TiO₂P25-900.

compared with literature.^{7,14-21} Formation of expected sulphonamides is evidenced by disappearance of single and strong absorption band for N–H stretching bond and appearance of two stretching bands for SO₂ group in their IR spectra.

4. Conclusion

In conclusion, we have developed a novel and highly efficient protocol for *N*-sulphonylation of amines and urazoles using nontoxic and inexpensive TiO₂P25-900 catalyst under conventional as well as ultrasound irradiation conditions. The effect of TiO₂ phase composition on *N*-sulphonylation of amines was analysed. Operational simplicity, short reaction times, simple procedure, reusability of the catalyst, and chemoselectivity are the main advantages of this method.

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