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Dehydroisomerisation of α -Pinene and Limonene to p-Cymene over Silica-Supported ZnO in the Gas Phase

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Abstract: Silica-supported zinc oxide possessing acid and dehydrogenation functions is an efficient, noble-metal-free bifunctional catalyst for the environment-friendly synthesis of p-Cymene from renewable monoterpene feedstock by gas-phase dehydroisomerisation of α -pinene and limonene in a fixed-bed reactor. The reaction involves acid-catalysed terpene isomerisation to p-menthadienes followed by dehydrogenation to form p-Cymene. Dehydroisomerisation of α -pinene produces p-Cymene with 90% yield at 100% conversion at 370 °C and WHSV = 0.01–0.020 h^{−1}. The reaction with limonene gives a 100% p-Cymene yield at 325 °C and WHSV = 0.080 h^{−1}. ZnO/SiO₂ catalyst shows stable performance for over 70 h without co-feeding hydrogen.

Keywords: α -pinene; limonene; p-Cymene; zinc oxide; bifunctional catalysis

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1. Introduction

p-Cymene (4-isopropyltolylene) has a variety of applications ranging from medicinal and cosmetic uses to industrial organic synthesis [1]. Its major application is as an intermediate for the synthesis of p-cresol, which is further processed to antioxidants [2]. p-Cresol could also be used for the production of terephthalic acid [3]. p-Cymene is commonly synthesised from the oil-based feedstock by environmentally harmful Friedel-Crafts alkylation of toluene with propene followed by isomer separation [1]. An alternative environmentally benign route to p-Cymene is through dehydroisomerisation of renewable terpene raw materials, α -pinene and limonene, using acid-redox bifunctional heterogeneous catalysis [1]. α -Pinene is an inexpensive major constituent (ca. 85%) of turpentine oils obtained from coniferous trees [4]. Crude sulfate turpentine, a by-product from the pulp and paper industry, is another cheap source of terpenes including α -pinene [1]. Limonene is obtained commercially from citrus fruits [4].

Dehydroisomerisation of α -pinene to p-Cymene is suggested to proceed through a bifunctional mechanism including α -pinene isomerisation on catalyst acid sites to monocyclic p-menthadienes and bi- and tricyclic terpenes followed by dehydrogenation of p-menthadienes on metal or oxo-metal redox sites [1] (Scheme 1). α -Pinene isomerisation has been extensively studied with a wide range of solid acid catalysts in liquid and gas phases [1]. Among the acid catalysts are zeolites [5–7], acid-activated clays [8,9], sulfated zirconia [10], ion exchange resins [11], and heteropoly acids [12–15]. Typically, it yields 30–60% of camphene together with a complex mixture of other monoterpene by-products [14,15]. The reaction is suggested to proceed through protonation of the α -pinene double bond to form pinanyl cation, followed by two parallel transformations: the rearrangement to bi- and tricyclic products (camphene, tricyclene, β -pinene, etc.) and 1–6 ring opening to form monocyclic p-menthadienes (limonene, terpinolene, terpinene, etc.) (Scheme 1) [1]. The first pathway is favourable at lower temperatures, whereas p-menthadienes form at higher

temperatures [1]. In the α -pinene-to-p-Cymene dehydroisomerisation, p-menthadiene dehydrogenation is suggested to be the rate-limiting step, whereas the isomerisation step is probably at quasi-equilibrium [1]. Usually, the synthesis of p-Cymene from α -pinene is carried out in the gas phase at ambient pressure. A range of heterogeneous catalysts have been reported for this reaction giving 100% α -pinene conversion at 300–460 °C [1,16–19]. These include $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ (390–460 °C, 53% p-Cymene yield) [16], zeolite Y (300 °C, 54% yield) [17], Pd/SiO₂ (300 °C, 67% yield) [1], Pd-Zn/Al-SBA-15 (300 °C, 77% yield) [18] and bulk Zn(II)–Cr(III) mixed oxide (350 °C, 78% yield) [19]. The supported Pd catalysts exhibit high activity at 300 °C, but require continuous hydrogen supply to reduce catalyst coking causing catalyst deactivation [1]. The noble-metal-free bulk Zn–Cr oxide gives practically the same p-Cymene yield as Pd-Zn/Al-SBA-15 without H₂ supply, although at a higher temperature of 350 °C [19].

Scheme 1. Dehydroisomerisation of α -pinene to p-Cymene.

p-Cymene can also be produced by dehydroisomerisation of limonene occurring through double bond migration on acid sites followed by dehydrogenation on metal or oxo-metal sites (Scheme 2), the latter probably being the rate-limiting step [20–25]. This reaction occurs easier than the α -pinene-to-p-Cymene conversion because it does not include C–C bond breaking. A number of heterogeneous catalysts have been reported for this reaction in liquid and gas phases [20–25], including Ti/SBA-15 (liquid phase, 160 °C, 56% p-Cymene yield) [21], Pd/HZSM-5 (liquid phase, 260 °C, 8 bar pressure, 82% yield) [22], Pd/Al₂O₃ (supercritical EtOH, 300 °C, 65 bar pressure, 80% yield) [23], TiO₂ (gas phase, 300 °C, 90% yield) [24], Pd/SiO₂ (gas phase, 300 °C, in H₂ flow, 99% yield) [25] and others [20]. Pd/SiO₂ gives the highest yield of p-Cymene in the gas phase, however, it requires continuous H₂ supply to prevent catalyst deactivation [25] as in the case of α -pinene dehydroisomerisation [1].

Scheme 2. Dehydroisomerisation of limonene to p-Cymene.

Here, the dehydroisomerisation of α -pinene and R-(+)-limonene (referred to as limonene) to p-Cymene is investigated in the presence of noble-metal-free silica-supported ZnO cata-

lyst in the gas phase in a continuous flow fixed-bed reactor. ZnO is an amphoteric oxide [26] known as a hydrogenation and dehydrogenation catalyst [2]: for example, for dehydrogenation of primary alcohols to aldehydes [27]. Silica support possesses mild Brønsted acidity due to its surface silanol groups; it can readily isomerise α -pinene and limonene at 300 °C [1,25]. Therefore, the silica-supported ZnO possessing both acidic and dehydrogenating functionalities has a potential for the dehydroisomerisation of these terpenes to p-Cymene. Here, it is demonstrated that this catalyst has a very high efficiency in the environment-friendly synthesis of p-Cymene from α -pinene and limonene, exhibiting stable performance without hydrogen supply.

2. Results and Discussion

2.1. Catalyst Characterisation

The texture of ZnO/SiO₂ catalysts was characterised by N₂ physisorption (Table 1), with particular attention to the ZnO/SiO₂(300) catalysts supported on Aerosil 300, which exhibited higher activities. These catalysts showed typical adsorption/desorption isotherms for mesoporous materials with a H1 hysteresis loop representative of amorphous silica (Figure S1). Bulk ZnO prepared by calcining Zn(NO₃)₂ hexahydrate at 400 °C had a very low surface area of 0.01 m²g^{−1}. As expected, supported ZnO/SiO₂ catalysts had much larger surface areas; their surface area and pore volume decreased with increasing ZnO loading. At a constant ZnO loading of 10 wt%, the catalyst surface area increased with increasing the surface area of silica support with an exception of ZnO/SiO₂(750), the surface area of which is smaller than that of ZnO/SiO₂(600). This may be explained by a larger contribution of microporosity in SiO₂(750) texture, which may be blocked by ZnO.

Table 1. Information about catalysts.

Catalyst ¹	S _{BET} ² (m ² g ^{−1})	Pore Volume ³ (cm ³ g ^{−1})	Pore Size ⁴ (Å)	Water Content ⁵ (wt%)
ZnO	0.01	–	–	–
SiO ₂ (300)	296	1.32	179	–
5%ZnO/SiO ₂ (300)	294	0.96	155	–
10%ZnO/SiO ₂ (300)	218	1.14	209	1.2 (1.3)
15%ZnO/SiO ₂ (300)	188	0.90	191	–
20%ZnO/SiO ₂ (300)	162	0.90	222	–
30%ZnO/SiO ₂ (300)	130	0.77	237	–
10%ZnO/SiO ₂ (200)	166	0.68	163	1.5 (1.4)
10%ZnO/SiO ₂ (600)	491	0.91	74	2.0 (2.0)
10%ZnO/SiO ₂ (750)	391	1.19	121	4.5 (3.5)

¹ Calcined at 400 °C for 2 h in air; in round brackets is the surface area of SiO₂ support (m²g^{−1}). ² BET surface area. ³ Single point total pore volume. ⁴ Average pore diameters by BET. ⁵ From TGA as weight loss in the temperature range of 40–100 °C and in round brackets in the range of 100–600 °C.

From TGA, the catalysts exhibited a water loss of 1.2–4.5% upon heating up to 100 °C, which can be attributed to physisorbed water, and a further loss of chemically bound water of 1.3–3.5% in the temperature range 100–600 °C (Table 1). The water loss increased with increasing the surface area of silica support. The loss of water at higher temperatures indicates the presence of silanol groups in the catalysts, which is also confirmed by DRIFT spectroscopy (see below). The silanol groups can act as active Brønsted acid sites in the dehydroisomerisation reaction [1,25].

Figure 1 shows XRD patterns of ZnO/SiO₂ catalysts together with the pattern of bulk ZnO [19,28]. While the bulk ZnO is a crystalline material (wurtzite structure), the ZnO/SiO₂ catalysts were amorphous in agreement with previous reports [29,30]. This indicates a fine dispersion of ZnO on the silica surface. Only ZnO/SiO₂(200) showed a trace of ZnO crystal phase due to a relatively low surface area of the silica support.

Figure 1. XRD patterns (CuK α) for (1) bulk ZnO, (2) 10%ZnO/SiO₂(200), (3) 10%ZnO/SiO₂(300), (4) 10%ZnO/SiO₂(600), (5) 10%ZnO/SiO₂(750).

The acidity of the catalysts was characterised by DRIFT spectroscopy of adsorbed pyridine. Both bulk ZnO and all ZnO/SiO₂ catalysts gave a strong band at 1450 cm^{−1} (Figure 2), which indicates the presence of Lewis acid sites [31]. On the other hand, the intensity of the characteristic band of Brønsted acid sites at 1540 cm^{−1} [31] does not exceed the level of noise. This points to the absence of Brønsted acid sites in the catalysts capable of protonating pyridine. This is in agreement with previous DRIFTS studies of ZnO catalysts [19,28–30].

Figure 2. DRIFT spectra of adsorbed pyridine (powdered KBr mixtures): (1) bulk ZnO, (2) 10%ZnO/SiO₂(300), (3) 10%ZnO/SiO₂(750).

As stated above, the TGA data (Table 1) indicate the presence of silanol groups SiOH in the catalysts, which are weak Brønsted acid sites incapable of protonating pyridine. Figure 3 shows the DRIFT spectra of silica supports and 10%ZnO/SiO₂ catalysts in the region of OH stretching modes of silanol groups. In the DRIFT spectra of SiO₂ supports (Figure 3A), the sharp peak at 3742 cm^{−1} is attributed to the free terminal silanol groups and the bands around 3682–3636 cm^{−1} to the hydrogen-bonded vicinal silanols. The broad band in the 3600–3100 cm^{−1} region is generally ascribed to silanol nests that consist of a number of silanol groups interacting through extended hydrogen bonding [32–34]. In ZnO/SiO₂ catalysts (Figure 3B), the free terminal silanol groups and silanol nests are clearly

present, whereas the hydrogen-bonded vicinal silanols are less pronounced. While being weak Brønsted acid sites, the silanol groups can isomerise α -pinene and limonene at 300 °C, as demonstrated previously [1,25].

Figure 3. DRIFT spectra of SiO₂ supports (A) and 10%ZnO/SiO₂ catalysts (B) calcined at 400 °C in air for 2 h (powdered KBr mixtures vs. KBr). The surface area of SiO₂ support (m²g⁻¹): (1) 200, (2) 300, (3) 600, and (4) 750.

2.2. Dehydroisomerisation of α -Pinene

Table 2 shows the results of initial testing of ZnO/SiO₂(300) catalysts (Aerosil 300 support) in α -pinene dehydroisomerisation. Among silica supports used, Aerosil 300 gave the best catalyst performance (see Table 3 below). The reaction was carried out for 5 h time on stream (TOS) at 370 °C and a weight hourly space velocity WHSV = 0.020 h⁻¹. ZnO loading in the catalysts was varied from 5 to 30 wt%. As seen, ZnO/SiO₂(300) catalysts exhibit high activity and p-Cymene selectivity, with α -pinene conversion varying between 98–100% and p-Cymene selectivity between 82–88%. The loading of ZnO in the range of 5–30 wt% had a relatively small effect on catalyst performance. Yet 10%ZnO/SiO₂(300) showed a better performance among the catalysts tested, giving 88% p-Cymene at 100% conversion (entry 4). The catalyst exhibited stable p-Cymene selectivity for over 5 h TOS (Figure 4). After reaction, initially the white catalyst became brown due to coke formation; 0.9% of carbon deposition was found by combustion analysis and catalyst surface area slightly reduced to 207 m²g⁻¹ (cf. 218 m²g⁻¹ in Table 1). Without ZnO, the silica support showed a high isomerisation activity (98% α -pinene conversion, entry 1), mainly producing limonene, camphene, and other p-menthadiene isomers (the other) together with some cracking products (the lights). Notably, no p-Cymene was formed on pure SiO₂ due to

the lack of dehydrogenation ability of SiO₂. p-Cymene formed only in the presence of ZnO as a dehydrogenation catalyst. These results agree with the reaction mechanism involving fast α -pinene isomerisation to p-menthadienes on acid sites (silanol groups of silica) followed by slow dehydrogenation of p-menthadienes on ZnO oxo-metal sites to form p-Cymene (Scheme 1) [1]. Bulk ZnO produced p-Cymene, although with a relatively low selectivity of 52% (entry 2), which can be explained by the low surface area of bulk ZnO (Table 1). Physical mixture ZnO + SiO₂(300) (1:9 w/w) of the same composition as the silica-supported 10%ZnO/SiO₂(300) catalyst produced mainly p-menthadienes, with a small amount of p-Cymene formed (21%, entry 5).

Table 2. Dehydroisomerisation of α -pinene to p-Cymene over ZnO/SiO₂(300). ¹

Entry	Catalyst	Conversion ² (%)	Selectivity (%mol) ²				
			Lights	Camphene	Limonene	p-Cymene	Other
1	SiO ₂ (300)	98	9	13	20	0	59
2	ZnO	98	8	5	0	52	35
3	5%ZnO/SiO ₂ (300)	100	10	0	0	86	4
4	10%ZnO/SiO ₂ (300)	100	12	0	0	88	0
5	ZnO+SiO ₂ (300) (1:9) ³	100	9	6	0	21	64
6	10%ZnO/SiO ₂ (300) ⁴	100	16	1	0	83	1
7	15%ZnO/SiO ₂ (300)	99	14	0	0	83	3
8	20%ZnO/SiO ₂ (300)	99	10	1	0	83	6
9	30%ZnO/SiO ₂ (300)	98	13	1	0	82	4

¹ 370 °C, 0.40 g catalyst, 0.48 kPa α -pinene partial pressure, 5 mL min^{−1} flow rate, 4–6 h TOS, WHSV = 0.020 h^{−1}. ² Average conversion and product selectivity over 5 h TOS. “Other” are unidentified p-menthadienes and “lights” are cracking products. ³ Physical mixture of bulk ZnO and SiO₂ (1:9 w/w). ⁴ At 0.88 kPa α -pinene partial pressure, WHSV = 0.037 h^{−1}.

Table 3. Dehydroisomerisation of α -pinene to p-Cymene over ZnO/SiO₂: effect of support. ¹

Catalyst	Conversion ² (%)	Selectivity (%mol) ²				
		Lights	Camphene	Limonene	p-Cymene	Other
10%ZnO/SiO ₂ (200)	100	13	0	0	87	0
10%ZnO/SiO ₂ (300)	100	10	0	0	89	1
10%ZnO/SiO ₂ (600)	99	16	0	0	83	1
10%ZnO/SiO ₂ (750)	99	17	0	0	83	0

¹ 370 °C, 0.80 g catalyst, 0.48 kPa α -pinene partial pressure, 10 mL min^{−1} flow rate, 6 h TOS, WHSV = 0.020 h^{−1}. ² Average conversion and product selectivity over 6 h TOS. “Other” are unidentified p-menthadienes and “lights” are cracking products.

Figure 4. Time course for α -pinene dehydroisomerisation over 10%ZnO/SiO₂(300): 0.40 g catalyst, 370 °C, 0.48 kPa α -pinene partial pressure, 5 mL min^{−1} flow rate, WHSV = 0.020 h^{−1}.

Figure 5 shows the effect of contact time, $(\text{WHSV})^{-1}$, on p-Cymene selectivity in the presence of 10%ZnO/SiO₂(300) at 370 °C. The contact time was varied by changing the flow rate (5–50 mL min^{−1}) and catalyst amount (0.4–0.8 g). The conversion of p-Cymene was 100% at such conditions. The results show that the selectivity increases monotonically with the contact time, as expected for a consecutive reaction (Scheme 1), reaching a plateau at 90% at a contact time 50–100 h ($\text{WHSV} = 0.01\text{--}0.02 \text{ h}^{-1}$).

Figure 5. α -Pinene conversion and p-Cymene selectivity over 10%ZnO/SiO₂(300) versus contact time at 370 °C and 0.48 kPa α -pinene partial pressure; the contact time varied by changing flow rate (5–50 mL min^{−1}) and catalyst amount (0.4–0.8 g).

Figure 6 demonstrates the effect of reaction temperature, varied between 200–400 °C, on p-Cymene selectivity in the presence of 10%ZnO/SiO₂(300) at an optimum contact time of 98 h. At this contact time, the conversion of α -pinene was 100% within the temperature range studied. It can be seen that the selectivity to p-Cymene increases with the temperature reaching 90% at 370 °C (90% p-Cymene yield). At the same time, the selectivity to p-menthadienes (the other) decreases. These results are in agreement with the mechanism shown in Scheme 1, where p-menthadienes are the intermediates to p-Cymene, with the rate-limiting step of p-menthadiene dehydrogenation to form p-Cymene [1]. Notably, the amount of the lights (cracking by-products) reduces as the temperature increases. This is not unexpected because the aromatic p-Cymene should be more stable towards cracking than α -pinene and its isomers.

The performance of 10%ZnO/SiO₂ catalysts containing different SiO₂ supports with the surface area of 200–750 m²g^{−1} is presented in Table 3 at the optimum temperature 370 °C and $\text{WHSV} = 0.020 \text{ h}^{-1}$. 10%ZnO/SiO₂(300) showed the best performance (89% selectivity at 100% conversion) closely followed by 10%ZnO/SiO₂(200) (87% selectivity at 100% conversion). The catalysts 10%ZnO/SiO₂(600) and 10%ZnO/SiO₂(750) comprising large-area silicas (600–750 m²g^{−1}) were less efficient, giving 83% selectivity at 99% conversion. This could be the result of many factors, such as catalyst pore structure, ZnO dispersion, density of silanol groups, etc. Thus, the larger density of silanol groups (Brønsted acid sites) in 10%ZnO/SiO₂(600) and 10%ZnO/SiO₂(750) may be responsible for the larger amounts of cracking by-products (the lights) formed on these catalysts.

Figure 6. Effect of temperature on α -pinene dehydroisomerisation over 10%ZnO/SiO₂(300): 0.80 g catalyst, 0.48 kPa α -pinene partial pressure, 5 mL min^{−1} flow rate, WHSV = 0.010 h^{−1}.

Figure S2 shows a longer-term test (72 h TOS) for α -pinene dehydroisomerisation over 10%ZnO/SiO₂(300) at 370 °C and WHSV = 0.020 h^{−1}. After 24 h on stream, the selectivity reduced from 89 to 83%, which was probably due to catalyst coking. Initially white, the catalyst turned dark brown; 2.3% of carbon deposition was found in the post reaction catalyst. The spent catalyst had a surface area of 87 m²g^{−1}, a pore volume of 0.71 cm³g^{−1} and an average pore diameter of 329 Å (N₂ adsorption isotherm is shown in Figure S3). As a result of coking, the surface area and pore volume significantly reduced, whereas the average pore diameter increased; probably due to the blocking of smaller pores by coke (cf. the data for the fresh 10%ZnO/SiO₂(300) catalyst in Table 1). The catalyst was regenerated in situ after 24 h TOS by air flow (10 mL min^{−1}) at 370 °C for 3 h, which allowed us to reduce coke deposition to 0.01% and restore catalyst activity. After 72 h TOS, with catalyst regeneration after each period of 24 h on stream, the average p-Cymene selectivity was 85% at 100% p-Cymene conversion.

In summary, the developed ZnO/SiO₂ catalyst has a high activity and selectivity in one-step α -pinene-to-p-Cymene dehydroisomerisation, providing 90% p-Cymene yield at 100% α -pinene conversion at 370 °C and WHSV = 0.01–0.02 h^{−1} (Figure 6). In terms of p-Cymene yield, it outperforms the catalysts reported previously such as Pd/SiO₂ [1], Pd-Zn/Al-SBA-15 [18], and bulk Zn(II)–Cr(III) mixed oxide [19]. Although the reported catalysts operate at lower temperatures, 300–350 °C, they provide considerably lower p-Cymene yields. Thus, the supported Pd catalysts operate at 300 °C to yield 67–77% p-Cymene; moreover, they require continuous hydrogen supply to prevent catalyst deactivation [1,18]. In contrast, the noble-metal-free Zn/SiO₂ gives stable performance without hydrogen supply and can be regenerated in situ by air at the reaction temperature.

2.3. Dehydroisomerisation of Limonene

Limonene-to-p-Cymene dehydroisomerisation occurs more easily and generally with higher p-Cymene yields than the reaction of α -pinene because it does not involve C–C bond breaking (Scheme 2). In the limonene dehydroisomerisation, ZnO/SiO₂ was found to be a highly effective catalyst, as in the case of α -pinene.

Table 4 shows the effect of ZnO loading (5–30 wt%) on limonene conversion and p-Cymene selectivity in the presence of ZnO/SiO₂(300) at 300 °C and WHSV = 0.080 h^{−1}. As seen, the reaction occurs practically with 100% limonene conversion regardless of ZnO loading. The catalysts exhibited stable p-Cymene selectivity for over 4 h TOS (Figure S4). The selectivity to p-Cymene increased with ZnO loading, reaching 98% with 30%ZnO/SiO₂(300). This is different from the reaction of α -pinene, where the optimal ZnO loading was at 10

wt% (Table 2). This difference could be due to the lower reaction temperature—300 °C for limonene and 370 °C for α -pinene—hence the higher loading of dehydrogenation component ZnO is required for limonene-to-p-Cymene conversion. Clearly, the reaction of limonene occurs more easily than that of α -pinene, which can be seen not only from the lower reaction temperature but also from a 4-fold shorter contact time.

Figure 7 shows the effect of contact time, $(\text{WHSV})^{-1}$, on limonene conversion and the selectivity to p-Cymene and α -terpinene in the presence of 30%ZnO/SiO₂(300) at 275 °C. The contact time was varied by changing the flow rate from 10 to 50 mL min^{−1}. The results show that limonene conversion and p-Cymene selectivity increase with the contact time, reaching 98% p-Cymene selectivity at 100% limonene conversion at a contact time of 12 h. As seen, the selectivity to p-Cymene increases at the expense of α -terpinene, which indicates that α -terpinene is the main reaction intermediate in agreement with the mechanism shown in Scheme 2.

Table 4. Dehydroisomerisation of limonene to p-Cymene over ZnO/SiO₂(300).¹

Catalyst	Conversion ² (%)	Selectivity (%mol) ²				
		Camphene	β -Pinene	α -Terpinene	p-Cymene	Terpinolene
5%ZnO/SiO ₂ (300)	>99	6	6	3	84	1
10%ZnO/SiO ₂ (300)	>99	1	2	0	97	0
20%ZnO/SiO ₂ (300)	100	0	3	0	97	0
30%ZnO/SiO ₂ (300) ³	100	0	2	0	98	0

¹ 0.20 g catalyst, 300 °C, 10 mL min^{−1} flow rate, 0.47 kPa limonene partial pressure, WHSV = 0.080 h^{−1}, 4 h TOS. ² Average conversion and product selectivity over 4 h TOS. ³ 0.2% of carbon deposition in spent catalyst.

Figure 7. Limonene conversion and product selectivity over 30%ZnO/SiO₂(300) (0.20 g) versus contact time at 275 °C and 0.47 kPa limonene partial pressure; the contact time varied by changing the flow rate (10–50 mL min^{−1}).

Figure 8 shows the effect of temperature on p-Cymene selectivity in the presence of 20%ZnO/SiO₂(300) and 30%ZnO/SiO₂(300) in the range of 275–350 °C at WHSV = 0.080 h^{−1}. For both catalysts, the conversion of limonene was 100% within this temperature range. It can be seen that the selectivity increases monotonically with the temperature, reaching 100% at 325 °C for 30%ZnO/SiO₂(300) (100% p-Cymene yield). These results are in agreement with the mechanism shown in Scheme 2, with the rate-limiting step of p-menthadiene dehydrogenation.

The best reported catalyst for the gas-phase dehydroisomerisation of limonene so far, Pd/SiO₂, provides 99% yield of p-Cymene at 300 °C, however, requires continuous

hydrogen supply to prevent catalyst deactivation [25]. Our noble-metal-free ZnO/SiO₂ catalyst gives 100% p-Cymene yield at 325 °C and exhibits stable performance without hydrogen supply.

Figure 8. Effect of temperature on limonene dehydroisomerisation over 20%ZnO/SiO₂(300) and 30%ZnO/SiO₂(300): 0.20 g catalyst, 0.47 kPa limonene partial pressure, 10 mL min^{−1} flow rate, 4 h TOS, WHSV = 0.080 h^{−1}; 100% limonene conversion in all cases.

3. Materials and Methods

3.1. Chemicals and Catalysts

α -Pinene (>98%), R-(+)-limonene (>96%) and Zn(NO₃)₂·6H₂O were from Sigma-Aldrich (Gillingham, Dorset, SP8 4XT, UK) and used as supplied without further purification. R-(+)-limonene is referred to as limonene for short. Aerosil 300 silica support ($S_{\text{BET}} \approx 300 \text{ m}^2\text{g}^{-1}$) was from Degussa. Other silicas with $S_{\text{BET}} = 200, 600$ and $750 \text{ m}^2\text{g}^{-1}$ were from Grace Catalysts & Carriers.

A series of silica-supported ZnO catalysts with ZnO loading of 5–30 wt% were prepared by impregnating silica support with Zn(NO₃)₂ from aqueous solution. The aqueous mixture was stirred overnight at room temperature followed by evaporation to dryness in a rotary evaporator. The catalysts were calcined in air at 400 °C for 2 h at a temperature ramp rate of 5 °C min^{−1} to decompose Zn(II) nitrate to Zn(II) oxide and finally grounded to 45–140 μm particle size. The loading of ZnO was determined using ICP-OES (inductively coupled plasma optical emission spectroscopy) analysis. In ZnO/SiO₂ catalysts thus prepared, ZnO loading agreed with the expected nominal loading within $\pm 1 \text{ wt}\%$. In contrast, catalyst preparation through precipitation of Zn(OH)₂ with ammonia [19] led to significant loss of silica support due to its interaction with the ammonia. Bulk ZnO was prepared by calcining Zn(II) nitrate at 400 °C. The catalysts were stored in a desiccator over P₂O₅. The catalysts were designated indicating their chemical composition and zinc oxide loading (wt%), with silica support surface area given in round brackets, for example, 10%ZnO/SiO₂(300) for 10 wt% ZnO supported on Aerosil 300.

3.2. Techniques

BET (Brunauer-Emmett-Teller) surface area and porosity of catalysts were determined from nitrogen adsorption measured at 77 K on a Micromeritics ASAP 2010 instrument. Prior (Micromeritics Instrument Corp., Norcross, GA, USA) to BET analysis, the catalysts were pre-treated at 240 °C in vacuum. ICP-OES analysis was carried out on a Spectro Ciros emission spectrometer (Spectro Analytical Instruments GmbH, Kleve, Germany) to determine zinc content in the catalysts. TGA (thermogravimetric analysis, Perkin Elmer

TGA 7 instrument (Perkin Elmer, Waltham, MA, USA) was used to measure water content in the catalysts.

XRD (powder X-ray diffraction) of catalysts was recorded on a Bruker D8 Discover diffractometer (Bruker, Billerica, MA, USA) using a monochromatic $\text{CuK}\alpha$ radiation ($\lambda = 1.541 \text{ \AA}$) in a 2θ range between 20 and 80° . DRIFT (diffuse reflectance infrared Fourier transform) spectra of adsorbed pyridine were taken on a Nicolet Nexus FTIR spectrometer (Nicolet Instrument Corp., Madison, WI, USA) to characterise acid sites in the catalysts, as described previously [28]. The amount of coke in post-reactor catalysts was determined by combustion elemental analysis.

GC-MS analysis of reaction products was carried out on a Thermo Scientific GC (Thermo Fisher Scientific, Waltham, MA, USA) interfaced to an ISQ Single Quadrupole equipped with a Zebron ZB-1701 capillary column ($30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \text{ }\mu\text{m}$).

3.3. Catalyst Testing

The dehydroisomerisation of α -pinene and limonene was carried out at 200 – 400°C and ambient pressure using nitrogen as a carrier gas in a continuous flow fixed-bed quartz tubular downflow reactor (9 mm internal diameter) with online GC analysis (Varian Star 3800 gas chromatograph equipped with a flame ionisation detector and Zebron ZB-1701 capillary column of 30 m length, 0.25 mm internal diameter, and $0.25 \text{ }\mu\text{m}$ film thickness). The catalyst powder (0.2 – 0.8 g) was loaded in the reactor supported by a glass wool plug. The length of catalyst bed was sufficient for the plug flow regime (1 cm for 0.2 g of ZnO/SiO_2). The temperature in the reactor was controlled by a Eurotherm controller using a thermocouple placed at the top of the catalyst bed. All reactor gas lines were made of stainless steel. The downstream lines and sampling valves were heated to 150°C to prevent product condensation. Prior to reaction, the catalyst was pre-treated at the reaction temperature for 1 h in nitrogen flow. Gas feed containing α -pinene or limonene at 0.2 – 1.0 kPa partial pressure was supplied to the reactor by passing nitrogen flow controlled by a Brooks mass flow controller through a stainless-steel saturator holding liquid substrate at a certain temperature to maintain the required substrate partial pressure. The downstream gas flow was analysed using the on-line GC to obtain terpene conversion and product selectivity. *p*-Cymene was the main reaction product together with small amounts of camphene, *p*-menthadiene isomers, and cracking products. The products were identified by GC and GC-MS using authentic samples from Sigma-Aldrich. For quantitative GC analysis, unidentified *p*-menthadienes were lumped together as “other” and the cracking products as “lights”. GC-FID response factors were assumed to be the same for all monoterpenes and *p*-Cymene since they have practically the same hydrocarbon composition. GC traces illustrating product analysis are shown in Figures S5 and S6 (Supplementary Information). Product selectivity was defined as molar percentage of α -pinene or limonene converted to a particular reaction product. Each catalyst test was repeated at least twice. The mean absolute percentage error in conversion and product selectivity was usually $\leq 5\%$ and the carbon balance was maintained within 95% . The reactions were carried out for 4 – 6 h time on stream (TOS) unless stated otherwise.

4. Conclusions

ZnO supported on silica is a highly efficient, noble-metal-free bifunctional catalyst for the environment-friendly synthesis of *p*-Cymene by the gas-phase dehydroisomerisation of α -pinene and limonene. Dehydroisomerisation of α -pinene over ZnO/SiO_2 produces *p*-Cymene with 90% yield at 100% conversion at 370°C and a contact time $\text{WHSV} = 0.01$ – 0.020 h^{-1} . The reaction with limonene gives a 100% *p*-Cymene yield at 325°C and $\text{WHSV} = 0.080 \text{ h}^{-1}$. ZnO/SiO_2 catalyst shows stable performance for over 70 h without co-feeding hydrogen.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/catal11101245/s1>, Figure S1: Nitrogen adsorption and desorption isotherms on $10\%\text{ZnO}/\text{SiO}_2(300)$; Figure S2: Long-term time course for α -pinene dehydroisomerisation over $10\%\text{ZnO}/$

SiO₂(300) with catalyst regeneration; Figure S3: Nitrogen adsorption and desorption isotherms on spent 10%ZnO/SiO₂(300) catalyst; Figure S4: Time course for limonene dehydroisomerisation over 20%ZnO/SiO₂(300); Figure S5: GC trace showing high resolution of product analysis; Figure S6: GC trace for limonene conversion over 30%ZnO/SiO₂(300).

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