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# A dual-functional Zr-MSU-3 catalyst for cascade MPV reduction and dehydration of 4'-methoxypropiophenone to anethole

Hongwei Zhang,<sup>[a]</sup> Candy Li-Fen Lim,<sup>[a]</sup> Muhammad Zaki,<sup>[a]</sup> Stephan Jaenicke<sup>[a]</sup> and Gaik Khuan Chuah(s)\*<sup>[a]</sup>

Dedication ((optional))

Abstract: Anethole is an ingredient in many flavour, fragrance and pharmaceutical formulations. To reduce the dependence of its supply from natural oils, a green route for anethole synthesis is designed based on Meerwein-Pondorf-Verley reduction and dehydration of 4'methoxypropiophenone. The one-pot cascade reactions were heterogeneously catalysed by dual-functional Zr-MSU-3, a predominantly Lewis acid catalyst with Si/Zr ratio of 10 and pores in the range of 3.2 - 4.2 nm. The use of 2-pentanol as solvent and hydrogen donor for the MPV reduction was advantageous as its high boiling point enhanced the rate of reactions, especially the dehydration of the MPV product, 1-(4-methoxyphenyl)-propan-1-ol. This dispenses with the need for a strong acid catalyst that could cause acid-catalyzed by-products. Anethole yields of 90 % with trans:cis isomer ratio ~ 92:8, similar to that of natural anethole, were obtained. In comparison, use of microporous Zr-Beta (Si/Zr 12.5) gave lower activity due to pore size constraints. Hence, through design of the reactions and catalyst, 4'-methoxypropiophenone could be efficiently converted to anethole in a sustainable and green manner.

#### Introduction

Anethole (*para*-methoxyphenylpropene), the main ingredient of anise oil, is widely used as a flavour substance.<sup>[1]</sup> It is certified as "GRAS" (Generally Recognized as Safe) by the US Food & Drug administration (FDA) and the Flavor Extract Manufacturers Association (FEMA). It exists as the *cis*- and *trans*-form with the latter being more abundant and preferred for use. Other applications of anethole include use as a masking agent in cosmetics, soap, and oral rinses.<sup>[1a, 2]</sup> Recent studies have focused on its medicinal properties because *trans*-anethole was found to exert anti-inflammatory<sup>[3]</sup> and anti-metastatic activity against fibro-sarcoma tumour cells.<sup>[4]</sup>

Natural anethole is obtained from essential oils extracted from a number of plant species by steam distillation<sup>[5]</sup> or supercritical fluid extraction (SFE).<sup>[5a, 6]</sup> The main sources are anise oil,<sup>[2b, 7]</sup> star anise oil <sup>[2b, 8]</sup> and fennel oil <sup>[9]</sup>, which contain 55 – 90 % anethole with 90 % in the *trans*-form <sup>[2a]</sup>. However, the content of essential

 H. Zhang, C. L.-F Lim, M. Zaki, Prof. S. Jaenicke, and Prof. G. K. Chuah\*
 Department of Chemistry
 National University of Singapore
 3 Science Drive 3, Kent Ridge, Singapore 117543
 E-mail: <u>chmcqk@nus.edu.sq</u>

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oil in the natural plant species is very low, e.g., ~1.5 - 5% in aniseed and 2 - 6% in fennel seeds.<sup>[10]</sup> The output and price of anethole fluctuate greatly due to changing weather and climate conditions so that there is a need to reduce the reliance on natural sources of trans-anethole. Anethole can also be obtained by rectification of crude sulfate turpentine, a by-product of the pulp and paper industry, where the anethole concentration is ~0.5 %. Despite the low concentration, the large quantity of turpentine leads to a significant output. However, due to forestry conservation, recycling of paper resources, and the trend towards paperless communication, there is a decline in yield from this source. It is also possible to obtain anethole by synthetic routes. Bauer and Molleken reported a two-step synthesis for anethole and 2-alkoxy-4-propen-1-yl phenols where condensation between anisole (4-methoxybenzene) and propionaldehyde is followed by acid-catalysed splitting at 100 - 300 °C to form o- and panetholes.<sup>[11]</sup> De Pasquale reported 91 % overall yield of anethole (cis:trans 13:87) from isomerization of estragole (1-allyl-4methoxybenzene) using an iron pentacarbonyl catalyst at 100 -140 °C.[12] Two recent patents reported the reduction of 4'methoxypropiophenone to 1-(4-methoxyphenyl)propan-1-ol followed by dehydration to anethole. Stoichiometric amounts of NaBH<sub>4</sub> and LiAIH<sub>4</sub> as reducing agent and concentrated sulfuric acid for dehydration were required.<sup>[13]</sup>

We investigated the feasibility of a green route for the synthesis of anethole from 4'-methoxypropiophenone using heterogeneous catalysts. Heterogeneous catalysts offer several advantages including recyclability of the catalyst and easy recovery of products.<sup>[14]</sup> 4'-Methoxypropiophenone can be readily synthesised from anisole and propionic anhydride, using zeolite H-Beta as an efficient solid acid catalyst.<sup>[15]</sup> Instead of using nonrecoverable reductants like NaBH<sub>4</sub> or LiAlH<sub>4</sub>, it is proposed to 4'-methoxypropiophenone to 1-(4-methoxyphenyl) reduce propan-1-ol by Meerwein-Ponndorf-Verley (MPV) transfer hydrogenation with a secondary alcohol as the reductant (Fig. 1). Although the atom economy of transfer hydrogenation is lower than direct hydrogenation using gaseous hydrogen, it is a safer alternative. Furthermore, it has the added advantage that precious metal catalysts need not be used.<sup>[16]</sup> For the subsequent dehydration step, a solid acidic catalyst advantageously replaces hazardous concentrated sulfuric acid. A dual functional catalyst capable of MPV transfer hydrogenation and dehydration should enable a direct transformation of 4'-methoxypropiophenone to anethole in one pot, eliminating the need for work-up steps to obtain the intermediate, 1-(4-methoxyphenyl)propan-1-ol.<sup>[17]</sup>

## **FULL PAPER**



Fig. 1. Proposed cascade MPV reduction and dehydration of 4'methoxypropiophenone to *trans*-anethole.

Zirconium-based catalysts are highly active for MPV reduction.<sup>[18]</sup> In particular, zirconium incorporated into the silica framework of zeolite beta shows excellent MPV reduction activity for a diverse range of substrates.<sup>[18c-g]</sup> Therefore, the feasibility of using Zr-Beta for the cascade MPV and dehydration reaction was first investigated in this study. Instead of the fluoride-assisted hydrothermal synthesis where the Si/Zr is limited to 75 or higher, a two-step post synthesis method was used to form the Zr-Beta with a high Zr content (Si/Zr 12.5). In the first step, Al-Beta with Si/Al 12.5 was dealuminated followed by introduction of zirconium via wet impregnation in the second step. This method allows the formation of zeolites with a high density of the catalytically active zirconium.<sup>[18a]</sup> The reaction mechanism for the MPV reduction is generally accepted to involve a cyclic six-membered transition state in which both the reducing alcohol and the carbonyl compound are coordinated to the same metal ion. Electron transfer from the oxygen of the carbonyl group to the lowest unoccupied molecular orbital of zirconium (dz<sup>2</sup>), activates the molecule and initiates a hydride transfer from the alcoholate.[19] Our previous study showed that Zr-Beta obtained by the two-step post synthesis method is more hydrophilic than the fluorideassisted sample, which is favourable for interaction with polar substrates. In view of the size of 4'-methoxypropiophenone, a catalyst with larger pores was synthesized for comparison. Mesoporous MSU-3 (in the nomenclature of MSU materials, the number "3" indicates that polypropylene oxide (PPO) polyethylene oxide (PEO) block copolymers were used as porogen) was chosen as the core material for substitution of zirconium into the silica framework. MSU-x mesostructures exhibit three-dimensional worm-like pore channels in contrast to the highly ordered mesoporous silicates such as M41S, SBA-15, KIT, etc.<sup>[20]</sup> It has been speculated that the interconnected random network of pores of MSU-3 could minimize diffusion limitations.<sup>[21]</sup> The synthesis of MSU materials requires neutral or mildly acidic conditions.<sup>[22]</sup> This is beneficial for the incorporation of zirconium as under more acidic conditions, the metal oxo-cation remains highly soluble, making it difficult to condense with the silica framework. The conditions necessary for zirconium incorporation into Zr-MSU-3 (hydrothermal treatment and addition of NaF) and the effect on catalytic activity are investigated in this study. The samples are denoted as SiZr-X-YD, where X and YD represent the Si/Zr molar ratio and hydrothermal duration (days), respectively.

#### **Results and discussion**

Physicochemical properties



Fig. 2. (a) Low and (b) high angle X-ray diffractograms of Zr-MSU-3 with varying Zr content.

The x-ray diffractograms of Zr-Beta show the characteristic peaks of zeolite beta (Fig. S1A). The position of the (302) peak at  $2\theta \sim 22.6^{\circ}$  is particularly sensitive to composition changes of the material. Dealumination of Al-Beta caused the (302) peak to shift towards higher angles as the spacing between the (302) planes, d<sub>302</sub>, decreased. Subsequently, with incorporation of zirconium into the Si tetrahedral framework, the d-spacing was increased to 3.921 Å. No diffraction planes corresponding to bulk ZrO<sub>2</sub> were observed.

The low angle x-ray diffractogram of the pure silica MSU-3 sample showed distinct and well resolved (100), (110) and (200) peaks, indicative of a 2D-hexagonal p6mm structure (Fig. 2a).<sup>[23]</sup> The peak intensity decreased with zirconium loading so that for SiZr-10-1D (Si/Zr 10), only the (100) peak was observed. The broadness of the peaks are typical of the MSU-X samples and are indicative of the formation of 3-dimensional disordered wormhole pore structure.<sup>[22, 24]</sup> A similar trend was observed for the samples formed in the presence of NaF as a condensation agent. The high angle x-ray diffractograms of the samples did not show any peaks of ZrO<sub>2</sub>, indicating that most of the zirconium was successfully incorporated into the silica framework (Fig. 2b). However, for the samples synthesized with the aid of NaF, peaks corresponding to zircon, ZrSiO<sub>4</sub> (PDF 03-0443), were observed. The intensity of the zircon diffraction peaks increased with zirconium loading. Increasing the duration of the hydrothermal treatment from 0 to 4 days for samples with Si/Zr 10 did not yield any significant changes in the x-ray diffractograms (Fig. S2).

Transmission electron micrographs of the pure Si-MSU-3 reveal the presence of well-ordered hexagonal channels with ~9.15 nm spacing (Fig. 3). This agrees well with the measured  $d_{100}$  ~9.20 nm from the x-ray diffractogram. Zirconium incorporation led to disruption of the long channels by increasing domains of disorder. For SiZr-10-1D, disordered wormhole pore structure was predominant with only small pockets of ordered channels. In contrast to the fluoride-free samples, the addition of NaF during synthesis resulted in better ordering of the channels with less disordered domains (Fig. S3).

The surface areas of the samples were  $520 - 730 \text{ m}^2 \text{ g}^{-1}$  (Table 1). In comparison, the Zr-Beta has a smaller surface area of 427 m<sup>2</sup> g<sup>-1</sup> with ~59 % due to the micropores. The nitrogen adsorption/desorption isotherms of the MSU-3 samples, with hysteresis loops between P/P° of 0.4 to 0.7, can be classified as a Type IV isotherm following the IUPAC convention (Fig. 4). The

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Fig. 3. TEM images for (a, b) Si-MSU-3 (c, d) SiZr-20-1D and (e, f) SiZr-10-1D.

pore sizes were calculated using the BJH model on the desorption isotherms. For SiZr-20-1D, the pores were in the range of 3.3 – 4.2 nm but decreased to 3.2 – 4.0 nm for SiZr-10-1D. The addition of NaF to the synthesis gel resulted in a bimodal pore distribution. This can be clearly seen in SiZr-10-1D-F where pores of ~3.2 – 4.0 nm and 5.2 – 6.1 nm formed. Furthermore, hydrothermal treatment of three days or longer led to larger pores with a wider distribution. The increase in the average pore diameter can be explained by the expulsion of water from the hydrophilic shell of the hybrid micelle.<sup>[25]</sup> With longer hydrothermal treatment, more water is lost from the hydrophilic PEO shells (from P123) of the hybrid micelles, stretching the PEO chains and resulting in larger pore sizes.<sup>[26]</sup>

Hydrothermal treatment of the synthesis gel was important for the incorporation of zirconium into the siliceous framework. Without any hydrothermal treatment, the Si/Zr ratio in SiZr-10-0D was only 11.1, less than in the synthesis gel. On the other hand, the Si/Zr molar ratio of the samples that had been subjected to hydrothermal treatment was between 9.6 - 10.3, close to the expected value of 10 (Table 1). The duration of hydrothermal treatment on the synthesis gel from 1 to 4 days did not



Fig. 4. (a) Nitrogen adsorption-desorption isotherms and (b) pore size distribution of mesoporous Zr-MSU-3 samples.

Table 1. Textural and chemical properties of Zr-MSU-3, Zr- and Al-Beta.

Sample	S <sub>BET</sub> (m <sup>2</sup> /g)	V <sub>pore</sub> (cm <sup>3</sup> /g)	Si/Zr	B/L <sup>[a]</sup>
Si-MSU-3	520	0.86	-	n.d.
SiZr-20-1D	730	0.93	19.9	0.24
SiZr-20-1D-F	713	1.13	20.8	0.17
SiZr-10-0D	615	0.56	11.1	n.d.
SiZr-10-1D	611	0.56	10.3	0.30
SiZr-10-1D-F	600	0.76	9.6	0.23
SiZr-10-3D	665	0.71	9.9	n.d.
SiZr-10-4D	583	0.64	10.2	n.d.
Zrβ-12.5	427 (251) <sup>[b]</sup>	0.84 (0.14) <sup>[b]</sup>	12.0	0.25
Alβ-12.5	568 (362) <sup>[b]</sup>	1.04 (0.19) <sup>[b]</sup>	-	0.80

[a] Brønsted/Lewis acid sites from pyridine IR after evacuation at 200 °C.[b] microporous area and volume.

significantly affect the Si/Zr ratio. These results confirm that the synthesis condition for MSU-3 is suitable for introduction of zirconium ions into the silica framework even to Si/Zr ~10. Elemental mapping analysis with SEM/EDS showed that the zirconium was uniformly dispersed throughout the particles (Fig. S4). Using diffuse UV/vis spectroscopy, the isolated nature of Zr<sup>4+</sup> in the tetrahedral configuration was inferred from the absorption at ~203–210 nm which has been ascribed to ligand-to-metal charge transfer from O<sup>2-</sup> to isolated Zr<sup>4+</sup> in tetrahedral configuration.<sup>[19a, 27]</sup> The absence of bulk ZrO<sub>2</sub> in Zr-MSU-3 samples is supported by the lack of a sharp absorption edge at ~240 nm (Fig. S5). The local environment of zirconium was deduced from <sup>29</sup>Si MAS NMR and XPS. The <sup>29</sup>Si spectrum of Si-MSU-3 shows two peaks, at ~ -110 ppm and -103 ppm in the Q<sup>4</sup>

and Q<sup>3</sup> range, which can be assigned to Si(4Si) and Si(3Si, 1OH), respectively (Fig. S6). The incorporation of zirconium in the framework is supported by a higher Q<sup>3</sup>/Q<sup>4</sup> intensity and the appearance of a small signal at - 91 ppm, in the Q<sup>2</sup> range.<sup>[28]</sup> The state of zirconium at the surface was studied using XPS. In bulk ZrO<sub>2</sub>, the binding energies of Zr 3d<sub>5/2</sub> and Zr 3d<sub>3/2</sub> are observed at 182.2 and 184.6 eV (Fig. S7). For Zr-Beta and Zr-MSU-3, these peaks are shifted to higher binding energies, in agreement with reported values for zirconium in silica framework.<sup>[29]</sup> The formation of Zr-O-Si bonds results in a more electropositive Zr<sup>4+</sup> as compared to zirconium in Zr-O-Zr due to a more electronegative Si<sup>4+</sup>. Consequently, the binding energy of Zr<sup>4+</sup> in the silica framework is higher than for ZrO<sub>2</sub>.

The substitution of zirconium into silica is known to create acidic sites which can be detected using ammonia TPD.<sup>[30]</sup> The desorption of ammonia occurred in a broad peak with onset at ~120 °C and extending to ~450 °C for the Zr-MSU-3 and Zr-Beta samples, showing that the samples had similar acid strengths. The broad desorption profiles indicate that the sites had a wide range of acid strength (Fig. 5). The density of acid sites for the Zr-MSU-3 samples was between 0.44-0.57 mmol g<sup>-1</sup> while it was only 0.31 mmol g<sup>-1</sup> for Zr-Beta. In contrast, only a very small desorption peak could be observed for Si-MSU-3 and dealuminated Beta samples, reflecting the low acidity of silica. The pyridine IR measurements showed the presence of both Brønsted (B) and Lewis (L) acid sites in the samples (Figs. 6 and S8). The adsorption of pyridine at Lewis acid sites is indicated by bands at ~1447-1460 cm<sup>-1</sup>, ~1575, and 1600-1630 cm<sup>-1</sup>, while the pyridinium ion formed by adsorption of pyridine at Brønsted acid sites shows bands at ~ 1540-1550 and 1640 cm<sup>-1</sup>. The peak at ~1490 cm<sup>-1</sup> is attributed to both Brønsted and Lewis acidities.<sup>[31]</sup> The relative density of Brønsted/Lewis acid sites were obtained from the areas of the 1545 and ~1447 cm<sup>-1</sup> peaks, respectively, after normalizing with the respective molar extinction coefficients.<sup>[31b]</sup> The B/L ratio for Zr-Beta was 0.25 while SiZr-20-1D and SiZr-10-1D have ratios of ~0.24 and 0.30, respectively (Table 1). The close B/L ratios suggest that the samples have very



Fig. 5. Ammonia TPD of (a) Si-MSU-3 (b) SiZr-20-1D (c) SiZr-20-1D-F (d) SiZr-10-1D (e) SiZr-10-1D-F (f) dealuminated Beta and (g) Zr-Beta-12.5.



Fig. 6. FTIR spectra of pyridine after evacuation at 200 °C for SiZr-20-1D, SiZr-20-1D-F, SiZr-10-1D, SiZr-10-1D-F and Zr-Beta-12.5.

similar acidic properties. In comparison, Zr-MSU-3 samples synthesized with NaF had lower acid density and smaller B/L ratios than those synthesized under fluoride-free conditions. After evacuation at 300 °C, the intensity of the pyridine peaks were reduced, indicating that the Zr-containing samples were of weak to moderate acidity. This contrasts with Al-Beta-12.5 which has pronounced Brønsted acidity with a high B/L ratio of 0.80. The intensity of the pyridine adsorption peaks remained high even after heating at 300 °C (Fig. S8a). Furthermore, the 1445 cm<sup>-1</sup> peak shifted to higher wavenumbers with increase of evacuation temperature, showing the presence of strong Lewis acid sites.

#### **Catalytic Activity**

#### Effect of mesoporosity

The initial MPV reduction and dehydration of 1 mmol 4'methoxypropiophenone in 10 mL of pentanol was carried out at 120 °C with 200 mg of an Al-Beta zeolite (Si/Al=12.5). However, the conversion of 4'-methoxypropiophenone was below 1 % even after 45 h (Table 2). Instead, autoetherification of 2-pentanol to 2-(pentan-2-yloxyl)pentane occurred which can be attributed to the presence of strong acid sites on the catalyst. In contrast, Zr-Beta-12.5, showed much better performance (Fig. 7a). The desired cascade reaction occurred with anethole forming the bulk of the products. After 45 h, 87.1% of 4'-methoxypropiophenone was converted with 90.5 % selectivity to anethole (3) (78.8 % yield). The trans:cis isomers were formed in the ratio of 92:8, similar to that for natural anethole. Besides anethole, about 2.4 % of the ether, 1-methoxy-4-(1-(pentan-2-yloxy) propyl)benzene (2), was detected (Scheme 1). This could be formed by etherification between the MPV product, 1-(4-methoxyphenyl)propan-1-ol (1), and 2-pentanol and/or by addition of 2-pentanol to anethole. However, the latter route can be ruled out as the ether concentration reached a maximum of ~ 4.5 % before decreasing, suggesting reversibility of the reaction. If the ether was formed by the second pathway, its concentration would be expected to grow with time as the concentration of anethole increased. At longer reaction times, 1-methoxy-4-propylbenzene (4) was detected which was due to transfer hydrogenation of C=C bond in the formed anethole. Notably, no side products due to acid-catalyzed

etherification or dehydration of 2-pentanol could be detected. Another striking feature is that the MPV product, 1-(4methoxyphenyl)propan-1-ol (1), was not observed, showing that once formed, it was rapidly dehydrated to anethole. The presence of Zr is necessary for the reaction as the siliceous Si-MSU-3 showed no activity.

Despite its activity, the rate of reaction over Zr-Beta is rather low. This is possibly due to the microporous zeolitic structure which limits access of bulky substrates to the active sites within the channels. The rate was increased when the Zr-MSU-3 material, SiZr-20-1D, was used as a catalyst. Despite a smaller zirconium content (Si/Zr = 20), the initial TOF (based on 4'methoxy propiophenone converted after 3 h per Zr site) was 0.14 h<sup>-1</sup> as compared to 0.11 h<sup>-1</sup> for Zr-Beta (Table 2). After 45 h, a higher conversion of 98.5 % was obtained (Fig. 7b). The selectivity to anethole remained high, 89.1 %, of which 93 % was trans-anethole. With SiZr-10-1D where zirconium content was closer to that of Zr-Beta, the reaction time was significantly shortened, so that close to 99 % conversion was obtained after 34 h (Fig. 8a). The yield of anethole increased to 89.7 % (92:8 trans:cis). The ether side product 2 was slightly higher. 4.3 %. than for Zr-Beta which is most probably caused by the larger pore size. In addition,



**Fig. 7.** Cascade MPV reduction and dehydration over (a) Zr-Beta-12.5 and (b) SiZr-20-1D. Reaction conditions: 1 mmol 4'-methoxypropiophenone, 10 mL 2-pentanol, 200 mg catalyst, 120 °C. (○) 4'-methoxypropiophenone (●) *trans*-anethole (▲) *cis*-anethole (♦) ether and (■) 1-methoxy-4-propylbenzene.



Scheme 1. Cascade reactions of *p*-methoxypropiophenone to anethole and side products.

Sample	TOF	Conv.	Selectivity (%) <sup>[b]</sup>		
	(h <sup>-1</sup> ) <sup>[a]</sup>	(%) <sup>[b]</sup>	Anethole (trans:cis)	2	4
deAl-Beta	0	0	-	-	-
Alβ-12.5	-	< 1	-	-	-
Zrβ-12.5	0.11	87.1	90.5 (92:8)	2.8	6.7
Si-MSU-3	0	0	-	-	-
SiZr-20-1D	0.14	98.5	89.1 (93:7)	2.8	8.1
SiZr-20-1D-F	0.13	79.5	74.2 (90:10)	23.4	2.4
SiZr-10-1D	0.14	98.1	91.5 (92:8)	4.1	4.4
SiZr-10-1D-F	0.13	90.5	77.1 (90:10)	20.3	2.6

[a] after 3 h

[b] after 34 h for SiZr-10-1D and SiZr-10-1D-F and 45 h for others.

some anethole underwent further transfer hydrogenation at the C=C bond to form 1-methoxy-4-propylbenzene.

As the duration of hydrothermal synthesis led to larger pore diameters as well as a wider distribution of pore sizes (Fig. 4), these effects on the catalytic activity were examined (Fig. S9). However, the most active catalyst was SiZr-10-1D, which had the smallest average pore size (3.6 nm) as well as the narrowest spread of pore size distribution of the samples. The initial rate of reaction (within 3 h) and anethole yield after 30 h were highest with this sample, suggesting an optimum pore size for the reaction.

The results show that the combination of Lewis and Brønsted acid sites on Zr-Beta and Zr-MSU-3 effectively catalysed the MPV reduction cascade and dehydration of 4'methoxypropiophenone. The tetrahedrally-sited framework Zr<sup>4+</sup> serves as the Lewis acid site for coordination of the carbonyl compound and the reducing alcohol for hydride transfer.<sup>[18]</sup> The presence of Brønsted acid sites with moderate strength facilitates the dehydration of 1-(4-methoxyphenyl)propan-1-ol to anethole, without competing acid-catalyzed side products. Although dehydration can be catalysed by Lewis acid sites, studies have shown that Brønsted acid sites are more active for alcohol dehydration.<sup>[32]</sup> In mixed oxides, protons associated with hydroxyl groups bridging Si and Zr form Brønsted acid sites which can be detected by pyridine IR spectroscopy. In addition, Brønsted acid sites can be created during the reaction as shown by Kung's group in a recent study on supported Sn complexes.<sup>[33]</sup> The binding of an alcohol to the Sn center forms an alkoxide and the released hydrogen is transferred to the neighbouring Sn-O-Si bond to form a Brønsted acid site.

#### Effect of zircon

Attempts to synthesize Zr-MSU-3 with even higher zirconium loading by this method were unsuccessful due to loss of ordered mesoporosity. Therefore, samples were synthesized with NaF as condensation catalyst. Although the materials had a bimodal pore distribution with bigger pores, the rate of reaction was decreased for both SiZr-10-1D-F and SiZr-20-1D-F and lower yields of anetholes were obtained as compared to the catalysts synthesized without NaF (Figs. 8b and S10). From the kinetic profiles, the concentration of the ether side product 2 built up to ~25 % before decreasing slowly with time. This clearly shows that the fluoride-synthesized catalysts were less efficient in the hydrolysis of the ether. From ammonia TPD, it was found that these samples have lower acid concentration which could be

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**Fig. 8.** MPV reduction and dehydration over (a) SiZr-10-1D and (b) SiZr-10-1D-F. Reaction conditions: 1 mmol 4'-methoxypropiophenone, 10 mL 2-pentanol, 200 mg catalyst, 120 °C. ( $\bigcirc$ ) 4'-methoxypropiophenone ( $\bullet$ ) *trans*-anethole ( $\blacktriangle$ ) *cis*-anethole ( $\blacklozenge$ ) ether and ( $\blacksquare$ ) 1-methoxy-4-propylbenzene.

attributed to the presence of crystalline zircon (Fig. 2b). The poor acidity of zircon has been reported previously by Melero et al.<sup>[34]</sup>

#### Effect of hydrogen donor

In the MPV reaction, the solvent also serves as the hydrogen donor. Hence, different solvents were investigated. Normally, isopropanol is the preferred reducing agent as the evaporation of the acetone formed in the reaction shifts the equilibrium towards product formation. However, the conversion was only 11.0 % after 30 h with 45 % selectivity to anethole (Table 3). Instead a substantial amount of 1-(4-methoxyphenyl)propan-1-ol was present, indicating that its dehydration to anethole was hindered (Fig. S11a). In an open system, the use of isopropanol as the hydrogen donor restricts the reaction temperature to 82 °C. As dehydration is an endothermic process, this temperature is probably too low for dehydration to occur as well as for removal of any water formed. To increase the reaction temperature, linear secondary alcohols with higher boiling points such as 2-butanol and 2-pentanol were used. With 2-butanol, the conversion of 4'methoxypropiophenone was slightly higher, 29.1 % (Fig. S11b). It notable that in 2-butanol at 100 °C, is 1-(4methoxyphenyl)propan-1-ol was not observed showing that its dehydration was no longer limited. The use of 2-pentanol at 120 °C resulted in a significant rate increase and the conversion was 90.6 % after 30 h. Due to the higher boiling point of 2pentanol, energy for the reaction as well as removal of water drove the reaction forward. For comparison, the reactions were also conducted in an autoclave. At 120 °C, the conversions were higher for 2-propanol and 2-butanol than under reflux. However, for 2-pentanol, only 30.8 % conversion was obtained as the 2pentanone and water formed remained in the closed system.

The effect of co-solvent was also investigated, keeping the ratio of 4'-methoxypropiophenone:2-pentanol between 1:1 to 1:10. However, it was difficult to find a suitable co-solvent. With anisole (4-methoxybenzene), the MPV product, 1-(4-methoxyphenyl) propan-1-ol (1), unexpectedly underwent C-C coupling and formed 1,1-bis(methoxylphenyl) propanes (Table S1). Increasing the alcohol to substrate ratio from 1:1 to 10:1 resulted in higher conversion, showing that excess alcohol did not inhibit the MPV reduction (Fig. S12). In polar aprotic DMF, the conversion was < 3 % even after 45 h. With dichlorobenzene, *o*- and *p*-xylene,

 Table 3. Influence of solvent types on conversion of 4'-methoxypropiophenone in open<sup>[a]</sup> and closed<sup>[b]</sup> systems.

Solvent	Т	Conv.	Selectivity (%)			
	(°C)	(%)	Anethole 3	1	2	4
2-propanol <sup>[a]</sup>	82	11.0	45.1	52.9	0	2.0
2-propanol <sup>[b]</sup>	120	51.2	78.3	17.3	0	4.4
2-butanol <sup>[a]</sup>	100	29.1	45.9	0	38.5	2.2
2-butanol <sup>[b]</sup>	120	45.4	86.8	0	9.1	4.1
2-pentanol <sup>[a]</sup>	120	90.6	90.1	0	6.0	3.9
2-pentanol <sup>[b]</sup>	120	30.8	90.4	0	9.6	0

Reaction condition: 1 mmol 4'-methoxypropiophenone, 200 mg SiZr-10-1D; solvent (10 mL), after 30 h of reaction.

dimerization of anethole occurred. Such products have been reported to form on acidic HY zeolites or under photoirradiation.<sup>[35]</sup> The dimerization of anethole in the presence of an aprotic solvent suggests a built-up of the molecule at the catalyst surface. Hence, for the designed cascade reactions to occur, it is best to use the alcohol as the reductant and solvent. Apparently, the high concentration of the alcohol helps in desorbing the anethole once it is formed, enabling a high selectivity to the desired product.

#### Optimization of reaction

The effect of substrate to catalyst ratio (S/C) was investigated using SiZr-10-1D. With a S/C ratio of 1.64, the conversion reached 84.7 % after 45 h. However, only about 50 mole % of the products formed was anethole. Of the side products, a significant fraction was ether 2 as its concentration reached a maximum of 34.4 mole % at 30 h before decreasing slightly to 33.2 mole % at 45 h (Fig. 9a). Lowering the S/C ratio increased the reaction rate and the ether concentration decreased. At a S/C ratio of 0.41, the ether concentration was < 1.3 % at 100 % conversion (Fig. 9b). However, the higher catalyst loading resulted in further hydrogenation of anethole to 1-methoxy-4-propylbenzene. Its concentration increased from < 1.5 to 36 mole % when the S/C ratio decreased from 0.66 to 0.16. While the enhancement in reaction rate can be attributed to an increase in the density of Lewis acid active sites, its effect on selectivity of the products is interesting. At the lowest catalyst loading, the high ether concentration indicates that there are insufficient acidic sites for



Fig. 9. Cascade MPV reduction and dehydration using S/C ratio of (a) 1.64 and (b) 0.41 in 10 mL 2-pentanol at 120 °C. (○) 4'-methoxypropiophenone; (●) trans-anethole (▲) cis-anethole (◆) ethers and (■) 1-methoxy-4-propylbenzene. Catalyst: SiZr-10-1D.

the hydrolysis. In contrast, at high catalyst loading, there are enough acid sites so that transfer hydrogenation at the C=C bond of anethole also occurred. Thus, an optimal S/C ratio is needed to ensure high selectivity to anethole.

The substrate concentration was next investigated. The reaction rate dropped drastically when the substrate concentration was decreased from 0.10 to 0.07 or 0.05 mol/L (Fig. 10). After 45 h, the conversion was only ~66 % due to the more dilute reaction conditions. A substantial proportion, 18 - 37 mole %, of the products comprised of the ether (2) rather than the desired anethole (Fig. S13). These results lend support to the hypothesis that etherification of the MPV product, 1-(4methyoxyphenyl)propan-1-ol, competes with its dehydration to anethole. Although the etherification reaction is reversible, excessive amounts of 2-pentanol (2-pentanol:4'methoxypropiophenone > 140: 1) shifted the equilibrium to the ether formation. At 0.20 mol/L substrate concentration, a higher reaction rate and a higher selectivity to anethole were achieved. After 23 h, 100 % conversion was reached with 91.2 % anethole vield.



Fig. 10. Anethole yield versus 4'-methoxypropiophenone concentration: (-) 0.20 (--) 0.10 (---) 0.07 and (...) 0.05 mol/L at 120 °C. Catalyst: SiZr-10-1D, 200 mg, S/C 0.82.

#### Recyclability of Zr-MSU-3

After the reaction, SiZr-10-1D was recovered by centrifugation, washed with ethanol and dried in an oven at 80 °C. It was recalcined at 500 °C for 5 h to remove any remaining organic residues. The conversion for three successive runs remained high with no significant change in the selectivity to anethole (Fig. 11).





The Si/Zr mole ratio of the sample recovered after three runs remained at 10.4, indicative that no leaching of Zr had occurred during reaction. Therefore, the mesoporous SiZr-10-1D is a useful recyclable heterogenous catalyst for the one-pot cascade transformation of 4'-methoxypropiophenone to anethole.

#### Conclusions

A direct one-pot synthesis of anethole was successfully carried out by MPV reduction of 4'-methoxypropiophenone to 1-(4methyoxyphenyl)propan-1-ol followed by its dehydration. The cascade reactions were efficiently catalyzed by mesoporous Zrcontaining MSU-3 with a high density of zirconium active sites. Hydrothermal treatment of the synthesis gel at 100 °C for one day resulted in guantitative incorporation of zirconium into the silica, forming Zr-MSU-3 with Si/Zr of 10. The material possessed a disordered wormhole structure which allowed easier access to active sites within the pore channels. In comparison, the cascade reactions were slower when a microporous Zr-Beta zeolite was used as catalyst. Compared to lower alcohols, the use of 2pentanol as solvent and hydrogen donor in the MPV reaction enabled a high reaction rate and also facilitated the dehydration of 1-(4-methyoxyphenyl)propan-1-ol. A high anethole yield of ~90 % was obtained over SiZr-10-1D. The catalyst could be reused with no observable loss of activity after three cycles.

#### **Experimental Section**

#### Synthesis of Zr-beta and Zr-MSU-3

The two-step post-synthesis method for Zr-Beta zeolite was carried as follows.<sup>[18a]</sup> Commercial Al-Beta zeolite (Si/Al 12.5, Zeolyst CP814E) was first calcined at 500 °C for 6 h before dealumination in 12 M nitric acid at 80 °C for 20 h (10 mL g<sup>-1</sup>). The dealuminated zeolite was recovered by filtration, washed with deionized water and dried overnight at 80 °C. It was suspended in water and a calculated amount of Zr(NO<sub>3</sub>)<sub>4</sub> to give Si/Zr 12.5 was added. The slurry was heated under stirring to remove the water, dried overnight at 80 °C in an oven and calculated at 600 °C for 8 h.

Zr-MSU-3 with Si/Zr molar ratio of 10 and 20 were synthesized by a one pot hydrothermal method. In a typical synthesis, solution A was prepared by dissolving 1 g of Pluronic® P-123 (Sigma Aldrich) in a 100 mL beaker containing 50 mL deionised water at 35 °C, followed by the addition of zirconyl oxychloride octahydrate, ZrOCl<sub>2</sub>·8H<sub>2</sub>O (Merck). Solution B containing 5 g of tetraethyl orthosilicate (TEOS) (Sigma Aldrich), 0.5 mL of 2 M HCl and 5 mL deionized water was stirred at room temperature till the TEOS was fully hydrolysed. Subsequently, solution B was added to solution A, stirred for 22 h and placed in a Teflon-lined stainless autoclave. The mixture was hydrothermally treated at 100 °C for various duration (0 4 days). The resulting precipitate was recovered by centrifugation, washed with deionized water and dried overnight in an oven at 90 °C. The sample was calcined in a muffle furnace at 500 °C for 5 h. The samples were denoted as SiZr-X-YD, where X and YD represent the Si/Zr molar ratio and hydrothermal duration (days), respectively. To investigate the effects of sodium fluoride as a condensation catalyst, 0.02 g of NaF was added to the solution A and the final calcined samples were denoted as SiZr-X-YD-F.

## **FULL PAPER**

#### Characterization

X-ray diffractograms were measured using a Bruker D8 x-ray diffractometer. A step size of 0.005° and a dwell time of 0.02 s was used in the low-angle range,  $2\theta \sim 0.5$  to  $4^\circ$ , with the aid of a knife edge accessory to cut off the direct beam. High angle measurements for  $2\theta \sim 10$  to  $80^{\circ}$ were taken using a step size of 0.02° and a dwell time of 0.02 s. The surface area and porosity were determined by nitrogen adsorption/desorption (Micromeritics Tristar 3000). Pore size distributions were calculated using the Barrett-Joyner-Halenda (BJH) model. Prior to the measurement, samples were thoroughly degassed at 300 °C under nitrogen flow for 5 h. <sup>29</sup>Si MAS NMR spectra were measured on a Bruker Avance Neo 400 WB spectrometer with a 4 mm double resonance MAS probe operating at a resonance frequency of 79.49 MHz. The measurement parameters are: spinning rate of 12 kHz, 20 ms acquisition time, 593 ppm sweep width, 3  $\mu$ s pulse length, 100 kHz 1H decoupling and a recycle delay of 20 s. The chemical shifts were referenced to DSS (4,4dimethyl-4-silapentane-1-sulfonic acid) as the secondary standard at -10.2 ppm. The Si/Zr molar ratio was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The samples were dissolved with HNO<sub>3</sub>/HF/H<sub>2</sub>O (1 mL/0.5 mL/1 mL) using microwave digestion. Temperature programmed desorption (TPD) of ammonia was used to evaluate the strength and density of acid sites of the samples. Approximately 0.15 g of sample was placed in a quartz reactor and pretreated under a flow of helium at 500 °C for 2 h. The sample was cooled to 100 °C before dosing with NH<sub>3</sub> for 15 minutes. After flushing with helium at 100 °C for 1 h to remove any physically adsorbed ammonia, the sample was heated at 10 °C/min to 500 °C. The evolved ammonia was monitored using a guadrupole mass spectrometer (Balzers QMS 200), Pyridine infrared spectra were recorded on a PerkinElmer Spectrum II spectrometer with a resolution of 4 cm<sup>-1</sup>. The samples were pressed into self-supported wafers of 8-10 mg and mounted in a quartz IR cell with CaF2 windows. The samples were evacuated under vacuum (10<sup>-3</sup> mbar) for 2 h at 300 °C. After cooling to room temperature, a background spectrum was recorded. Pyridine was introduced for 15 min before evacuating the system for an hour and measuring the spectrum at room temperature. Further IR measurements were made after evacuation at 100, 200 and 300 °C for one hour. Transmission electron microscopy (TEM) was carried out using a JEOL 3010 transmission electron microscope operated at 300 kV. About 5 mg of the finely ground sample was suspended in 5 mL of 2-propanol and after sonication, a drop of the suspension was placed onto a carbon coated grid and dried at room temperature overnight. Scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS) was carried out on a JEOL JSM-6701F SEM (field-emission) equipped with JEOLJED-2300 EDS system at a resolution of 136 eV. The electron beam for the scanning electron microscope and digital X-ray mapping were 5 kV and 15 kV, respectively. The samples were placed on double sided carbon tape and coated with Pt for SEM/EDS measurements. X-ray photoelectron spectroscopy (XPS) was carried out on a VG Scientific Escalab Mark 2 spectrometer, equipped with a twin anode x-ray source, Omicron EA125 U7 hemispherical electron spectrometer and a 7-channel detector. Spectra were obtained using a magnesium anode (Mg = 1253.6 eV) operating at 300 W. The powdered samples, placed on double sided tape, were analyzed using a constant analyzer energy of 20 eV with 15° emission angle and an analyzing area of 3.0 nm (diameter). The C 1s adventitious carbon line at 284.6 eV was used for charge referencing. The diffuse reflectance spectra (DRS) were taken using a Shimadzu UV-2450 UV-Visible spectrophotometer with BaSO<sub>4</sub> as standard.

#### Catalytic activity

In a typical reaction, 1 mmol (0.164 g) of 4'-methoxypropiophenone, 10 mL of 2-pentanol and 0.2 g of catalyst were added to a 25 ml two-necked round bottom flask. The reaction mixture was heated to reflux (120  $^{\circ}$ C). Besides

2-pentanol, other secondary alcohols such as 2-propanol and 2-butanol were tested as well. For comparison, the reaction was also carried out in a 25 ml Parr autoclave at 120 °C. Other parameters investigated include (i) 4'-methoxypropiophenone to catalyst ratio (S/C, g/g) from 0.41 to 1.64 in 10 mL 2-pentanol and (ii) 4'-methoxypropiophenone concentration from 0.05 to 0.2 mol/L, using SiZr-10-1D as catalyst. Aliquots were removed at different intervals and analyzed with an Agilent HP 6890 gas chromatograph equipped with a HP-5 capillary column and a flame ionization detector. The reaction products were identified by gas chromatography-mass spectrometry (GC-MS).

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#### Entry for the Table of Contents (Please choose one layout)

Layout 1:

## FULL PAPER

Zirconium-incorporated MSU-3 is an active dual functional catalyst with accessible 3-dimensional wormhole pore structure and Lewis acidic sites. Through a cascade of MPV transfer hydrogenation and dehydration, 4'methoxypropiophenone is efficiently transformed to anethole with yields up to 90 %.



Hongwei Zhang, Candy Li-Fen Lim, Muhammad Zaki, Stephan Jaenicke and Gaik Khuan Chuah(s)\*

Page No. – Page No.

A dual-functional Zr-MSU-3 catalyst for cascade MPV reduction and dehydration of 4'methoxypropiophenone to anethole