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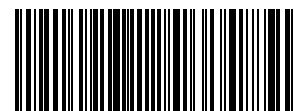
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FEATURE ARTICLE

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Synergy between Brønsted acid sites and Lewis acid sites

Selvedin Telalović,^a Jeck Fei Ng,^b Rajamanickam Maheswari,^c
Anand Ramanathan,^d Gaik Khuan Chuah^b and Ulf Hanefeld^{*a}

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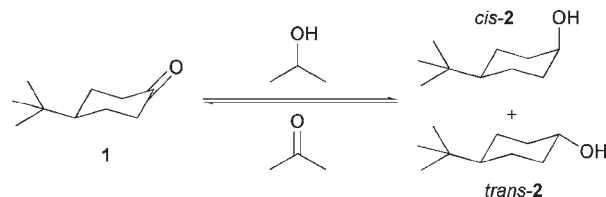
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Synergy between Brønsted acid sites and Lewis acid sites in mesoporous Al-Zr-TUD-1 was demonstrated to exist in Brønsted acid catalysed reactions, but not in Lewis acid catalysed reactions.

Heterogeneous acidic catalysts are of great importance for the environmentally benign synthesis of bulk and fine chemicals.¹ Zeolites and mesoporous silicates (MPS) in particular have been widely used for this purpose.^{2,3} While purely siliceous zeolites and MPSs show low acidity, Brønsted and Lewis acidity can be imparted by the incorporation of metals such as Al into the framework of these materials. The influence of the Brønsted acid sites on the Lewis acid sites (and *vice versa*) in the thus obtained materials has long been a topic of debate. In particular, possible synergy was and is a focus of interest. A recent study on dealuminated HY zeolite supports the notion that synergy does indeed exist, demonstrating interactions between Al induced Brønsted and Lewis acid sites.⁴ While Al induces both Brønsted and Lewis acid sites, tetrahedrally coordinated Zr tends to impart only Lewis acidity to the material.^{5,6} It should therefore be possible to vary the ratio of Brønsted and Lewis acid sites in a material by incorporating both metals in different ratios. When Al-Zr-beta was prepared, only marginal synergy was observed in the isomerisation of *m*-xylene,⁷ while adding Zr to Al-MCM-41 only allowed for an increase of its Lewis acidity in line with the amount of Zr added, no experiments to probe for a possible synergy effect were performed.⁸

Recently we prepared Al-TUD-1, a sponge like MPS with a three dimensional pore structure.^{3,9} This Brønsted and Lewis acidic material proved to be a good catalyst in the Friedel–Crafts alkylation.¹⁰ In contrast, the novel Zr-TUD-1 was demonstrated to have exclusively Lewis acidity.^{11,12} It catalysed the Meerwein–Ponndorf–Verley (MPV) reduction of **1**, a reaction that is catalysed by Lewis acids only (Scheme 1).^{13–15} It also showed activity in the Prins cyclisation of citronellal **3**, a Brønsted and Lewis acid catalysed reaction (Scheme 2).^{12,16–18} Based on these results we designed a series of mixed Al-Zr-TUD-1s with different Al/Zr ratios and an

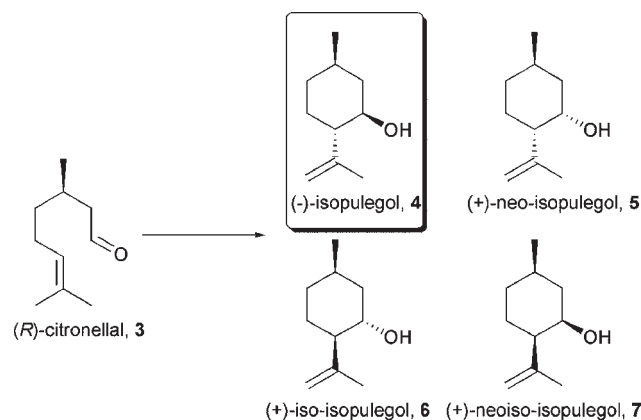


Scheme 1 Meerwein–Ponndorf–Verley reduction of 4-*tert*-butyl cyclohexanone.

overall Si/M ratio of 25. By comparing the activity of these catalysts with physical mixtures of Al-TUD-1 and Zr-TUD-1 with Si/M of 25, synergy should become detectable.

Al-Zr-TUDs with Si/M ratios of 25 and Al : Zr ratios of 3 : 1, 2 : 2 and 1 : 3 (denoted Al-Zr-3:1-TUD-1, Al-Zr-2:2-TUD-1 and Al-Zr-1:3-TUD-1) were prepared in an analogous manner to Al- and Zr-TUD-1, *via* a one-pot procedure based on the sol–gel technique.^{10,12} Triethanolamine as a complexing reagent for both Al and Zr ensured their incorporation as isolated species, a process also known as the “atrane route”.¹⁹ The three catalysts obtained were mesoporous with surface areas, pore volumes and pore diameters comparable to the earlier prepared Al-TUD-1 and Zr-TUD-1 (Table 1). While the composition of the M-TUD-1s is identical to the synthesis mixture and thus highly predictable when only one metal is introduced, some deviation from the composition of the synthesis mixture was observed for the Al-Zr-TUDs. This might be due to differences in ionic radii of the tetrahedral Al(III), Zr(IV) and Si(IV) in the framework.

HR-TEM and powder X-ray diffraction studies unambiguously demonstrated the material to be structured and mesoporous, containing no crystalline phase (Fig. 1). This strongly indicates that both Al and Zr are framework incorporated in



Scheme 2 Prins cyclisation of citronellal yields isopulegol and its stereoisomers.

^a Gebouw voor Scheikunde, Technische Universiteit Delft, Julianalaan 136, 2628 BL Delft, The Netherlands. E-mail: u.hanefeld@tudelft.nl; Fax: +31 15 278 1415; Tel: +31 15 278 9304

^b Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 11754, Republic of Singapore. E-mail: chmeggk@nus.edu.sg; Fax: +65 6779 1691; Tel: +65 6516 2839

^c Department of Chemistry, Anna University, Chennai – 600025, India. E-mail: maheswarianand@annauniv.edu

^d Department of Chemistry, National Institute of Technology, Tiruchirappalli – 620015, India. E-mail: ranand@nitt.edu

Table 1 Physical properties of Al-TUD-1, Zr-TUD-1 and the different Al-Zr-TUD-1s

M-TUD-1	Synthesis mixture		After calcination ^a		$S_{\text{BET}}^b/\text{m}^2 \text{g}^{-1}$	$d_{\text{P,BJH}}^c/\text{nm}$	$V_{\text{P,BJH}}^d/\text{cm}^3 \text{g}^{-1}$	Uptake $\text{NH}_3/\text{mmol g}^{-1e}$
	$n_{\text{Si}}/n_{(\text{Al}+\text{Zr})}$	$n_{\text{Si}}/n_{\text{Al}}$	$n_{\text{Si}}/n_{\text{Zr}}$	$n_{\text{Si}}/n_{(\text{Al}+\text{Zr})}$				
Zr-TUD-1	25	—	25	25	764	8.8	1.23	0.69
Al-Zr-1:3-TUD-1	25	92	45	30	877	3.3	0.70	0.38
Al-Zr-2:2-TUD-1	25	47	69	28	686	4.6	0.85	0.32
Al-Zr-3:1-TUD-1	25	31	135	25	705	4.2	0.70	0.33
Al-TUD-1	25	26.6	—	26.6	956	3.7	0.95	0.40

^a From elemental analysis. ^b Specific surface area. ^c Mesopore diameter from adsorption branch. ^d Specific mesopore volume. ^e Data from NH_3 -TPD.

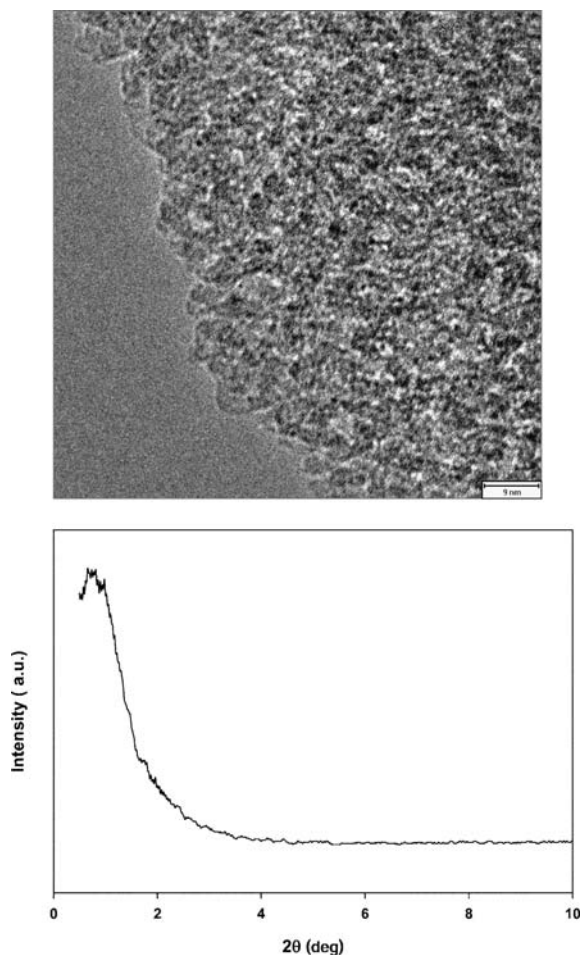
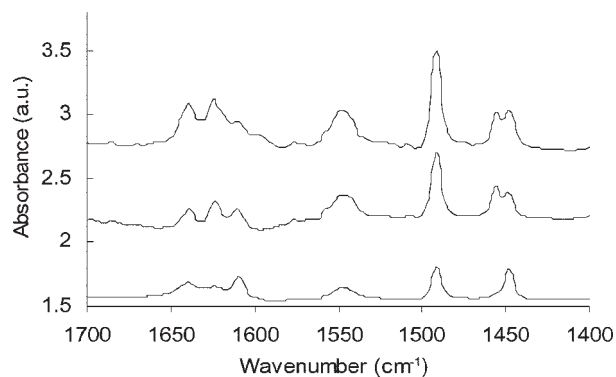
the Al-Zr-TUD-1s, similar to Al-TUD-1 and Zr-TUD-1. Temperature-programmed desorption (TPD) of ammonia revealed that Al-TUD-1 and all the Al-Zr-TUD-1 samples have a very similar total acidity, while Zr-TUD-1 differs significantly (Table 1). This is surprising and might indicate that Al strongly influences the overall acidity of the materials.

FT-IR spectra of Al-Zr-TUD-1 samples after pyridine desorption at 200 °C clearly show the presence of Brønsted (1547 cm^{-1}) and Lewis acidity (Al: 1456 cm^{-1} ,¹⁰ Zr: 1448 cm^{-1} ,¹² Fig. 2). With an increase of Zr the signal for the Lewis acidic site due to Al decreases, as does that for Brønsted acidity. Overall the ratio Brønsted/Lewis acidity decreases from approximately 1.1 for Al-Zr-3:1-TUD-1 and

Al-Zr-2:2-TUD-1 to 0.7 for Al-Zr-1:3-TUD-1. Thus a range of MPS materials with either Al or Zr or mixtures thereof was available to study the influence of Brønsted acid sites on Lewis acid sites and *vice versa*.

In order to probe for synergy between Brønsted acid sites and Lewis acid sites, the Lewis acid catalysed MPV reduction of **1** was investigated (Scheme 1). Reaction conditions were chosen to match earlier optimisation studies.¹² Reduction of **1** in all cases yielded *cis*-**2** and *trans*-**2** in ratio *cis* : *trans* of ~13 : 87, in line with a non-selective reduction.¹² As expected for a Lewis acid catalysed reaction, Zr-TUD-1 catalysed the reaction significantly better than Al-TUD-1, which has a less Lewis acidic character (Fig. 3A). With increasing Zr content Al-Zr-3:1-TUD-1, Al-Zr-2:2-TUD-1 and Al-Zr-1:3-TUD-1 display increasing activity in the MPV reduction (Fig. 3B). In order to evaluate whether the Al-induced and Zr-induced acidity influence each other in the Al-Zr-TUD-1s, physical mixtures of Al-TUD-1 and Zr-TUD-1 with the same metal-concentration as in Al-Zr-TUD-1 were also tested (Fig. 3A). This revealed that the activities of all samples were dependent only on the concentration of Zr in the sample and virtually independent of the Al-concentration. This clearly demonstrates that there is no synergy between Brønsted acid sites and Lewis acid sites in the MPV reduction of **1**.

In dealuminated zeolite HY, synergy between Brønsted acid sites and Lewis acids sites was shown to be present.⁴ However, no reaction demonstrating this was performed. Since no synergistic influence of Brønsted acid sites on Lewis acid sites could be detected in the MPV reduction, we then turned to the Prins cyclisation of citronellal (**3**), yielding isopulegol (**4**) and its stereoisomers **5–7**. Employing earlier described reaction

**Fig. 1** HR-TEM (top, the bar represents 9 nm) and XRD (bottom) of Al-Zr-1:3-TUD-1.**Fig. 2** FT-IR spectra after pyridine desorption at 200 °C: top Al-Zr-3:1-TUD-1, middle Al-Zr-2:2-TUD-1 and bottom Al-Zr-1:3-TUD-1.

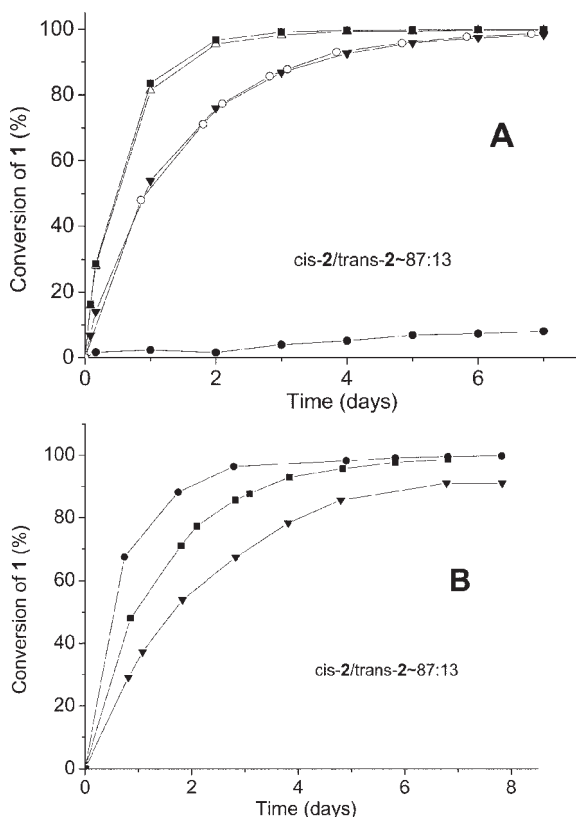


Fig. 3 Reduction of **1** over Al- and Zr-TUD-1 catalysts. Reaction conditions: 2 mmol **1**, 4 ml isopropanol, 80 °C, 50 or 100 mg catalyst. A: ● Al-TUD-1 (50 mg), ■ Zr-TUD-1 (50 mg), ○ Al-Zr-2:2-TUD-1 (50 mg), ▼ Al-TUD-1 (25 mg) and Zr-TUD-1 (25 mg), △ Al-TUD-1 (50 mg) and Zr-TUD-1 (50 mg); B: ▼ Al-Zr-3:1-TUD-1 (50 mg), ■ Al-Zr-2:2-TUD-1 (50 mg), ● Al-Zr-1:3-TUD-1 (50 mg).

conditions, this Brønsted acid catalysed reaction was performed with Zr-TUD-1, Al-TUD-1, Al-Zr-3:1-TUD-1, Al-Zr-2:2-TUD-1 and Al-Zr-1:3-TUD-1 (Fig. 4). Zr-TUD-1 had the lowest activity, while Al-TUD-1 displayed significantly higher activity. Remarkably, the activities of all Al-Zr-TUD-1s were higher than that of either Zr-TUD-1 or Al-TUD-1. As the metal concentration in the mixed Al-Zr-TUD-1s is the same as in either Zr-TUD-1 or Al-TUD-1 and given the fact that the overall acidity is virtually identical to Al-TUD-1 and lower than Zr-TUD-1 this is unambiguous proof of synergy between the Al induced Brønsted acid sites and the Zr induced Lewis acid sites.

In conclusion, mixed Al-Zr-TUD-1 samples clearly demonstrate synergy for the Brønsted acid catalysed Prins cyclisation of **3**. In contrast, no synergy was observed in the Lewis acid catalysed MPV reduction of **1**.

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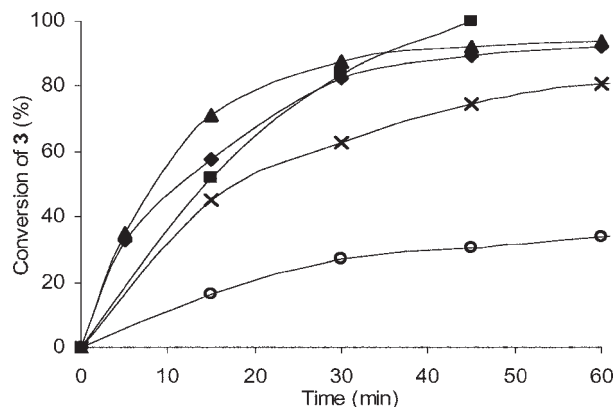


Fig. 4 Cyclisation of **3** over Al- and Zr-TUD-1 catalysts. Reaction conditions: 4 mmol **3**, 5 g toluene, 80 °C, 50 mg catalyst. (○) Zr-TUD-1, (×) Al-TUD-1, (■) Al-Zr-1:3-TUD-1, (◆) Al-Zr-2:2-TUD-1 and (▲) Al-Zr-3:1-TUD-1.

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