

## Phenol hydroxylation using Ti- and Sn-containing silicalites†

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New bimetallic framework and non-framework titanium and tin silicalite have been investigated for phenol hydroxylation with H<sub>2</sub>O<sub>2</sub> in different solvents, and the optimized catalyst composition showed 26% higher initial rate than reference TS-1.

Ti-containing molecular sieves have been in great demand in oxidation reactions since the invention of Ti-containing silicalite (TS-1) in 1983.<sup>1</sup> These include the commercially practiced reaction of phenol hydroxylation to dihydroxybenzenes, hydroquinone (HQ) and catechol (CT), and benzoquinone (BQ) with aqueous hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) as illustrated below.<sup>2</sup>

Many studies have been devoted to this reaction. Some reaction parameters such as solvent effects, catalyst properties (external surface, pore size, and crystal size), and different metal incorporation have been identified for TS-1.<sup>3–11</sup>

Recently, UOP LLC's scientists investigated the redox-silicalites, incorporated with both titanium and tin into the framework structure (Ti–Sn–S-1) for epoxidation of olefins.<sup>12</sup> Ti–Sn–S-1 shows excellent improved catalytic activity and stability. Its activity was unchanged even after several hundred hours of use. Moreover, the literature shows that the isomorphous incorporation of Sn into the beta-zeolite framework results in a unique catalyst. Sn-Beta showed enzyme-like selectivity in some oxidation reactions, because the catalyst acidity was optimized.<sup>12</sup>

In this work Ti–Sn–S-1 was used for the phenol hydroxylation with H<sub>2</sub>O<sub>2</sub> and its catalytic activity was compared to TS-1. In order to understand the effect of Sn on the reaction, the different Sn incorporated catalysts were synthesized in framework and non-framework positions.

The reference catalyst, TS-1, was obtained from NCL Pune, India. Ti–Sn–S-1 and Sn–S-1 were prepared according to the literature.<sup>13</sup> Ti or Sn impregnated on Sn–S-1 and TS-1 were prepared *via* impregnation with Ti(OC<sub>3</sub>H<sub>7</sub>)<sub>4</sub> in ethanol or SnCl<sub>4</sub> × H<sub>2</sub>O in water. The impregnated catalyst was calcined at 550 °C for 2 h.

All catalyst samples were characterized by different techniques (Chemical Composition, XRD, SA, Porosity, NH<sub>3</sub>-TPD, and SEM). The relevant characterisation results are summarized in Table 1. The XRD results indicated that all catalyst samples contained the well-defined single-phase XRD patterns and were consistent to those already reported for TS-1.<sup>†</sup>

The phenol hydroxylation was carried out in a high-pressure-resistant tube (Aldrich, Catalog # Z-18, 106–4) placed in a

Table 1 Catalyst characterization summary

Catalyst	Si/Ti <sup>a</sup>	Si/Sn <sup>a</sup>	BET surface area/m <sup>2</sup> g <sup>-1</sup>	Crystal size/nm	NH <sub>3</sub> -TPD/mmol NH <sub>3</sub>
TS-1	54	—	398	204	0.030
Sn–S-1	—	270	455	189	0.072
Ti–Sn–S-1 [1]	57	3830	404	174	0.040
Ti–Sn–S-1 [2]	62	527	420	155	0.049
Ti–Sn–S-1 [3]	97	100	446	126	0.106
Sn on TS-1 <sup>b</sup>	56	510	400	204	0.036
Ti on Sn–S-1 <sup>c</sup>	54	270	400	189	0.059

<sup>a</sup> Si to Ti or Sn molar ratio; <sup>b</sup> Sn was impregnated on calcined TS-1; <sup>c</sup> Ti was impregnated on calcined Sn–S-1

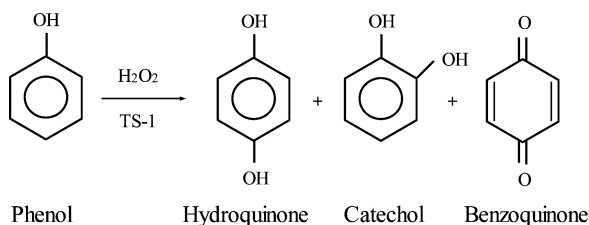
stirring block heater. The reaction was performed at atmospheric pressure with H<sub>2</sub>O<sub>2</sub> (30 wt% in water, Aldrich) at 60 °C for 6 h. Typically, 1 wt% of catalyst was used with a phenol to H<sub>2</sub>O<sub>2</sub> molar ratio of 2 : 1. The products were collected and analyzed using a gas chromatograph equipped with a PONA (Hewlett Packard) capillary column. Peroxide consumption was determined by iodometric titrations (ASTM, D 2340–96).

First we studied the effect of solvent (Table 2) using TS-1 and Ti–Sn–S-1 [1]. We found that in water, the hydroxylation reaction was very fast and selective to the desired products, (HQ and CT) although there was some BQ produced in the system. This is most likely related to the interaction of water with the hydrophilic Ti sites and the strong adsorption between water and phenol, which can enhance the conversion.<sup>14</sup> However, this adsorption, has been observed only when the Ti active sites are incorporated in the framework. BQ, produced during the reaction, was believed to change to tar. This tar can plug the catalyst pores and then decrease catalytic activity.<sup>4</sup> When solvents, which can dissolve the tar, such as acetonitrile, methanol, and acetone, were used, good performance and solubility were observed. Furthermore, higher BQ selectivity was also observed. This suggests that BQ formation may occur more on catalyst pores than the external surface. However, more work is needed for a more comprehensive understanding. For practical applications in this work, water was chosen for detailed study.

Table 2 Phenol hydroxylation using H<sub>2</sub>O<sub>2</sub> at 60 °C in different solvents with various catalysts after 6 h

Catalyst	Solvent	Phenol conversion (%)	Selectivity (%)	
			HQ <sup>a</sup> + CT <sup>b</sup>	BQ <sup>c</sup>
TS-1	Water	50.0	97.7	2.3
	Acetonitrile	29.0	93.7	6.3
	Methanol	26.1	81.6	18.4
	Acetone	15.0	66.4	33.6
Ti–Sn–S-1[1]	Water	50.0	99.1	0.9
	Acetonitrile	31.9	100.0	–
	Methanol	31.4	96.7	3.3
	Acetone	17.3	78.8	21.2

<sup>a</sup> Hydroquinone; <sup>b</sup> Catechol; <sup>c</sup> Benzoquinone



† Electronic supplementary information (ESI) available: XRD pattern of Ti–Sn–S-1s. See <http://www.rsc.org/suppdata/cc/b3/b303455k/>

**Table 3** Phenol hydroxylation using H<sub>2</sub>O<sub>2</sub> at 60 °C in water with different catalysts after 6 h

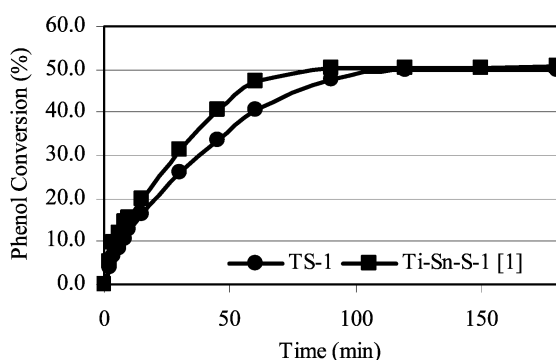
Catalyst	Conversion (%)		Selectivity (%)	
	Phenol	H <sub>2</sub> O <sub>2</sub>	HQ <sup>a</sup> + CT <sup>b</sup>	BQ <sup>c</sup>
1. TS-1	50.0	99.9	97.7	2.3
2. Sn-S-1	1.4	35.0	95.3	4.7
3. Ti-Sn-S-1 [1]	50.0	99.9	99.1	0.9
4. Ti-Sn-S-1 [2]	46.8	99.5	98.8	1.2
5. Ti-Sn-S-1 [3]	38.6	94.4	99.2	0.8
6. Sn on TS-1	47.5	99.4	98.4	1.6
7. Ti on Sn-S-1	5.0	37.6	88.8	11.2

<sup>a</sup> Hydroquinone; <sup>b</sup> Catechol; <sup>c</sup> Benzoquinone

We tested the synthesized catalysts in water under the same standard conditions. According to Table 3, Ti-Sn-S-1 [1] and TS-1 show similar final conversions to products. Nevertheless, the kinetic study of TS-1 and Ti-Sn-S-1 [1] (Fig. 1) shows that the Ti-Sn-Silicalite [1] converted phenol to dihydroxy compounds faster than TS-1. The initial reaction rate is  $6.4 \times 10^{-8}$  and  $8.1 \times 10^{-8}$  mol m<sup>-2</sup> s<sup>-1</sup> for TS-1 and Ti-Sn-S-1 [1], respectively. This means that the small amount of Sn incorporation results in 26% higher activity than TS-1. However, only Sn incorporation generated a silicalite catalyst with much less activity than TS-1 (Table 3, exp. 2).

When a small amount of Sn was incorporated (exp. 4 and 5), two main catalyst properties were modified; smaller crystal size and higher acidity (see Table 1). Generally, the liquid phase zeolite catalyzed reactions are controlled by the diffusion step; the smaller crystal size catalyst gives the higher catalytic activity.<sup>6</sup> However, when Sn incorporation was increased, the increased acidity has more effect on the phenol conversion than the decreasing crystal size.

The acidity of Ti-Sn-S-1s increased with the increasing of Sn incorporation. The NH<sub>3</sub> adsorption data (Table 1) indicate that increasing of Sn incorporation increased the acid strength of the catalyst. Sn incorporation may alter the reaction mechanism by changing the adsorption of phenol and phenol hydroxylation products thereby increasing the phenol conversion.<sup>13,14</sup> The small increase in acidity has the benefit for of the faster adsorption of phenol, and results in a faster reaction.



**Fig. 1** Phenol conversion at 60 °C vs. time.

When the acid strength is too high, the products desorption is probably limited and the catalyst is deactivated faster; hence relative catalytic activity is lower.

Furthermore, when more Sn was incorporated, the catalytic activity decreased. This indicated that not all Sn introduced was active. Some of Sn was in the form of Sn<sup>6+</sup> or SnO<sub>2</sub>. Both of which are not active for the phenol hydroxylation.

Non-framework incorporation of Sn by impregnation, exp.6, gave a catalyst with a lower performance than TS-1 or Ti-Sn-S-1 [1], which contains framework Sn atoms. The reason for this is because the active Sn sites are only on the external surface and some of them are in the non-active form. When Ti is impregnated on Sn-S-1 (exp.7), a non-framework catalyst, its activity is lower than TS-1. This is due to Ti sites that are only on the external surface. Some of them are in the non-reactive form such as TiO<sub>2</sub> or anatase, which is not active for the phenol hydroxylation but is active for hydrogen peroxide decomposition.

In summary, Ti-Sn-S-1 opens up an alternative for the phenol hydroxylation with H<sub>2</sub>O<sub>2</sub> to dihydroxybenzenes. The highest product selectivity to hydroquinone and catechol was achieved with water as a solvent. Sn incorporated in TS-1 framework promoted greater catalytic activity for phenol hydroxylation in comparison to TS-1 due to crystal morphology and acidity optimization and/or modification. The framework of Ti or Sn incorporation is critical for the phenol hydroxylation.

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