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Effect of Stannic Species Modification on the Acidity of Silicalite-1 and Its Enhancement in Transforming Ethylenediamine to Heterocyclic Amines

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Abstract: In this study, a series of SnO₂ modified zeolite catalysts (Snx-S-1; x is the weight percentage of Sn) were prepared with SnCl₂ and a defective Silicalite-1 (S-1) zeolite via facile deposition–precipitation method. It was found that the stannic species modified all-silica zeolite catalysts were active for the intermolecular condensation of ethylenediamine (EDA) to 1, 2-Diazabicyclo [2, 2, 2] octane (TEDA) and piperazine (PIP). The best catalyst Sn6-S-1 (6 wt.% Sn loading) showed 86% EDA conversion and 93% total selectivity to TEDA and PIP. By contrast, the defective S-1 zeolite parent showed only approximately 9% EDA conversion under the same conditions. With the help of catalyst characterization techniques including hydroxyl vibration and pyridine adsorption FT-IR spectroscopy (transmission mode), the enhancement of the catalytic activity of the SnO₂ modified zeolite catalysts (Snx-S-1) was mainly attributed to the formation of mild Lewis acid sites in the siliceous zeolite. Both the hydroxyl nests of the defective S-1 zeolite and the dispersed SnO₂ clusters should be the important factors for the formation of mild Lewis acid sites on the modified zeolite. Based on the catalytic performance of the modified zeolite in the conversion of EDA to PIP and TEDA, it is inferred that the mildly acidified defective S-1 zeolite by the SnO₂ deposition modification might become a very active and durable catalyst for reactions involving strongly alkaline reactants and products.

Keywords: defective Silicalite-1; SnO₂ modification; acidity; condensation of ethylenediamine

1. Introduction

Zeolitic solid acids with strong acidic sites have attracted attention in the past because they are good catalysts for a long list of hydrocarbon transformation reactions in both oil refining and petrochemical industries [1]. Aluminosilicate zeolites are generally strongly acidized, and they belong to a big family that has already more than 200 different topologic structures so far [2]. However, the conversions of reactants with strong basicity such as nitrogen-containing compounds [3], which are useful reactions for the synthesis of functional organic molecules, often need zeolitic solid acids with mild acidity. One important example of this kind of reaction is the conversion of ethylenediamine (EDA) to heterocyclic amines like 1, 2-Diazabicyclo [2, 2, 2] octane (TEDA) and piperazine (PIP). TEDA is an excellent catalyst for producing polyurethane foams [4], while PIP has found a lot of applications in medical and industrial fields [5]. PIP can also be used as an antioxidant to scavenge free radicals and as a promoter for the removal and recovery of CO_2 [6].

In the 1990s, H-ZSM-5 zeolite had been used as catalyst for the conversion of EDA to TEDA and PIP [7,8]. Generally, H-ZSM-5 zeolite has high initial EDA conversion, but it deactivates fast due to the strong adsorption of highly alkaline EDA, TEDA, and PIP on the strong acid sites (bridging



hydroxyl groups) of H-ZSM-5 zeolite. For this reason, some modification methods such as alkali metal ion modification [7] and dealumination [9], etc. have been proposed to weaken the strength of acidic sites in H-ZSM-5. However, such efforts often cause negative effects such as worse diffusivity due to pore channel blocking. In 2003, titanium silicalite-1 (TS-1) was patented for the reaction of EDA to TEDA and PIP [10]. Later, people conducted a detailed study on the intermolecular condensation of EDA to make PIP and TEDA over TS-1 zeolite [11]. Silicalite-1 (S-1) zeolite is an aluminum-free crystalline silicate with the same MFI topological framework as the Al-containing ZSM-5 zeolite and Ti-containing silicate zeolite (TS-1). It is well known that the presence of defective sites in S-1 lattice can form mild acidity (silanol nests). The defective S-1 zeolite has been reported as an active Beckmann rearrangement catalyst [12–15]. However, previous study indicated that the defective S-1 zeolite itself was not very active and selective for the reaction of EDA to TEDA and PIP, giving only 19.5% EDA conversion and 7.5% TEDA selectivity [11]. This implies that the acidity of defective S-1 is too weak to be an efficient catalyst for the conversion of EDA.

In recent years, $Sn-\beta$ zeolite has attracted increasing attention because its isolated framework Sn is an active Lewis acid site for many reactions, including Baeyer–Villiger oxidation, sugar isomerization, and Meerwein–Ponndorf–Verley reaction [16,17]. Sn-MFI zeolite was also found active for the hydroxylation of phenol [18] and the synthesis of N-methylaniline by aniline alkylation with methanol [19], etc. Sn-containing zeolites can be obtained by direct hydrothermal synthesis. However, the direct hydrothermal synthesis is a time-consuming, corrosive, and noxious route due to the use of a large amount of HF. Recently, Dapsens et al. [20–22] developed an alkaline-assisted metalation method to prepare Sn-MFI zeolite by simply contacting a commercial S-1 zeolite with a Sn-containing alkaline solution. It seems that the alkaline-assisted metalation strategy is environmentally benign and relatively easy to scale up.

In this study, inspired by the Lewis acidity of Sn- β zeolite and the facile alkaline-assisted metalation strategy in making Sn-containing zeolite, we attempted to enhance the acidity of a defective S-1 zeolite by introducing different amounts of Sn into the defective S-1 zeolite with deposition–precipitation (DP) method. In this way, a series of Sn-containing S-1 zeolites with different Sn loadings were obtained and characterized by different techniques. The intermolecular condensation of EDA to TEDA and PIP was also employed as a probe reaction to characterize the catalytic performance of the acidity of the Sn-containing S-1 zeolites. Results indicate that the introduction of Sn species into the defective S-1 is a good way to activate the originally less active material, which showed remarkably enhanced catalytic activity and selectivity in the conversion of EDA compared with the defective S-1 zeolite parent. To the best of our knowledge, such work has not been reported so far. We think that the Sn-containing S-1 zeolite, as a kind of mild solid acid catalyst, might find many applications in the future, especially in the area of transforming strongly alkaline N-containing organic molecules.

2. Results and Discussion

2.1. Sn Species and their Locations in the Modified Defective S-1 Zeolite

First of all, we would like to note that when the defective S-1 zeolite was used as parent for the DP modification (see experimental section for detail), the resulted catalysts were coded as Snx-S-1, where x denoted the weight percentage of Sn in the catalyst. For the purpose of comparison, a "perfect" S-1 zeolite (coded as Si-S-1) with low density of hydroxyl nests was prepared by treating the defective S-1 zeolite parent with $(NH_4)_2SiF_6$ aqueous solution. The Si-S-1 zeolite together with a fume SiO₂ matrix were also subjected to the DP modification, and the resulting catalysts were named Sn3-Si-S-1 and Sn3-fume SiO₂, respectively. Here, the Sn loading was fixed at 3 wt.%.

The scanning electron microscope (SEM) characterization revealed that the defective S-1 zeolite parent was composed of 400–500 nm clean plate crystals. However, the surface of Sn-containing samples (Snx-S-1, x = 1, 3, 6, 8) was attached by a lot of small aggregates, as shown by Figure 1. As the number of the aggregates in the samples increased with Sn loading (Snx, x = 1, 3, 6, 8 (wt.%)), it is

reasonable to assign them to Sn species. Table 1 indicates that treating the defective S-1 zeolite parent by the DP method only caused a marginal decrease of the zeolitic specific surface area and that the decrease was mainly due to the decline of external surface area. In view of the fact that the external surface of the Sn-containing zeolitic samples (Snx-S-1) was attached by many small aggregates of Sn species, the decline of their external surface area is reasonable.



Figure 1. SEM images of Sn-containing defective S-1 (Snx-S-1) zeolite samples.

Sample	Sn content (wt.%)	S _{BET} (m ² g ⁻¹)	S _{micro} (m ² g ⁻¹)	S _{extra} (m ² g ⁻¹)	V_{tol} (cm ³ g ⁻¹)	V _{micro} (cm ³ g ⁻¹)
S-1	0	379	288	91	0.23	0.14
Sn1-S-1	1	371	279	92	0.23	0.13
Sn3-S-1	3	361	298	63	0.23	0.15
Sn6-S-1	6	366	300	66	0.23	0.14
Sn8-S-1	8	364	289	76	0.22	0.13

Table 1. Textural properties of defective S-1 zeolite and its Sn-containing counterparts (Snx-S-1).

Figure 2 shows the UV–VIS spectra of Sn-containing catalysts with different matrixes (A) and the Sn-containing defective S-1 zeolite catalysts with different Sn loadings (B). So far, the UV–VIS spectroscopic technique has been widely used as an informative characterization method for Sn species

in Sn-containing zeolites and molecular sieves [16]. Generally, from UV–VIS spectra, three kinds of Sn species have been identified in these Sn-containing materials. They are isolated tetracoordinated framework Sn species, nano-sized SnO₂ clusters, and bulky SnO₂ particles, corresponding to UV absorption at about 200–220 nm, 230–255 nm, and 280–290 nm, respectively [20,23–26]. In the present work, the absence of 200–220 nm absorption band for the Sn-containing samples with different matrixes (Figure 2A) and the Sn-containing defective S-1 zeolite samples with different Sn loadings (Figure 2B) indicates that there is substantially no isolated tetrahedral Sn species in these Sn-containing materials. That is, the DP process used in this study did not introduce Sn atoms into the zeolitic framework of S-1. However, all the samples had absorption bands at around 230 nm and 270 nm instead, and their intensities gained with the increase of Sn loading. Thus, from the absorption bands at around 230 nm and 270 nm, it is concluded that the Sn species in the catalysts of this study should mainly exist in the forms of hexa-coordinated nano-sized SnO₂ clusters and bulky SnO₂ species.



Figure 2. UV–VIS spectra of Sn-containing catalysts with different matrixes (**A**) and the Sn-containing defective S-1 zeolite catalysts with different Sn loadings (**B**).

The H₂-TPR profiles in Figure 3 show that, roughly speaking, there are two kinds of hydrogen-consuming peaks in the Sn-containing catalysts. The peak centered at around 500 °C could be assigned to nano-sized SnO₂ clusters, while the other peak centered around 600 °C could be assigned to the bulk SnO₂ species [27]. The profiles of H₂-TPR suggested that the defective S-1 zeolite matrix facilitated the formation of nano-sized SnO₂ clusters in the catalyst (Sn3-S-1), while the "perfect" S-1 zeolite matrix that had low density of hydroxyl nests led to the formation of more bulky SnO₂ particles and fewer SnO₂ clusters in the catalyst (Sn3-Si-S-1). In addition, for the defective S-1 zeolite matrix, the increase of the Sn loading resulted in the increase of the content of bulky SnO₂ particles. This is easy to understand. Nevertheless, it is interesting to note that the deposition of SnO₂ onto the amorphous fume SiO₂ matrix also formed a large number of nano-sized SnO₂ clusters. To this, we speculate that the abundant surface silanols of fume SiO₂ should be attributed.



Figure 3. H_2 -TPR profiles of Sn-containing catalysts with different matrixes (**A**) and the Sn-containing defective S-1 zeolite catalysts with different Sn loadings (**B**).

As shown in Figure 4, in agreement with the previous study [28], the hydroxyl stretching FT-IR spectra of the fume SiO_2 matrix had a very intensive and sharp band at 3745 cm⁻¹ in its IR spectrum. This band can be assigned to the stretching mode of surface isolated silanols. The tail at the low-frequency side of the main band was a complex, which is supposed to relate to the stretching mode of geminal silanols and weakly perturbed vicinal silanols [28]. In short, the surface of the amorphous fume SiO₂ matrix was rich in hydroxyls, and at least part of them were relatively active (for example, the weakly perturbed vicinal silanols). Different from the fume SiO_2 , the hydroxyl IR spectrum of the defective S-1 zeolite featured three weak bands at 3740 cm⁻¹, 3725 cm⁻¹, and 3680 cm⁻¹, and one large and broad band centered at around 3450 cm⁻¹. These bands could be assigned to external surface isolated silanols, internal surface isolated silanols, weakly hydrogen-bonded vicinal silanols, and medium-strength hydrogen-bonded silanol nests, respectively [29]. Except for the external surface isolated silanols, the other internal surface hydroxyls were expected to be located in the hydroxyl nests of the defective S-1 zeolite. Compared with the defective S-1 zeolite, a big difference of the "perfect" S-1 zeolite, Si-S-1, obtained with $(NH_4)_2SiF_6$ aqueous solution treatment was the lack of both 3680 cm⁻¹ and 3450 cm^{-1} bands. This means that the treatment of the defective S-1 zeolite with $(NH_4)_2SiF_6$ had effectively repaired most of the defects of the original zeolite parent. When 3 wt.% Sn was deposited into these matrixes by DP method, it was easy to find that the absorptions of all the silanol groups on the different matrixes became weakened to certain degrees (Figure 4B–D). This phenomenon indicates that SnO₂ was deposited on both external and internal surfaces of the S-1 zeolites. From Figure 5 it can be seen that when Sn loading was small (e.g., Sn loading 3.0 wt.%), the deposit of the Sn resulted in relatively more considerable attenuation of 3450 cm⁻¹, 3680 cm⁻¹, and 3725 cm⁻¹ bands, if the intensity of the 3740 cm⁻¹ band is used as a reference. This means that at low-level Sn loading, the SnO₂ species were mainly deposited into the internal hydroxyl nests of the defective S-1 zeolite. As was mentioned above in the H₂-TPR characterization, at such a low Sn loading level the SnO₂ species mainly existed as nano-sized SnO_2 clusters. When Sn loading was big enough (8.0 wt.%, for example), on the other hand, the deposit of SnO₂ on the defective S-1 zeolite also resulted in the obvious attenuation of the 3740 cm⁻¹ band as well. This indicates that the excess SnO₂ species were deposited on the external surface of the defective S-1 zeolite if Sn loading was high. Therefore, the results of hydroxyl stretching FT-IR spectroscopy agreed well with those of H₂-TPR characterization.



Figure 4. Hydroxyl stretching FT-IR spectra of different samples: S-1, Si-S-1, and fume SiO₂ matrixes (**A**); fume SiO₂ and Sn3-fume SiO₂ (**B**); S-1 and Sn3-S-1 (**C**), Si-S-1 and Sn3-Si-S-1 (**D**).



Figure 5. Hydroxyl stretching FI-IR spectra of defective S-1 and the Sn-containing defective S-1 zeolite catalysts with different Sn loadings.

2.2. Acidity of the Sn-Containing Defective S-1 Zeolite

Pyridine adsorption FT-IR spectroscopy is currently a commonly adopted method for determining the type and number of acid sites of Sn-containing zeolites and molecular sieves. According to the literature reports [30–37], the Sn-containing zeolites and molecular sieves mainly have Lewis acid sites, and they usually give pyridine absorption bands in the range of 1450 to 1455 cm⁻¹ and 1610 to 1615 cm⁻¹. These bands are often accompanied by another important band at 1490 cm⁻¹, which is generally considered as the contribution of pyridine adsorbed on both Brønsted acid sites and Lewis acid sites. However, in the Sn-containing zeolites and molecular sieves, Brønsted acid sites (1540–1545 cm⁻¹) are seldom detectable unless a small number of trivalent metal ions such as Al³⁺ ions appear in the zeolitic framework as a result of impurity or survival [25,34]. Therefore, in the cases of Brønsted acid sites being undetectable, the band at around 1490 cm⁻¹ was directly assigned to Lewis acid sites by some researchers [31,33]. In addition to the abovementioned features, the bands related to hydrogen-bonded pyridine (at ca. 1445, 1485, and 1596 cm⁻¹) [37] and the bands belonging to physically adsorbed pyridines (at ca. 1438 and 1589 cm⁻¹) [11] may also be observed. In some studies, there are bands in between 1575 and 1581 cm⁻¹, though their assignments are still disputed [11,35].

The pyridine adsorption FT-IR spectra of Sn-containing catalysts with different matrixes and Sn-containing defective S-1 zeolite catalysts with different Sn loadings are shown by Figures 6 and 7. The dependences of the number of Lewis acid sites of the catalysts on matrix and Sn loading are illustrated by Figure 8, where the number of Lewis acid sites of the catalysts was determined with the 1455 cm⁻¹ band on the their pyridine adsorption FT-IR spectra evacuated at 350 °C, following the reported procedures [38,39]. From Figure 6A it can be seen that, after being evacuated at 200 °C, all the Sn-containing samples except the one obtained with fume SiO₂ matrix exhibited very similar absorption bands, corresponding to physically adsorbed pyridines (1438 cm⁻¹ and 1589 cm⁻¹), hydrogen-bonded pyridines (1446 cm⁻¹, 1485 cm⁻¹, and 1598 cm⁻¹), and the Lewis sites bonded pyridines (1455 cm⁻¹ and 1614 cm⁻¹, both were shoulder peaks), respectively. The typical feature of Brønsted acid sites in the range of 1540 to 1545 cm⁻¹ was not detectable for all Sn-containing samples of this study. However, from the complex in the region of 1450 to 1500 cm⁻¹, the 1490 cm⁻¹ band can be found. Therefore, by referring to what has been done in the literature [31,33], here we simply assign the 1490 cm⁻¹ band to the pyridines adsorbed on Lewis sites. Different from the Sn-containing zeolitic samples, which had a very intensive absorption band at around 1580 cm⁻¹ and an intensive band complex in the area of 1450 to 1500 cm^{-1} , Sn-containing fume SiO₂ catalyst had a weak band at 1580 cm^{-1} and a very weak band in the area of 1450 to 1500 cm⁻¹. In addition, the Sn-containing fume SiO₂ catalyst also lacked the bands at 1438 cm⁻¹ and 1614 cm⁻¹. After degassing at 350 °C, the bands related to physically adsorbed pyridines (1438 cm⁻¹ and 1589 cm⁻¹) basically disappeared. Meanwhile, the hydrogen-bonded pyridines related band at 1485 cm⁻¹, which was a component of the band complex in the area of 1450 to 1500 cm⁻¹, also disappeared due to the high-temperature treatment.

Figure 7 clearly shows that the defective S-1 zeolite only showed a small number of Lewis acid sites as indicated by the weak bands of pyridine adsorption (degassed at $350 \,^{\circ}$ C) at $1455 \,^{\circ}$ C) at $1450 \,^{\circ}$ C) at $1455 \,^{\circ}$ C) at $1455 \,^{\circ}$ C) at $1450 \,^{\circ}$ C) at $1455 \,^{\circ}$ C) at $1450 \,^{\circ}$ C) at $1450 \,^{\circ}$ C) at $1455 \,^{\circ}$ C) at $1450 \,^{\circ}$ C) at $1455 \,^{\circ}$ C) at $1450 \,^{\circ}$ C) at $1450 \,^{\circ}$ C) at $1455 \,^{\circ}$ C) at $1450 \,^{\circ}$ C) at 1450

After being treated by the DP method, SnO_2 species were deposited to the defective S-1 zeolite, which resulted in the pronounced increase of the intensities of the Lewis acid sites related absorption bands at 1455 cm⁻¹, 1614 cm⁻¹ and 1490 cm⁻¹. Furthermore, it seems that the increase of the Sn loading (when the Sn loading was less than 6 wt.%) was accompanied by the increase of the intensities of the Lewis acid related absorption bands at 1455 cm⁻¹, 1614 cm⁻¹. These phenomena

clearly indicate that the stannic species modification via the DP process can notably enhance the Lewis acid amount and acid strength of the defective S-1 zeolite. However, just as is indicated by Figure 7A, the same stannic species modification method does not give so many Lewis acid sites on the matrixes of amorphous fume SiO_2 and the "perfect" S-1 zeolite with low density of hydroxyl nests obtained with $(NH_4)_2SiF_6$ aqueous solution treatment. The influences of both matrix and Sn loading on the formation of Lewis acid sites on Sn-containing catalysts prepared with the DP process can be seen more clearly from Figure 8. It is obvious that the defective S-1 zeolite and its defect density are of significance for the acidity enhancement. Further, taking the H₂-TPR profiles (Figure 3) and the hydroxyls stretching FT-IR spectra of defective S-1 and the Sn-containing defective S-1 zeolite catalysts with different Sn loadings (Figure 5) into consideration, it is reasonable to think that the combination of nano-sized SnO₂ clusters with the hydroxyl nests of the defective S-1 zeolite should be the necessities of the increases of Lewis acid amount and acid strength in the S-1 zeolite.



Figure 6. Pyridine adsorption FT-IR spectra of Sn-containing catalysts with different matrixes (**A**) and Sn-containing defective S-1 zeolite catalysts with different Sn loadings (**B**) (thick lines: evacuated at 200 $^{\circ}$ C; thin lines: evacuated at 350 $^{\circ}$ C).



Figure 7. Pyridine adsorption FT-IR spectra (evacuated at 350 °C) of Sn-containing catalysts with different matrixes (**A**), Sn-containing defective S-1 zeolite catalysts with different Sn loadings (**B**) and the deconvolution of the main absorption band of Sn1-S-1 sample at low frequency (**C**).





Figure 8. Dependences of the number of Lewis acid sites (estimated with the 1455 cm⁻¹ band of pyridine adsorption FT-IR spectra after evacuation at 350 °C, following the procedures reported in [39,40]) of the Sn-containing catalysts on matrix (**A**) and Sn loading (**B**).

2.3. Catalytic Performance of the Stannic Oxide Modified Defective S-1 Zeolite

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In order to evaluate the catalytic performance of the acidity of defective S-1 zeolite and its Sn-containing counterparts, the intermolecular condensations of EDA to PIP and TEDA were chosen as a probe reaction. The main reaction paths of EDA on solid acid catalyst is as Scheme 1 [8,11].

$$\begin{pmatrix} NH_2 \\ NH_2 \end{pmatrix} + \begin{pmatrix} NH_2 \\ NH_2 \end{pmatrix} \longrightarrow \begin{pmatrix} H \\ N \\ N \\ H \end{pmatrix} + 2NH_3$$
(1)
(EDA) (PIP)

$$\begin{pmatrix} n \\ N \\ N \\ H \end{pmatrix} \longrightarrow \begin{pmatrix} N \\ N \end{pmatrix} + 3H_2$$
(3)

$$(NH_2 \longrightarrow CH_3NH_2 + CH_3CH_2NH_2$$
(4)

$$CH_{3}NH_{2} + CH_{3}CH_{2}NH_{2} + \left(\bigvee_{N}^{N} \right) \longrightarrow \left(\bigvee_{N}^{N} \right) + \left(\bigvee_{N}^{N} \right) + \left(\bigvee_{N}^{N} \right)$$
(5)

Scheme 1. The main reaction paths of ethylenediamine (EDA) over solid acid catalyst [8,11]. ((1)–(2): Main reactions; (3)–(5): Side reactions).

The condensation of EDA over solid acid catalyst is commonly conducted at atmospheric pressure and gas-phase condition. The reactant and the major products involved are of strong organic bases. Accord to literature [41], the gas-phase basicity (GB) of EDA, PIP, and TEDA are very close to that of pyridine. Moreover, the heterocyclic amines like PIP and TEDA also have a similar molecule structure to pyridine. This is one of the reasons why the intermolecular condensation of EDA was selected as a probe reaction for studying the catalysts' reaction performance.

Figure 9 shows that the conversion of EDA over bulk SnO_2 and fume SiO_2 was near zero. Both the defective S-1 zeolite and the "perfect" S-1 (Si-S-1) zeolite with low density of hydroxyl nests have inferior activity for the conversion of EDA as well. However, the activity of the former was much higher than that of the latter. Looking back to the acidity characterization in Figure 7B, one can see that the defective S-1 zeolite matrix certainly had a little acidity as indicated by the appearance of a small absorption band at 1490 cm⁻¹ after evacuation at 350 °C, but the acidity of the "perfect" Si-S-1 zeolite, especially that of the fume SiO₂, was too weak to be observed at evacuation at 350 °C. Therefore, the conversions of EDA over different matrixes agreed well with the acidities of these siliceous materials. The modification of fume SiO₂, Si-S-1, and S-1 with SnO₂ via the DP process remarkably enhanced the conversion of EDA over these modified matrixes. By contrast, the modification of defective S-1 zeolite with SnO₂ resulted in the most active catalyst (Sn3-S-1), which exhibits 79% EDA conversion, while the catalysts obtained with Si-S-1 and fume SiO₂ acquired much lower activities; the EDA conversions over them were 59% and 12%, respectively. One can again see from Figure 7A that conversions of EDA over the Sn-containing catalysts (Sn loading was 3 wt.%) coincided well with their acidities characterized by pyridine adsorption FT-IR (bands at 1614 cm⁻¹, 1490 cm⁻¹, and 1455 cm⁻¹). The ratios of TEDA/PIP over Sn3-fume SiO₂, Sn3-Si-S-1, and Sn3-S-1 catalysts were calculated to be 0.67, 0.78, and 1.63, respectively. Generally, the formation of TEDA from the condensation of PIP with EDA needs stronger acid sites. Therefore, the increase of the TEDA/PIP ratio in the sequence of Sn3-fume SiO₂, Sn3-Si-S-1, and Sn3-S-1 also suggested an increase of the acidity of the Sn-containing catalyst in the sequence of Sn3-fume SiO₂, Sn3-Si-S-1, and Sn3-S-1. From these results we inferred that the defects of the S-1 zeolite, or in other words, the hydroxyl nests of the defective S-1 zeolites, took an important role in the acidity enhancement of SnO₂ deposition modification.



Figure 9. Catalytic performance of different catalysts in the intermolecular condensation of EDA to piperazine (PIP) and 1, 2-Diazabicyclo [2, 2, 2] octane (TEDA) (reaction conditions: $340 \degree C$, EDA/H₂O mass ratio = 0.9, weight hourly space velocity (WHSV) of reactant solution = $1.3 h^{-1}$, time on stream (TOS) = 24 h).

Figure 10 shows that Sn loading also has a significant influence on the catalytic performance of the SnO_2 deposited defective S-1 zeolite catalyst. First of all, this can be seen from the evolution of EDA conversion. As the Sn loading increased, the EDA conversion increased first and then declined

slightly. The maximum EDA conversion was obtained with 6 wt.% Sn loading. Interestingly, at low Sn loading (1 wt.%), a small increase of Sn loading had a very big promotion effect on the conversion of EDA; the conversion of EDA was increased from 9% (S-1) to 70.55% (Sn1-S-1), and the increment was almost 7 times. In addition, the dependence of the product (PIP and TEDA) selectivity on Sn loading is also impressive. The defective S-1 zeolite matrix produced more PIP than TEDA. However, in the case of Sn-containing zeolite catalysts, the product was dominated by TEDA, and this overturn happened right in the lowest Sn loading (1 wt.%). Once more, from Figures 7B and 10 it is easy to see that the change of the acidity of the Sn-containing defective S-1 zeolite as Sn loading increased is in line with the catalytic performance change of the catalyst series. The enhancement of the acidity of the defective S-1 zeolite by the SnO_2 deposition modification not only increased the catalytic activity of the defective S-1 zeolite but also adjusted the product selectivity of the zeolite in the intermolecular condensation of EDA. On account of the higher additional value of TEDA than PIP, the increase of TEDA selectivity via enhancing the acidity of the defective S-1 zeolite with SnO₂ deposition modification has practical significance for the intermolecular condensation of EDA. As to the slight decline of the activity of the modified catalyst with very high Sn loading (e.g., 8 wt.%), we tend to think that it was mainly caused by the inaccessibleness of some of the catalysts' active sites at very high Sn loading, but this issue must be made certain in the future work.



Figure 10. Effect of Sn loading on the conversion of EDA and the selectivity (to PIP and TEDA) of Sn-x-S-1 catalysts (for reaction conditions, see Figure 9).

In order to know whether or not the highly alkaline EDA reactant and TEDA and PIP products involved in the intermolecular condensation can avoid the strong adsorption on the acidity enhanced defective S-1 zeolite, so as to guarantee a stable reaction activity, a preliminary durability test was conducted with selected catalyst Sn6-S-1. Figure 11 shows that the condensation of EDA could conduct smoothly over the SnO₂ modified catalyst within 80 h, which implies that the acidification of the defective S-1 zeolite by SnO₂ deposition modification did not result in the strong adsorption of the highly alkaline EDA and TEDA and PIP on the modified catalyst. Thus, the defective S-1 zeolite modified with the SnO₂ deposition method could be a suitable catalyst for reactions involving highly alkaline reactants and products. In future study, the coking deactivation and coke-burning regeneration of the Sn-containing defective S-1 catalyst will be investigated in detail.



Figure 11. Reaction stability of Sn-containing defective S-1 zeolite catalyst Sn6-S-1 (6 wt.% Sn loading) in the intermolecular condensation of EDA to PIP and TEDA (for reaction conditions, see Figure 9).

3. Materials and Methods

3.1. Catalyst Preparation

The defective S-1 zeolite parent was manufactured by DQ Tech Chemical Technology (Dalian, China). Before use, the defective S-1 parent was dried at 110 °C and then calcined at 550 °C. For the purpose of comparison, a "perfect" S-1 zeolite (Si-S-1) with low density of silanol nest was prepared by treating the defective S-1 parent with 0.025 M (NH_4)₂SiF₆ (Aladdin, Shanghai, China)aqueous solution at 80 °C for 10 h according to the described procedure [42]. Then, the treated zeolite was recovered and dried at 110 °C overnight, which was followed by calcination at 540 °C for 6 h. In addition to the S-1 zeolites, a kind of amorphous silica (fume SiO₂) (Evonik Industries AG, Frankfurt, Germany) was also employed as a matrix in the DP process for comparison.

Details of the DP process used in this study are as follows. First, an alcohol solution was prepared by dissolving a certain amount of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (Damao, Tianjin, China) in it. Second, powder sample of the calcined S-1 zeolites or fume SiO_2 was dispersed in the solution under vigorous agitation. The dispersion was allowed for 20 min. It was followed by adding excess ammonium hydroxide solution (25 wt.%) into the slurry. After that, the mixture was agitated at 80 °C for 5 h. Finally, the mixture was evaporated to dryness at 110 °C and calcined at 550 °C for 6 h to obtain the Sn-containing catalyst samples.

3.2. Catalyst Characterizations

Catalyst samples were characterized by scanning electron microscope (SEM), UV–visible spectroscopy (UV–VIS), nitrogen physisorption, Fourier transform infrared spectroscopy (FT-IR), and H₂-TPR techniques. SEM images were taken on a Hitachi S-4800 microscope. The UV–VIS spectra were recorded on a JASCOV-550 spectrometer (JASCO, Tokyo, Japan) using BaSO₄ as reference. The H₂-TPR experiments were carried out with a Quanta chrome ChemBet 3000 chemisorb (Shimadzu, Kyoto, Japan) instrument. In order to obtain the TPR profiles, sample (150 mg, 380–830 μ m sieve

fraction) was placed in a quartz tube between two quartz wool plugs and introduced into an oven. Prior to reduction, the sample was calcined at 450 °C (10 °C min⁻¹) in 5% O₂ in He for 1 h. Then, the sample was cooled down to room temperature in a N2 flow. The temperature-programmed reduction (TPR) measurements were performed in a flow of 5 vol.% H₂ in N₂ under heating at a ramp of 10 °C min⁻¹ until the temperature of 800 °C was reached. The spectrum of surface hydroxyl (OH) vibration was obtained with a Nicolet is10 FT-IR spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) using transmission mode. To do this, catalyst sample was pressed into a self-supporting thin wafer (approximately 15 mg) and decontaminated at 400 °C under vacuum (10^{-3} pa) for 4 h in a quartz IR cell equipped with CaF_2 windows. After the pretreatment, the cell was cooled down to room temperature for spectrum recording. The spectrum was recorded from 4000 to 400 cm⁻¹ with an optical resolution of 4 cm^{-1} . The hydroxyl vibration spectra were obtained by subtracting the background spectrum (recorded with an empty IR cell in the absence of sample) from the measured sample spectra. The pyridine IR spectra were also recorded with a Nicolet 10 FT-IR spectrometer using transmission mode in the range from 4000 to 400 cm⁻¹ with an optical resolution of 4 cm⁻¹. The pretreatment of catalysts was the same as that for obtaining surface hydroxyl spectra. The spectra of the adsorbed pyridine were obtained as follows: First, pyridine adsorption was carried out at 35 °C; second, the evacuation treatment (10⁻³ pa) was conducted for 30 min at 200 °C and 350 °C; then the cell was cooled down to room temperature for spectra recording; finally, the spectra were obtained by subtracting the background spectrum (sample spectrum before pyridine adsorption) from the measured spectra. All IR spectra have been normalized by sample mass.

3.3. Catalytic Tests

The probe reaction of EDA intermolecular condensation was carried out on a top-flow fixed-bed tubular reactor at atmospheric pressure. The inner diameter of the fixed-bed reactor was 10 mm (catalyst loading 1 g). Binder-free catalysts, which were always loaded in the thermostatic region of the reactor, were pressed and crushed in the size of 20–40 mesh and calcined at 540 °C for 3 h before use. The reaction conditions were as follows: 340 °C, EDA/H₂O mass ratio = 0.9, and the weight hourly space velocity (WHSV) of the reactant solution was 1.3 h⁻¹. Liquid products of the reaction were collected by a cooling trap and sampling every 12 h. The products were analyzed by a Shimadzu 2010 gas chromatograph equipped with a SE-54 column (30 mm × 0.53 mm × 1.0 μ m) and a FID detector. The conversion of EDA and the selectivity of TEDA and PIP were calculated as follows:

Conversion of EDA: EDA conv. = $\sum Ai/(\sum Ai + A_{EDA in products}) \times 100\%$ Selectivity of TEDA: TEDA selec. = $A_{TEDA}/\sum Ai \times 100\%$ Selectivity of PIP: PIP selec. = $A_{PIP}/\sum Ai \times 100\%$

where A_{TEDA}, A_{PIP}, and A_{EDA in products} were obtained according to the following formula:

$$Ai = fi \times A'i$$

where A'i is the area percentage of TEDA, PIP, and EDA obtained in the gas chromatograph analysis. fi is the relative mass correction factor which was determined with a self-prepared standard solution containing given amounts of TEDA, PIP, and EDA. Σ Ai is the sum of the A value of all the products that appeared in the gas chromatograph analysis, including not only TEDA, PIP, and EDA but also other impurities. The relative mass correction factors of the impurities were arbitrarily determined as 1.0.

4. Conclusions

The acidity of defective S-1 zeolite was successfully enhanced by a facile SnO₂ precipitation– deposition method. The acidified defective S-1 zeolite catalyst showed remarkably improved catalytic performance for the intermolecular condensation of EDA to PIP and TEDA, compared with the inactive zeolite parent. Catalyst characterizations suggest that both the hydroxyl nests of the defective S-1 zeolite and the dispersed SnO₂ clusters should be the important factors for the formation of mild Lewis acid sites on the defective zeolite. Based on the catalytic performance of the stannic species modified defective S-1 zeolite in the conversion of EDA to PIP and TEDA, it is estimated that the SnO₂ mildly acidified defective S-1 zeolite might become a very active and durable catalyst for reactions involving highly alkaline reactants and products.

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