Priority Communication

Sn-containing hexagonal mesoporous silica (HMS) for catalytic dehydrogenation of propane: An efficient strategy to enhance stability

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A B S T R A C T

Sn-containing hexagonal mesoporous silica (Sn-HMS) has been synthesized and evaluated for catalytic dehydrogenation of propane. XRD, HRTEM and XPS characterizations jointly evidence that, the Sn species are probably embedded into the lattice of HMS bulk at a relatively low Sn loading amount. Compared with Sn/SiO_2 samples prepared by conventional impregnation method, Sn-HMS catalyst exhibits inspiringly higher propane conversion (~40%) and better dehydrogenation stability up to 170 h, even after three oxidative regenerations. The improved stability of Sn-HMS catalyst is probably resulted from the inhibition of Sn reduction to low-melting-point metallic Sn species due to a strong Sn—O—Si bond, as well as the stabilization of the Sn species induced by the mesoporous structure of HMS substrate. Further, the reaction route of propane dehydrogenation over Sn-HMS catalyst has been proposed.

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Catalytic dehydrogenation of abundant alkanes, as an effective route to produce high-valued light alkenes, has attracted great attention recently. Due to the detrimental effect of Cr_2O_3-based catalyst and high cost of Pt-based catalyst, the exploration of a novel non-toxic dehydrogenation catalyst with low cost is still one of the urgent issues. Since 1960s, an abundance of research has been focused on the promoting effects of Sn in Pt-based catalyst. It is widely accepted that, the improved selectivity to olefin and good stability of PtSn catalyst [1–4], are mainly attributed to the geometric [5–7] and electronic [8–10] effects of the introduced Sn.

In people's traditional understanding, Sn alone is inactive in dehydrogenation reaction [11,12]. Inspiringly, Sn-based catalyst has been proved to be efficient for propane dehydrogenation in our recent work [13]. The dehydrogenation performance of Sn-based catalyst is even comparable to that of the industrially relevant Cr and Pt-based catalysts. That is, Sn alone can act as the active component for dehydrogenation, instead of only a promoter for Pt-based catalyst. However, the catalyst suffers irreversible deactivation during a 70 h run, which is primarily attributed to the migration and partial removal of low-melting-point (around 503 K) Sn species. To improve the catalyst stability, an appropriate support with high surface area should be chosen to anchoring and incorporating the Sn species more stably. Herein, the facilely synthesized [14] hexagonal mesoporous silica (HMS) has been selected, given its appropriate physical and chemical properties. The thick walls (2.0–3.0 nm) [15,16] and short channel length [17] of HMS guarantee good thermal stability up to 1073 K [18] and fast diffusion of products, respectively. Moreover, its weak acidity [19] facilitates prompt desorption of olefins, thereby reducing the occurrence of undesired secondary reactions.

In this work, a series of Sn-containing HMS samples with SnO_2 content of 2, 5 and 10 wt%, has been synthesized and reduced in H_2 flow prior to reaction (experimental details are given in the Supporting Information). Small-angle XRD patterns in Fig. 1a demonstrate that, the characteristic peak of (100) plane of HMS-type materials [15,20] at around 2θ of 2–3° is detected over almost all these samples, except for 10Sn-HMS. Thereby, it is speculated that, as for 10Sn-HMS, the partial collapse of HMS ordered structure possibly occurs, which is also evidenced by the SEM images in Fig. S1. Moreover, wide-angle XRD pattern of 10Sn-HMS (see Fig. S2) displays distinct diffraction peaks corresponding to crystalline SnO_2. On the contrary, no SnO_2 diffraction peak is observed in the pattern of 5Sn-HMS. This result indicates that, Sn species are highly dispersed over the HMS substrate or even embedded into the lattice of HMS bulk at low Sn contents, instead of aggregating together to form big crystals.

When Sn species are introduced into HMS substrate, both the BET surface area and the pore volume decrease to some extent, especially for the 10Sn-HMS sample (see Table 1). Meanwhile,
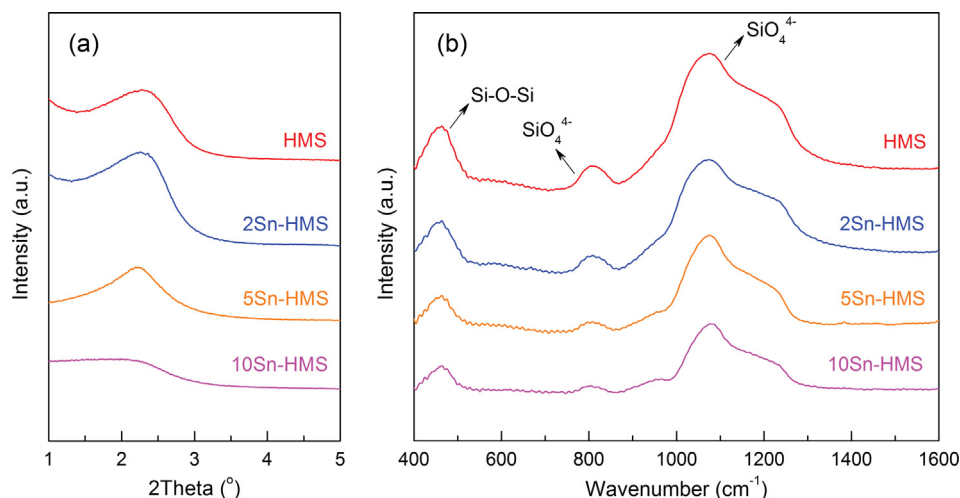
Fig. 1. (a) Small-angle XRD patterns of Sn-containing HMS catalysts; (b) FT-IR spectra of Sn-containing HMS catalysts.

Table 1
Structural and reaction characteristics of Sn-containing HMS catalysts.

	HMS	2Sn-HMS	5Sn-HMS	10Sn-HMS
Surface area, m^2/g	1163	1065	960	799
Pore diameter, nm	2.92	3.03	3.11	3.3
Pore volume, cm^3/g	0.79	0.73	0.71	0.53
d_{100}, nm	4.12	4.2	4.41	4.4
a_0[a], nm	4.76	4.85	5.09	5.08
W_d[b], nm	1.84	1.82	1.98	1.78
Sn density, Sn atom/nm^2	–	0.08	0.21	0.5
TOF $\times 10^3$, mole propene/(mole of added Sn·s)	–	3.38	2.70	1.25

[a] a_0 is the unit cell parameter calculated from XRD distance by $a_0 = 2d_{100}/\sqrt{3}$..
[b] W_d is the wall thickness calculated by $W_d = a_0$ – Pore diameter.

the pore diameter expands progressively upon the incorporation of Sn atoms, which is probably caused by a larger size of Sn^{4+} (0.055 nm) than Si^{4+} (0.026 nm) [21], while the wall thickness data are comparable among all these samples in spite of different Sn contents, being consistent with the results reported by Abdel-Fattah and Pinnavaia [22]. Notably, all these samples possess thicker framework walls than the mesoporous silica MCM-41 (about 1 nm) [23], thereby guaranteeing a good thermal stability of the catalyst. Furthermore, the Sn-containing HMS samples exhibit even better thermal stability than the raw HMS material, as indicated by the TG-DTA profiles in Figs. S3 and S4.

FT-IR characterization has also been conducted over Sn-HMS samples (see Fig. 1b). Infrared bands around 810 and 1090 cm^{-1}, respectively corresponding to the symmetric and anti-symmetric vibration modes of tetrahedral SiO_4 structure unit [18], can be detected over all these samples. A peak assigned to the Si—O—Si vibrational mode [24] can also be observed at 475 cm^{-1}. In addition, the intensity of all IR bands decreases with increasing Sn content, indicating the partial destruction of the ordered mesoporous structure at higher Sn loadings. Moreover, an additional band around 960 cm^{-1} is detected. In the literature, the understanding of this IR band is controversial. Some researchers [25–28] believed that, the presence of the infrared band at 950–970 cm^{-1} is a direct evidence for the isomorphous substitution. While the others [29,30] held different opinions, they attributed the band to Si—O stretching vibration in the Si—OR group instead of Sn—O—M. To further probe into the existing state of Sn species in HMS, the HRTEM and EDS elemental mapping were taken (see Fig. 2). A typical wormhole structure of HMS substrate is clearly observed for 5Sn-HMS sample, and no obviously aggregated particles of Sn spe-

cies are detected. The corresponding EDS mapping verifies that, the Sn species incorporated into HMS are uniformly dispersed over the substrate and suffer from negligible agglomeration.

In the O 1s XPS spectra of 5Sn-HMS (see Fig. S5), only one peak located at the binding energy of 532.7 eV, which is reported to be characteristic of SiO_2 in transition-metal-incorporated mesoporous silica [31], is observed, while for the lattice oxygen of SnO_2, the characterization peak of O 1s is primarily around 530–531 eV [32,33]. These facts further evidence that, the Sn species are probably embedded into the framework of HMS substrate.

Fig. 3 shows the initial dehydrogenation performance over the different Sn-HMS samples. It can be clearly seen that, the pure-silica HMS delivers an extremely low activity toward propane dehydrogenation. Notably, this propane conversion level is close to that achieved with no catalyst being loaded, indicating that the low activity is primarily attributed to homogeneous reactions. When Sn species are introduced, the conversion of propane increases continuously to 40% with Sn content up to 5 wt%. Afterward, the propane conversion demonstrates a slight decreasing trend with increasing Sn content to 10 wt%, probably attributed to the partial collapse of the ordered HMS mesoporous structure and the appearance of aggregated SnO_2 crystals. The selectivity to propene, however, exhibits a monotonically increasing trend with the content of Sn. In general, a maximum propene yield of 36% is obtained over 5Sn-HMS catalyst, which is significantly higher than that obtained over the conventional Sn/SiO_2 catalyst even with a smaller space velocity. It is also worth noting that, the turnover frequencies (TOF) of propene (see Table 1) decrease with the increase of Sn content, indicating that the utilization efficiency of Sn atoms also decreases with the increasing Sn loading.