

Synthesis, characterization and catalytic activity of SnAPO-5 in hydrogenation reaction

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Received 5 October 2010; revised and accepted 10 January 2011

Tin containing aluminophosphate molecular sieve with AFI structure (SnAPO-5) has been synthesized hydrothermally by using Sn(II) and Sn(IV) salts as precursors. The SnAPO-5 materials have been thoroughly characterized by powder X-ray diffraction, FTIR, UV-vis spectroscopy, scanning electron microscopy, thermal analysis, N₂ sorption and surface area measurements, and elemental analysis using ICP. FTIR and UV-vis spectral data of calcined SnAPO-5 reveal that Sn can be substituted for the phosphorous sites up to 2 mole% in the framework lattices. Substitution of Sn preferably occurs at the phosphorous sites rather than for Al at lower metal concentration [Sn(II) or Sn(IV) $\leq$ 2 mole% SnO₂] but higher loading leads to octahedral tin species. The calcined SnAPO-5 material exhibits good hydrogenation activity for the reduction of cyclohexanone to cyclohexanol using 2-butanol as hydrogen donor molecule under the liquid-phase reaction conditions. Other metallophosphates such as CoAPO-5, MnAPO-5 and FeAPO-5 fail to undergo this hydrogenation reaction under similar experimental conditions.

Keywords: Catalysis, Aluminophosphates, Tin, Molecular sieves, Metallophosphates, Hydrogenation, Cyclohexanone

The incorporation of transition metals in microporous and mesoporous molecular sieves is a challenging area of research because of the potential use of these materials as eco-friendly heterogeneous catalysts in chemical industries¹⁻⁴. A large variety of phosphate based molecular sieves can be synthesized in the presence or absence of template molecules⁵⁻⁸ and their synthesis under mild acidic to neutral pH conditions favors the smooth incorporation of the transition metals in the framework as compared to the silicate based molecular sieves. The transition metal ion can either be incorporated in true framework sites or anchored to the framework in defect sites, or be present as isolated/clustered extra framework cations, which can be monitored by careful controlling of various synthesis parameters involved under hydrothermal synthesis of these materials. Thus, the substitution of transition metals like Co²⁺, Mn²⁺, V⁴⁺, Ti⁴⁺, Sn⁴⁺ and Cr³⁺ in the framework of AFI molecular sieves⁹⁻¹⁷ induces the well known redox property; this property is utilized for the oxidation of various organic molecules either using molecular O₂ or dilute H₂O₂ as oxidant. Although the use of these transition metal-containing aluminophosphates are well studied in the field of oxidation, polymerization, and vapor-phase Friedel-Crafts reactions, very little research has

been focused in the field of catalytic hydrogenation¹⁸. Furthermore, tin containing microporous and mesoporous molecular sieves showed excellent catalytic activities in liquid-phase organic transformations¹⁹⁻²³. However, detailed investigation of incorporation of tin in the microporous aluminophosphates and its applications as a catalyst in hydrogenation reaction under mild liquid-phase conditions has not been studied.

Herein we report the successful utilization of SnAPO-5 molecular sieve in liquid phase hydrogenation of cyclohexanone using 2-butanol as hydrogen donor molecule. The SnAPO-5 materials synthesized here are thoroughly characterized with XRD, TG-DTA, SEM, FTIR, UV-vis, sorption and surface area measurements, and elemental analysis. The activity of SnAPO-5 is also compared with that of other metallophosphate analogues such as CoAPO-5, MnAPO-5, and FeAPO-5, suggesting the catalytic role of framework tin in this liquid phase hydrogenation reaction.

Materials and Methods

All chemicals were purchased commercially and used without further purification. Phosphoric acid (85 wt%, Wako pure) and pseudo boehmite (75 wt%,

Table 1 – Input and output gel composition and physiochemical properties of SnAPO-5

Sample	Gel composition ^a		Product composition		Surface area (m ² /g) ^e
	SnO ₂	Al ₂ O ₃	SnO ₂	P ₂ O ₅	
SnAPO-5 ^b	0.03	0.5	0.01	0.49	365
SnAPO-5 ^b	0.06	0.5	0.02	0.48	343
SnAPO-5 ^{b,c}	0.1	-	-	-	-
SnAPO-5 ^d	0.03	0.5	0.02	0.48	318
SnAPO-5 ^d	0.06	0.49	0.03	0.47	303
SnAPO-5 ^d	0.1	0.49	0.045	0.465	298

^aAl₂O₃: 1; P₂O₅: 1.^bSnCl₄ was used as tin source.^cMixture of chabazite, aluminophosphotridymite; AFI phase was observed.^dSnCl₂ was used as tin source.^eBET surface area was measured with BELSORP 28 A using N₂ at 77 K.

Pural^R,) were the respective sources of phosphorous and aluminum. The tin sources were SnCl₄ (99%, Aldrich) and SnCl₂·2H₂O (96%, Nacalai Tesque Inc., Japan). Triethylamine (97%, TCI) was used as structure-directing agent for synthesis of AFI framework.

XRD powder patterns were obtained using a MAC Science MXP-18VTZ diffractometer with Cu-K_α radiation. TG-DTA measurements were carried out with a MAC Science TG-DTA 2100 instrument in dried air. Diffused reflectance UV-visible spectra were recorded on a JASCO V-550 spectrometer using BaSO₄ as a reference. FTIR spectra were recorded with a Nicolet 750 FTIR apparatus and KBr technique was used to study the framework stretching vibrations. Morphology of the samples was observed with a Hitachi S-800 scanning electron microscope. Surface area was measured by N₂ adsorption at 77 K on a BELSORB 28SA analyzer after evacuation at 473 K for 3 h.

Hydrothermal synthesis of SnAlPO-5

The synthesis of SnAPO-5 was carried out with the molar gel composition Al₂O₃ : P₂O₅ : *x* SnO₂ : 0.75 TEA : 17.5 H₂O (where *x* is 0.03 – 0.1) and the amount of tin present in the calcined materials is shown in the Table 1. In a typical synthesis, phosphoric acid was mixed with distilled water at 273 K followed by addition of the required amount of SnCl₂·2H₂O and alumina under constant stirring. Then the triethylamine was added dropwise with the temperature being controlled at around 273 K since the addition of amine causes an exothermic reaction. Then the contents were stirred for an extended period of time to get the homogeneous thick gel which was

crystallized in a Teflon lined autoclave at 473 K for 24 h under tumbling conditions. After crystallization, the white powder was filtered, washed thoroughly with distilled water, dried, and calcined at 803 K for 8 h to burn off the organics. Similarly, other metal containing AFI materials were synthesized according the reported literature procedure¹⁵.

Hydrogenation of cyclohexanone

In a typical reaction, 5 mmol of cyclohexanone, 100 mmol of 2-butanol (anhydrous), and 20 wt% of the catalyst with respect to cyclohexanone were mixed in a round bottom flask. The flask was fitted with a reflux condenser and the contents were vigorously stirred using a magnetic stirrer at 368 K while circulating cold water through the condenser. After 10 h of reaction, the catalyst was separated and the reaction mixture was analyzed through a GC equipped with capillary column. The products were identified using authentic samples.

Results and Discussion

Phase purity and crystal morphology

The XRD patterns of calcined SnAPO-5 synthesized using SnCl₄ (diffractogram a and b) and SnCl₂·2H₂O (diffractogram c-e) are shown in Fig. 1. In the case of SnCl₄, the SnAPO-5 is readily crystallized when the amount of Sn in the synthesis gel is less than 0.06 mole. Further increase of SnCl₄ to 0.1 mole produced a mixture of chabazite, aluminophosphotridymite, and AlPO-5 (Table 1). However for SnCl₄ as source, elemental analysis indicated that the amount of tin present in the final calcined sample was 2 mol% of SnO₂, which is less than that of the initial synthesis gel. Furthermore, in

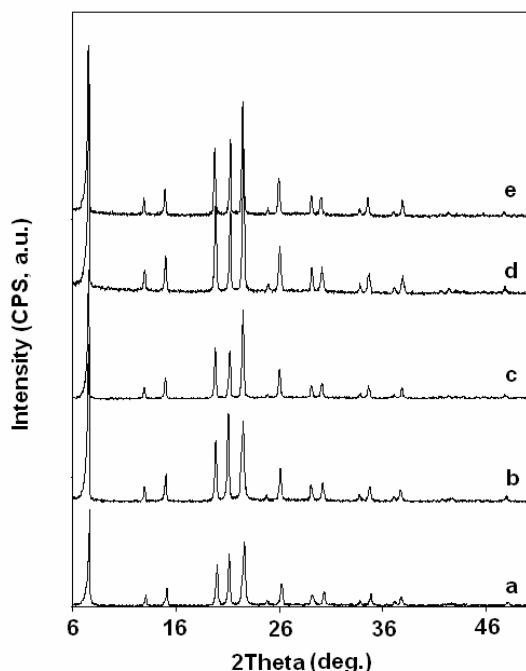


Fig. 1—XRD patterns of different calcined SnAPO-5 samples. [a and b refer to 1 and 2 mole% SnO_2 synthesized with SnCl_4 , c-e refer to 2, 3, and 4.5 mole% SnO_2 synthesized using $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ as precursor].

the case of synthesis with $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ the gel crystallized with a wide input ratio of 0.03 – 0.1 mole (diffractogram c-e). The XRD patterns show that all the SnAPO-5 samples are completely crystalline and free from amorphous or other crystalline impurities. The unit cell analysis of the dry calcined SnAPO-5 (sample 2, Table 1) gave parameters of $a = 13.77(2) \text{ \AA}$ and $c = 8.42(2) \text{ \AA}$, with a cell volume of $1385(7) \text{ \AA}^3$. Comparison of these values with that of pure AlPO-5 [$a = 13.78(2) \text{ \AA}$; $c = 8.37(2) \text{ \AA}$] suggests that incorporation of tin in the framework results in an increase in the c -dimension and the unit cell parameter c has been observed to increase linearly with amount of tin in the SnAPO-5 samples¹³. A similar change in the unit cell parameters for the substitution of heavy metals such as Co^{2+} has also been reported²⁴. Thus the introduction of larger Sn^{4+} with ionic radii 0.069 nm into the AFI framework would also affect the unit cell parameter in a similar way.

Figure 2 shows SEM pictures of SnAPO-5 samples obtained from SnCl_4 and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$. SnAPO-5 synthesized with SnCl_4 exhibits fairly regular hexagonal prisms (Fig. 2A) with crystal size of 2-3 μm , but a large number of small crystals along

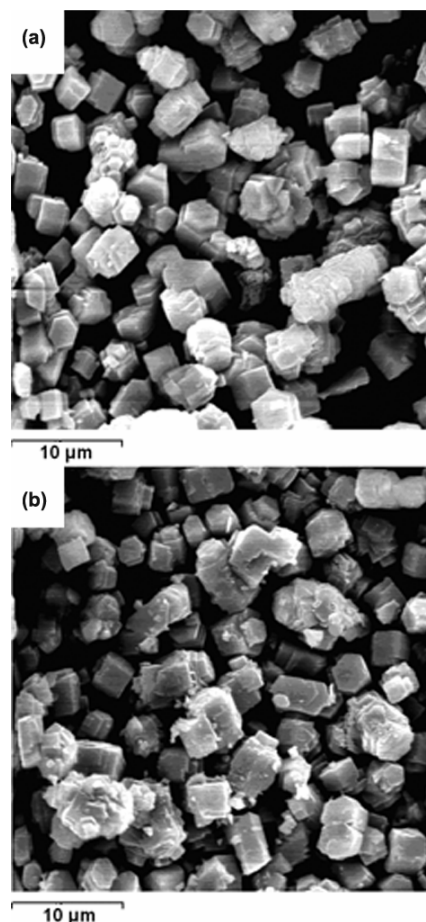


Fig. 2—SEM images of SnAPO-5. [(A) synthesized with SnCl_4 ; (B) synthesized with SnCl_2].

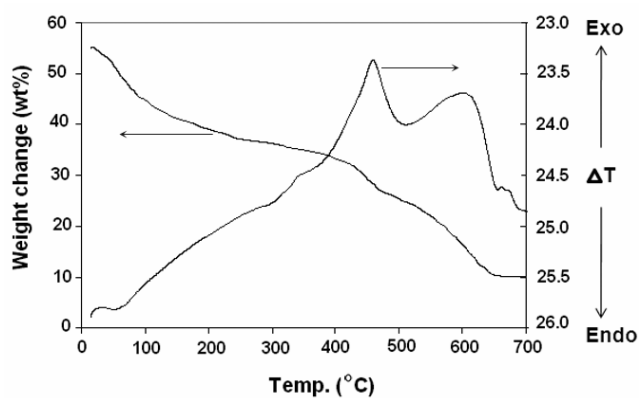


Fig. 3—TG-DTA of SnAPO-5; sample with 2 mole% SnO_2 synthesized with SnCl_4 .

with hexagonal prisms are formed with $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (Fig. 2B) as the tin source. Also, the SEM images confirm that all the above synthesized samples are highly crystalline without any amorphous materials. Figure 3 exhibits the TG-DTA of the as-synthesized SnAPO-5 and obviously, the calcination process

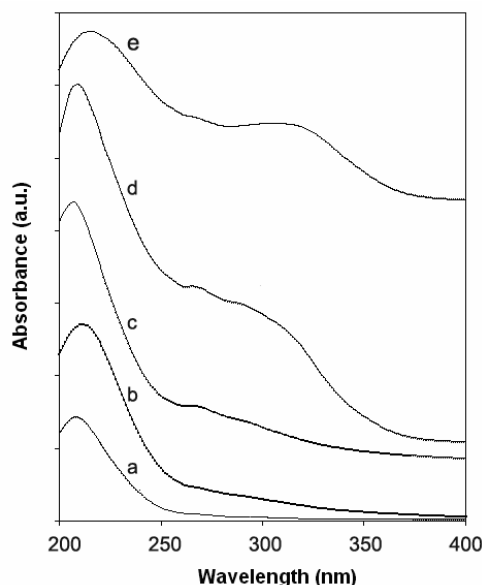


Fig. 4—UV-vis spectra of different calcined SnAPO-5 samples. [a and b refer to 1 and 2 mole% SnO_2 synthesized with SnCl_4 , c-e refer to 2, 3, and 4.5 mole% SnO_2 synthesized using $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$].

proceeds in two different stages as exhibited in the DTA curve. After desorption of water at low temperature, the first exothermic decomposition of triethylamine begins at 753 – 773 K and the second exotherm appears around 843 – 873 K. The decomposition of organics at higher temperature between 843 and 873 K is attributed to the removal of triethylamine from four membered ring structure, which requires relatively higher energy than that required for the removal of triethylamine present in the channels and/or pores. Furthermore, the heat treatment of SnAPO-5 over 923 K resulted in collapse of crystalline framework. However literature reports suggest that pure AlPO-5 without tin in the framework position is thermally stable above 1273 K. Thus, the relatively low thermal stability of SnAPO-5 suggests that substitution of tin in the AFI framework.

Spectral characterization

The incorporation of tin in the AFI framework is further evidenced from the UV-vis spectra (Fig. 4). Samples with less than 2 mole% of SnO_2 exhibit a sharp absorption band around 220 nm (spectra a-c). However, the absorption band extends to 250 – 280 and 300 – 350 nm as the amount of SnO_2 increases (spectra d and e) to 4.5 mole%. The appearance of sharp absorption band around 220 nm is attributed to finely dispersed tin in the framework position²⁵, whereas the bands at 250 – 280 nm and above 300 nm

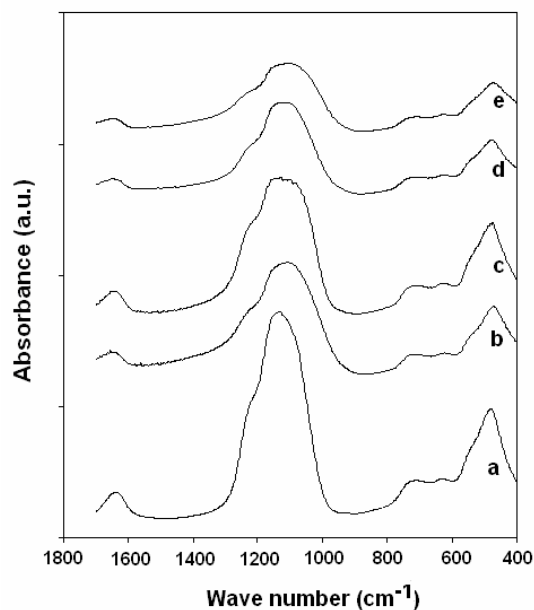


Fig. 5—Infrared spectra of different calcined SnAPO-5 samples. [a and b refer to 1 and 2 mole% SnO_2 synthesized with SnCl_4 , c-e refer to with 2, 3, and 4.5 mole% SnO_2 synthesized using $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$].

may arise from the extra-framework species and bulk SnO_2 , respectively. Thus, the observed spectra of different SnAPO-5 materials indicate that while at low metal concentration, the framework substitution occurs predominantly, considerable amount of bulk SnO_2 and extra-framework species are formed with increased amount of tin in the final crystalline products.

The FTIR spectra of various calcined SnAPO-5 materials recorded by using KBr pellet technique in the region of framework vibrations are exhibited in Fig. 5. Spectra a and b refer to samples with 1 and 2 mole% SnO_2 synthesized using SnCl_4 as the metal source and clearly show that the SnAPO-5 with minimum amounts of tin in the lattice position exhibits less deformation or broadening in the region of 1050 – 1250 cm^{-1} ; broadening of the band takes place as the amount of SnO_2 increases. The broadening is quite pronounced for SnAPO-5 with 2, 3, and 4.5 mole% SnO_2 (spectra c and e) due to highly distorted environments in the framework vibration region. Thus, in the 950 – 1250 cm^{-1} region, the stretching vibrations of T-O-T and T-O-Sn, (where T stands for the central atom of the TO_4 tetrahedra) are prominent. Therefore, the marked changes in the IR bands of different SnAPO-5 materials in the region of 1050 – 1250 cm^{-1} may be

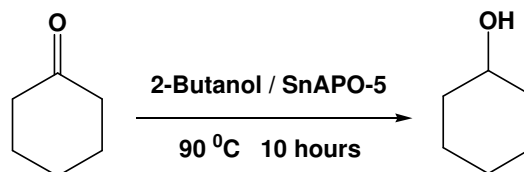
associated with distortion of the lattice caused by the incorporation and/or anchoring at the defect sites by the heavy metals.

Catalytic hydrogenation over SnAPO-5

The activity of various SnAPO-5 catalysts for the selective reduction of cyclohexanone to cyclohexanol (Scheme 1) under liquid-phase conditions is shown in Table 2. The hydrogenation activity of SnAPO-5 synthesized with SnCl_4 precursor increases with increase in the amount of tin in the AFI structure. As seen from Table 2, the catalyst with 1 mole% of tin exclusively in the tetrahedral position exhibits lower activity (7.1% conversion) than that observed over catalyst with 2 mole% of tin (14.8% conversion). The activity of SnAPO-5 synthesized with SnCl_2 precursor also shows the same trend as that of Sn(IV) and the sample with 3 mole% tin exhibits the best activity (16.5% conversion) here. However, the catalyst with 4.5 mole% tin shows lower activity in spite of its higher tin content, which is attributed to the presence of a large amount of bulk SnO_2 and extra-framework species in that catalyst, as evidenced from the UV-visible spectroscopy. Furthermore the absence of activity over 2 wt% bulk SnO_2 confirms that the observed activity is indeed catalyzed by the tin atom in tetrahedral position of AFI structure rather than the bulk SnO_2 . CoAPO-5 and MnAPO-5 exhibit lower activity than that observed over SnAPO-5. FeAPO-5 does not show any activity over the hydrogenation of cyclohexanone. Thus, the observed hydrogenation activity over different metallophosphates follows the order: SnAPO-5 > CoAPO-5 > MnAPO-5 > FeAPO-5.

Incorporation of Sn and its role in catalytic reactions

UV-visible spectra of calcined SnAPO-5 shows a band at 220 nm arising from tetrahedral coordination of both Sn^{4+} and Sn^{2+} ions in the samples. Furthermore, reported literature reveals that a similar absorption band for bulk SnO_2 is observed at 310 nm corresponding to the six coordinated Sn species²⁵. In the present study using Sn^{4+} ions, the spectrum (Fig. 4, spectra a and b) shows a band at 220 nm confirming the presence of tetrahedral Sn species in the framework lattices. A similar absorption band has also been reported over microporous Sn-silicates²⁶ (Sn-MFI), where the Sn^{4+} ions located in the tetrahedral coordination appears at 210 nm, at a relatively higher energy than the SnAPO-5. The observed shift is attributed to the environment of four



Catalytic hydrogenation of cyclohexanone over SnAPO-5

Scheme 1

Table 2 – Selective reduction of cyclohexanone to cyclohexanol over SnAPO-5 catalysts. [React. cond.: cyclohexanone: 5 mmol; 2-butanol: 100 mmol; catalyst: 20 wt%; temp.: 368 K; reaction time: 10 h]

Catalyst	SnO_2 (mole%)	Conv. of cyclohexanone (%)	Cyclohexanol (%)
SnAPO-5 ^a	1	7.1	100
SnAPO-5 ^a	2	14.3	100
SnAPO-5 ^b	2	9.5	100
SnAPO-5 ^b	3	16.5	100
SnAPO-5 ^b	4.5	14.9	100
SnO_2	2.0	Nil	Nil
CoAPO-5 ^c	-	4.2	100
MnAPO-5 ^d	-	2.4	100
FeAPO-5 ^e	-	Nil	Nil
AlPO-5	-	Nil	Nil
SnAPO-5 ^f	2	13.4	100

^aThe catalysts were synthesized using SnCl_4 .

^bThe catalysts were synthesized with $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$.

^c2 mole% cobalt oxide.

^d2 mole% manganese oxide.

^e1 mole% iron oxide.

^fActivity after 4 successive reuse.

–O–P attached to Sn in SnAPO-5 instead of four –O–Si in Sn-silicates²⁷. Furthermore, the SnAPO-5 materials synthesized with Sn(II) exhibited both tetrahedral as well as octahedral Sn species (Fig. 4, spectra c-e). Similar to Sn^{4+} ions, the incorporation of up to 2 mole% Sn^{2+} produced exclusively pure tetrahedrally coordinated SnAPO-5, whereas bulk SnO_2 phase begins to appear with high metal loading. In some cases the formation of octahedral species (absorption band at 270 nm) is also noticed possibly due to the attachment of Sn at the defect sites. The elemental analysis of the above materials (Table 1) also suggests that Sn^{4+} substitution leads to exclusively four coordinated species. However, octahedral and extra-framework species are formed at

higher metal loading with Sn^{2+} . The FTIR spectra of SnAPO-5 in the stretching vibration region of $1000 - 1250 \text{ cm}^{-1}$ suggest that the incorporation of Sn in the framework leads to distortion or broadening of bands. The presence of Sn is characterized by the stretching vibrations²⁸ around 1070 cm^{-1} . In the present study, a sharp band is observed at 1095 cm^{-1} for the samples containing less amount of tin (Fig. 5, spectrum a) in the framework position and the band gradually shifts to lower wave number (1078 cm^{-1}) as the amount increased further (spectra b-e in Fig. 5). The incorporation of tin in the AlPO-5 structure is further confirmed by the catalytic hydrogenation of cyclohexanone.

For the catalytic hydrogenation of cyclohexanone over SnAPO-5 materials under liquid-phase conditions, 2-butanol acts as a hydrogen donor. The conversion of cyclohexanone increases with increase in the amount of tin for catalysts synthesized with SnCl_4 . However, catalysts obtained with SnCl_2 exhibit less activity for the reduction of cyclohexanone due to the presence of extra-framework Sn species. It is worthwhile to mention that no hydrogenation activity was observed over AlPO_4 catalyst under similar experimental conditions, confirming the possible role of active Sn sites in the hydrogenation reactions. The introduction of Lewis acidic Sn^{n+} ions in the AFI framework position and its strong interaction with carbonyl groups of cyclohexanone may possibly promote the reaction as reported in the case of microporous Sn-beta^{29,30}. However, the CoAPO-5 and Mn-APO-5 exhibit less activity than SnAPO-5, possibly due to lower Lewis acidity and weak interaction of cyclohexanone with these catalysts. FeAPO-5 fails to undergo hydrogenation under similar conditions. The possible reason for the lack of activity over FeAPO-5 may be because most of the iron may exist as iron oxide outside the framework structure rather than finely dispersed in the aluminophosphate network. The stability and reusability of SnAPO-5 was examined after activating the catalyst at 300°C for 2 h. The catalytic activity of SnAPO-5 with 2 mol% SnO_2 exhibited 93.7% of its original activity after four successive recycling.

Conclusions

SnAPO-5 was synthesized up to 2 mole% of SnO_2 in the final product without formation of octahedral and bulk SnO_2 species. Tetrahedral substitution predominantly occurred for Sn^{4+} , whereas Sn^{2+}

favoured both tetrahedral as well as octahedral coordinated Sn species. SnAPO-5 exhibited good hydrogenation activity for the reduction of cyclohexanone using 2-butanol as hydrogen donor molecule. CoAPO-5 and MnAPO-5 exhibited less activity than SnAPO-5, whereas FeAPO-5 could not catalyze the hydrogenation of cyclohexanone under identical reaction conditions.

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