

SYNTHESIS OF FRUCTONE AND ACYLAL USING HEXAGONALLY ORDERED MESOPOROUS ALUMINOSILICATE CATALYST

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Hexagonally ordered mesoporous AISBA-15 with different n_{Si}/n_{Al} ratios have been hydrothermally synthesized using the non-ionic copolymer Pluronic P123 surfactant as the structure directing agent and characterized by XRD, N_2 adsorption-desorption, and ammonia-temperature programmed desorption (pyridine-TPD). Acetal and acylal formation reactions of organic carbonyl compounds were efficiently catalyzed by AISBA-15 under liquid-phase reaction conditions and the results were compared with the MFI, BEA and AIMCM-41(23). Of the catalysts studied, AISBA-15(45) showed the highest activity in both the acetalization and acylal reactions of the carbonyl compounds under the optimized reaction conditions, and could be recycled several times without loss in activity. AISBA-15(45) catalyst is highly stable, efficient, chemoselective, and environmental friendly, which could open the possibility for environment benign approach for the synthesis of acetals, acylals and its derivatives under mild reaction conditions.

Keywords: Adsorption; Mesoporous; AISBA-15; Silica; Acetal; Acylal.

The acylal preparation is generally used to protect the carbonyl groups in the selective synthesis of various value-added natural products, which typically require several steps, owing to the stability of acylals in basic as well as in mildly acid media¹⁻³. Besides the interest of acetals as protecting groups, they can be used in various applications including the fragrances, the additives for foods, beverages, and detergents⁴⁻⁸. The acetals are generally prepared from carbonyl compounds using either an alcohol or an orthoester, in the presence of acid catalysts including the protic acids, Lewis acids (zinc chloride)⁹, alumina¹⁰, montmorillonite¹¹, zeolites^{12,13}, and cation exchange

resins¹⁴. Acetalization of aldehydes can be performed in the presence of weak acids, while ketones generally need stronger ones like sulfuric, hydrochloric or *p*-toluenesulfonic acid (4-methylbenzene-1-sulfonic acid) and larger amounts of catalyst than aldehydes. However, many of the methods mentioned above present limitations as a result of use of expensive and toxic mineral acids, rigorous reaction conditions, tedious work-up procedure, and necessity of neutralisation of the strongly acidic media accompanied by the production of undesired wastes¹⁵⁻¹⁸.

The preparation of fructose 3,3-(ethylenedioxy)butanoate, a flavouring material with apple scent, involves the acetalization of ethyl acetoacetate with ethylene glycol¹⁶ whereas acylals are usually prepared from the carbonyl compounds using acetic anhydride (Ac₂O) as the acylating agent¹⁸. Homogeneous catalysts such as sulfuric acid, hydrochloric acid, triflic (trifluoromethanesulfonic) acid orthophosphoric acid, *p*-toluenesulfonic acid, etc. and heterogeneous catalysts such as zeolites, clays, and sulfated zirconia generally catalyze these above processes for the production of the above substituted acetals or acylals¹⁶⁻²⁵. However, the efficiency of the strong homogenous acid catalysts is low as the strong acid and water formed during the acetalization can cause the hydrolysis of the ester, leading to the reduction of the yield of the final desired product. On the other hand, high temperatures, high catalyst loadings, longer reaction times, and cumbersome procedures are required if the zeolites, sulfated zirconia, and clays are used in the process. Moreover, some of these are not selective in terms of aldehyde and keto functional groups. Thus, it is highly critical to find a cost-effective, mild and simple selective protocol, and the efficient catalysts for synthesis of acylals from aldehydes.

Mesoporous materials have received a lot of attention in the recent years owing to their excellent textural characteristics such as high surface area, uniform mesopores, and large pore volume, which help them to find applications in various fields including adsorption, separation, nanotechnology, and sensors²⁶⁻⁴⁵. Mesoporous materials with different structures such as MCM-41, MCM-48, SBA-15 and so on, are prepared by soft templating approach using the organic surfactant molecules as the structure directing agents²⁶⁻³². Of these mesoporous materials, SBA-15 is an interesting mesoporous silica material which possesses highly ordered hexagonal mesopores with considerably thicker pore walls as compared with MCM-41. This material was synthesized using an amphiphilic triblock copolymer as the structure-directing agent in highly acidic media⁴²⁻⁴⁵. It has been reported that SBA-15 exhibits improved hydrothermal stability as compared with MCM-41^{26,43} due to its thicker pore walls. As the framework charge of

SBA-15 mesoporous silica is neutral, the aluminum was incorporated into the silica framework in order to introduce the acid function⁴⁶. Very recently, Vinu et al.^{47,48} have successfully reported the synthesis of AISBA-15 materials with a high aluminum content and tunable pore diameters by simply adjusting the water-to-hydrochloric acid ratio ($n_{\text{H}_2\text{O}}/n_{\text{HCl}}$). They also found that the catalyst is highly stable and showed excellent activity in various acid-catalyzed reactions such as *tert*-butylation of phenol and isopropylation of *m*-cresol⁴⁷⁻⁴⁹.

Here, we tried to use the above highly acidic AISBA-15 catalyst with different aluminum contents for the synthesis of fructose, and acylals and the results are compared with AlMCM-41, BEA, and MFI. Of the catalysts studied, AISBA-15 was found to be the most active, showed superior catalytic performance compared with other catalysts in both acetalization and acylal reactions. In addition, the catalysts could be regenerated without appreciable loss in catalytic activity and selectivity.

EXPERIMENTAL

Materials

Aluminum triisopropoxide and tetraethyl orthosilicate (Merck) were used as the source for aluminum and silicon, respectively. Triblock copolymer poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) (Pluronic P123, molecular weight 5800, $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$) (Aldrich) was used as structure-directing template. Ethyl acetoacetate, ethylene glycol, toluene, benzaldehyde, and Ac_2O were purchased from Wako. All the chemicals were used as received without further purification.

Preparation of the Catalysts

AISBA-15 samples with different $n_{\text{Si}}/n_{\text{Al}}$ ratios were synthesized using triblock copolymer, poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) as a structure-directing agent with the following molar gel composition: TEOS : 0.02–0.15 Al_2O_3 : 0.016 P123 : 0.46 HCl : 127 H_2O . In a typical synthesis, 4 g of Pluronic P123 was added to 30 ml of water. After stirring for a few hours, a clear solution was obtained. To the solution, 70 g of 0.28 M hydrochloric acid was added and the solution was stirred for 2 h. Then, 9 g of tetraethyl orthosilicate and the required amount of an aluminum source were added and the resulting mixture was stirred at 40 °C for 24 h. The resulting gel was transferred to polypropylene bottle, kept in a hot air oven, and heated at 100 °C for 24 h under hydrothermal conditions. The solid product obtained was recovered by filtration, washed with water several times, and dried overnight at 100 °C. Finally, the product was calcined at 540 °C in air atmosphere to remove the template. The samples are denoted as AISBA-15(x) where x denotes the $n_{\text{Si}}/n_{\text{Al}}$ ratio.

Characterization

The powder X-ray diffraction patterns of AISBA-15 and AlMCM-41 materials were collected on a Siemens D5005 diffractometer using $\text{CuK}\alpha$ ($\lambda = 0.154$ nm) radiation. The diffractograms were recorded in a 2θ range of 0.8 to 10° with a 2θ step size of 0.01° and a step time of 10 s. Nitrogen adsorption and desorption isotherms were measured at -196°C on a Quantachrome Autosorb 1 sorption analyzer. The samples were evacuated at 250°C for 3 h in the adsorption analyzer. The specific surface area was calculated using the BET model.

The density and strength of acid sites of AISBA-15 and AlMCM-41(23) materials were determined by temperature-programmed-desorption (TPD) of pyridine. About 100 mg of the materials was evacuated at 250°C for 3 h under vacuum ($p < 10^{-5}$ hPa). Thereafter, the samples were cooled to room temperature under dry nitrogen followed by exposure to a stream of pyridine in nitrogen for 30 min. Subsequently, the physisorbed pyridine was removed by heating the sample to 120°C for 2 h in a nitrogen stream. The TPD of pyridine was performed by heating the sample in stream (50 ml/min) from 120 to 700°C at a rate of $10^\circ\text{C}/\text{min}$ using a high-resolution thermogravimetric analyzer (SETARAM setsys 16MS). The observed weight loss was used to quantify the number of acid sites, assuming that each mole of pyridine corresponds to one mole of proton.

Catalyst Testing

Acetalization reactions were carried out according to the procedure reported elsewhere^{12b}. Typically, in acetalization of ethyl acetoacetate, the catalyst was freshly activated at 500°C for 2 h, and the required quantity was weighed in the 50 ml glass batch reactor attached to a Dean-Stark apparatus to remove the water formed in the reaction. Ethyl acetoacetate (12.0 mmol) and ethylene glycol (24.0 mmol) in toluene (40 ml) were added to the glass reactor and the reaction temperature was maintained with a silicon oil bath equipped with a thermostat and magnetic stirrer. The resulting suspension was continuously stirred and heated at 146°C in a silicone oil bath with an automatic temperature control system. On the other hand, acylal reactions with benzaldehyde (7.4 mmol) and Ac_2O (22.2 mmol) were carried out in a 50 ml glass batch reactor with an anhydrous CaCl_2 tube at the reaction temperature 40°C . Samples were taken at the end of the each reaction and analyzed with a Shimadzu GC-2010 gas chromatograph using a DB-5 capillary column, coupled with a thermal conductivity detector. The product identification was carried out using GC-MS.

RESULTS AND DISCUSSION

Structural Characterization

The powder XRD patterns of AISBA-15(45) and AISBA-15(7) show all the four well resolved peaks, which are indexed to (100), (110), (200) and (210) reflections of the ordered hexagonal space group $P6mm$ (Fig. 1). The length of the hexagonal unit cell a_0 is calculated using the equation $a_0 = 2d_{100}/\sqrt{3}$ and is given in Table I. The observed d spacings are compatible with the hexagonal $P6mm$ space group. The unit cell constant of AISBA-15(7) is larger than that of AISBA-15(45), indicating the incorporation of aluminum

TABLE I
Textural parameters and acidity of AISBA-15(45), AISBA-15(7), AIMCM-41(23), BEA and MFI catalysts

Catalysts	a_0 nm	$n_{\text{Si}}/n_{\text{Al}}$		A_{BET} m^2/g	Pore volume cm^3/g	Pore diameter $d_{\text{p.ads}}/\text{nm}$	Acid site/ mmol g^{-1}
		gel	product				
AISBA-15(45)	11.27	7	45	930	1.35	9.7	0.439
AISBA-15(7)	11.76	3	7	604	1.26	11.8	0.387
AIMCM-41(23)	3.63	23	22	1210	0.80	2.4	0.359
BEA	-	-	30	540	-	-	0.94
MFI	-	-	60	364	-	-	0.82

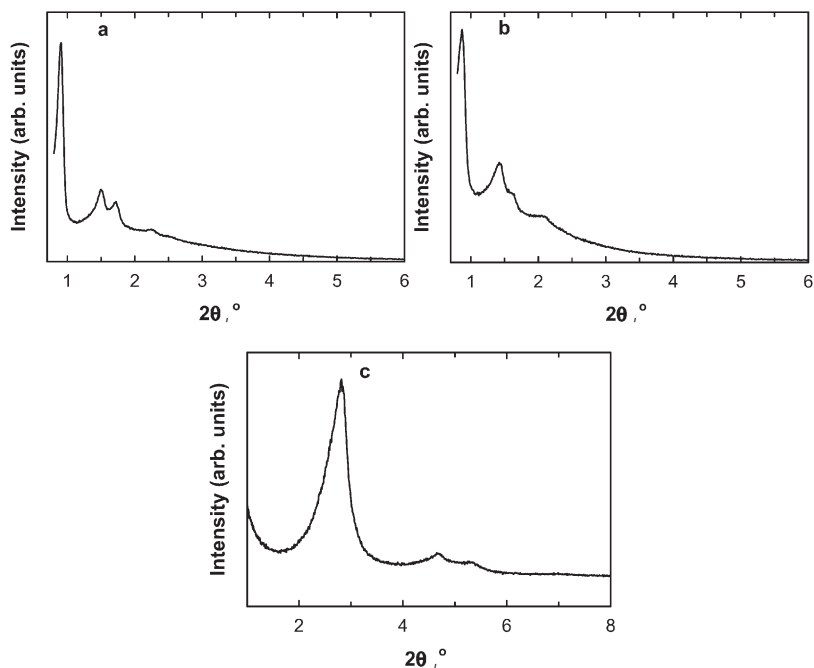


FIG. 1
Powder XRD patterns of calcined AISBA-15 with different $n_{\text{Si}}/n_{\text{Al}}$ ratio and AIMCM-41(23): AISBA-15(45) (a), AISBA-15(7) (b) and AIMCM-41(23) (c)

in the silica framework of SBA-15 (Table I). Elemental composition of AISBA-15 materials is also presented in Table I. In all cases, the $n_{\text{Si}}/n_{\text{Al}}$ ratio of the calcined materials is higher than the $n_{\text{Si}}/n_{\text{Al}}$ ratio in the synthesis gel, indicating a lower extent of Al incorporation. This could be due to a high solubility of the aluminum source in the acid medium. The powder XRD pattern of AIMCM-41(23) also exhibits a high degree of structural ordering as evident from the narrow (100) reflections and the presence of the higher-order (110) and (200) reflections which can be assigned to a hexagonal lattice, in good agreement with the reported patterns of MCM-41 materials (Fig. 1). More detailed characterization of these catalysts including nitrogen adsorption isotherms, pyridine-TPD, and ^{27}Al MAS NMR was reported elsewhere by Vinu et al.⁴⁷⁻⁴⁹

Catalytic Activity

Acetalization of aldehydes or ketones, in general, is initiated in the presence of an acid catalyst through a simple condensation reaction. Acetalization of ethyl acetoacetate with ethylene glycol was carried out over AISBA-15(45) at the reaction temperature 146 °C, reaction time 1 h, and the catalyst weight 0.09 g (3 wt.% of the total reaction mixture) and the results were compared with MFI and AIMCM-41(23). The reaction scheme and the activities of the studied catalysts in the acetalization of ethyl acetoacetate with ethylene glycol are shown in Scheme 1 and Table II, respectively. Regardless of the nature and the type of the catalysts, only one main product is formed, which is fructose. This is an industrially important product, which shows that the type of the catalyst does not play a role in controlling the selectivity of the products in this reaction. It can also be seen from Table II that the conversion of ethyl acetoacetate is significantly affected by the nature and the type of the catalysts investigated. According to Table I, of the catalysts studied, AISBA-15(45) was found to be the most active cata-



SCHEME 1

Reaction scheme of the formation of fructose (ethyl 3,3-ethylenedioxy)butanoate)

lyst; it exhibits the ethyl acetoacetate conversion 50% with 100% selectivity to fructose under the optimized reaction conditions. On the other hand, MFI gives the ethyl acetoacetate conversion 37% whereas only 24% of conversion was obtained for AIMCM-41(23).

As it is well documented, the acetal formation is a reversible reaction, which proceeds by a two-step mechanism. The first step is the formation of a hemiacetal, followed by removal of a water molecule. Acetal or ketal formation is strongly influenced by electronic and steric factors involved in the reaction. However, it is generally accepted that the rate-determining step of acetalization is the formation of a cation from the protonated hemiacetal. In order to compensate for the low rate of hemiacetal formation, the reaction media must be sufficiently acidic in order to promote the effective protonation of any hemiacetal formed, and polar to allow stabilization of the cationic intermediate. If the above concept is true, MFI catalyst, which exhibits the greatest number of acid sites of the other catalysts used in the study, should be the most active catalyst. However, the catalyst was found to be the least active, which is contrary to the above statement, revealing that the parameters other than acidity play a critical role in controlling the activity of the catalysts. When the textural parameters of the catalysts are compared with the catalytic activities (Tables I and II), it is found that the performance of the catalysts in the acetalization reaction could be less dependent on the specific surface area and the acidity of the catalysts, but more on the pore size of the catalysts. The pore diameter of the AISBA-15 is much larger than that of the other catalysts used in the study, which allows the mass transport of the reactant molecules inside mesochannels of

TABLE II

The comparison of the catalytic activity of the AISBA-15(45) on the acetalization of ethyl acetoacetate with ethylene glycol over MFI and AIMCM-41(23)

Catalyst	Ethyl acetoacetate conversion, mole %	Selectivity, mole %
AISBA-15(45)	50	100
MFI	37	100
AIMCM-41	24	100

Reaction conditions: ethyl acetoacetate 1.56 g, ethylene glycol 1.49 g, ethylene glycol/ethyl acetoacetate molar ratio 2, toluene 41 ml, catalyst weight 0.09 g (3 wt.% of total weight of the reactants), temperature 146 °C, time 1 h.

AlSBA-15 and really helps to achieve the highest conversion of ethyl acetoacetate. A similar trend was also observed by Corma et al.¹⁷ in the synthesis acetal fragrance using large-pore zeolites, in which toluene was used as the solvent. Another advantage of the AlSBA-15 catalyst is its high thermal and hydrothermal stabilities due to its thicker aluminosilicate walls, which are also highly critical for the regeneration of the catalyst and its repeated use. From these results, it is evident that the AlSBA-15 catalyst is highly active, efficient, and eco-friendly, which can replace the homogeneous and small micropore zeolites and zeotype catalysts, which are currently being employed in the industry for the production of acetals.

The effect of catalyst concentration on the conversion and the product selectivity in acetalization of ethyl acetoacetate with ethylene glycol was also studied using the AlSBA-15(45) catalyst. It was found that the conversion of ethyl acetoacetate increases from 41 to 87.5% with catalyst weight increasing from 1 to 5 wt.% for a reaction time of 1 h (Table III). However, the selectivity of the product was not at all affected if the catalyst weight was increased. The increase in the activity with increasing catalyst weight is mainly attributed to the fact that the number of active sites, which are required for the reaction, increase with increasing catalyst weight.

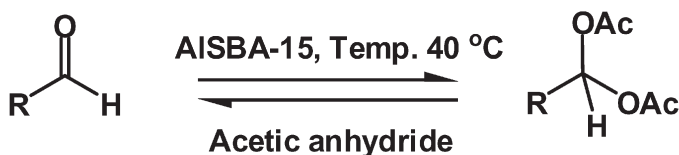
The use of the AlSBA-15 catalyst was also extended to acylal reactions. Scheme 2 shows the selective formation of acylal compounds by the reaction of benzaldehyde with acetic anhydride, which is carried out using AlSBA-15(45) and other catalysts such as MFI, BEA, AlMCM-41(23), and AlSBA-15(7) in the distillation mode; the results are presented in Table IV. It should be noted here that the reactions were carried out under solvent-free conditions at 40 °C. These conditions are mild, cost-effective, and

TABLE III

The effect of catalyst concentration on the catalytic activity of the acetalization of ethyl acetoacetate with ethylene glycol over AlSBA-15(45)

Catalyst wt. %	Ethyl acetoacetate conversion, mole %	Selectivity, mole %
1	41.0	100
3	50.0	100
5	87.5	100

Reaction conditions: ethyl acetoacetate 1.56 g, ethylene glycol 1.49 g, ethylene glycol/ethyl acetoacetate molar ratio 2, toluene 41 ml, temperature 146 °C, time 1 h.



SCHEME 2

Reaction scheme of acylal formation

environment-friendly. Interestingly, 100% selectivity to acylal was obtained regardless of the nature and the type of the catalysts. As can be seen in Table IV, AISBA-15 with the highest aluminum content shows a low activity compared with AISBA-15(45), which records the highest activity with the benzaldehyde conversion 81% under the optimized reaction conditions. The low activity of AISBA-15(7) could be mainly due to the presence of a large amount of octahedral aluminum in the catalyst, which provides Lewis acid sites, where the aldehyde may interact and form the intermediates, resulting in a low reactivity. Of the catalysts studied, MFI was found to be the least active catalyst, which is mainly due to the fact that the pore diameter of the MFI is much smaller than that of the other catalysts investigated in this study. It is also interesting to note that the conversion of benzaldehyde increases with increasing weight of the AISBA-15(45)

TABLE IV

The comparison of the catalytic activity of the AISBA-15(45) with other catalysts on the acylal formation with benzaldehyde and Ac_2O

Catalyst	Catalyst wt.%	Benzaldehyde conversion, mole %	Selectivity mole %
AISBA-15(45)	0.1	9.4	100
AISBA-15(45)	0.2	46.8	100
AISBA-15(45)	0.3	66.8	100
AISBA-15(45)	0.5	81	100
AISBA-15(7)	0.5	11	100
BEA	0.5	31	100
MFI	0.5	5.6	100
AlMCM-41	0.5	31.9	100

Reaction conditions: benzaldehyde 0.79 g, Ac_2O 2.28 g, Ac_2O /benzaldehyde molar ratio 3, temperature 40 °C, time 15 min.

catalyst. The conversion increased from 9.4 to 81% with increasing the weight percentage of the catalyst from 0.1 to 0.5. A similar trend was also observed in the acetalization of ethyl acetoacetate using ethylene glycol.

The acylal formation has also been studied with benzaldehyde derivatives such as 4-methoxybenzaldehyde and 4-methylbenzaldehyde with acetic anhydride to see the effect of aldehyde structure on the formation of the acylals. The results are presented in Table V. It is noteworthy to mention that catalyst activity decreases when the aldehydes with electron-donating substituents are used as the reactants. The aldehyde conversions decreases in the order: benzaldehyde > 4-methylbenzaldehyde > 4-methoxybenzaldehyde. This could be mainly due to preferential adsorption of the aldehyde with electron-donating substituents on the catalyst surface, which blocks the accessibility of acetic anhydride to the active site of the catalyst. This causes a possible poison effect due to strong adsorption of the aldehydes with electron-donating groups, leading to a low catalytic activity. Moreover, the presence of the Lewis acid sites in the catalyst systems where some aldehydes may interact and form the intermediates with the Lewis acid sites also favors a low reactivity, which is clearly reflected in the AISBA-15(7) catalyst.

It is important to study whether the aluminium leakage of the AISBA-15(45) catalysts under the reaction conditions used. This can help in enhancing the repeatability of the catalytic reaction as industrial application demands assessment of the process economy. To check this aspect, the acetalization reaction was stopped after 15 min and the catalyst was separated while still hot. The hot filtrate was monitored in further reaction for 1 h. As expected, the filtrates obtained from all the catalysts did not show any change in conversion. This observation confirms that the aluminium is fixed in the solid catalyst and does not leak out under acid conditions.

TABLE V
Acylal preparation from benzaldehyde and its derivatives with acetic anhydride over AISBA-15(45) catalyst

Substrate	Conversion, %	Selectivity, %
Benzaldehyde	81	100
Tolualdehyde	15	100
<i>p</i> -Anisaldehyde	1.6	100

Reaction conditions: acetic anhydride/aldehyde molar ratio 3, catalyst weight 0.015 g (0.5 wt.% of the total weight of the reactants), temperature 40 °C, time 15 min.

Further, recyclability of the catalyst was studied in acetalization of ethyl acetoacetate using the most active catalyst AISBA-15(45) under the reaction conditions 146 °C, 1 wt.% catalyst, ethylene glycol/ethyl acetoacetate molar ratio equal to 2 in 40 ml toluene for 30 min in the distillation mode. The catalyst was recycled twice without any appreciable loss in its activity after calcination of the separated catalyst at 500 °C for 3 h in air. Even after two recyclings, the product with a similar yield and purity as those obtained in the first cycle was achieved. This shows that the catalyst could be regenerated several times and that it is highly stable under the reaction conditions.

CONCLUSIONS

Aluminum-containing mesoporous molecular sieves AISBA-15 with different $n_{\text{Si}}/n_{\text{Al}}$ ratios were synthesized using aluminum triisopropoxide as the source of aluminum and characterized by physicochemical methods, viz. XRD, AAS, N_2 adsorption, and pyridine-TPD. Fructose was synthesized by the acetalization of ethyl acetoacetate with ethylene glycol. Acylal reactions with aldehydes and acetic anhydride were carried out over AISBA-15 catalysts and their results were compared with MFI, BEA and AIMCM-41(23). Of the catalysts studied, AISBA-15(45) was the most active catalyst, showing superior catalytic performance in the synthesis of fructose and acylals as compared with other catalysts investigated. In addition, the deactivated catalyst could be regenerated without appreciable loss in catalytic activity and selectivity in several cycles.

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