

# Novel Highly Acidic Nanoporous Catalysts and their Application in Acid Catalyzed Reactions

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## Abstract

Three dimensional cage type mesoporous aluminosilicates (AIKIT-5) with different  $n_{Si}/n_{Al}$  ratios have been successfully synthesized hydrothermally using pluronic F127 as a template under highly acidic medium (Srinivasu et al. Adv. Funct. Mater. (2008) in press). The catalysts have been unambiguously characterized by XRD,  $N_2$  adsorption, and TPD of  $NH_3$ , and utilized for the acetylation of veratrole, and other aromatic substrates such as anisole, isobutylbenzene, and 2-methoxynaphthalene, using acetic anhydride (AA) as an acylating agent under liquid phase conditions. The effect of various parameters such as the reaction temperature, reaction time, reactant mole ratios, and amount of aluminium, on the AA conversion in the acetylation of veratrole has been investigated in detail to discover the optimized reaction condition. The reaction conditions were optimized to get more conversion of acetic anhydride and the activity of these catalysts has been compared with zeolite catalysts namely HY, H $\beta$ , H-mordenite, and HZSM-5 zeolites, and the results are discussed in detail. It has been found that the AIKIT-5 catalysts showed excellent performance in the acetylation of veratrole over zeolites and other mesoporous catalysts studied under the optimized reaction conditions. Among the catalysts studied, AIKIT-5(10) was found to be the best catalyst, showing high conversion of AA and very high selectivity to the desired products. The conversion of AA decreases in the following order: AIKIT-5(10)>AIKIT-5(28)>HY(13.5)>H $\beta$ (30)>AIKIT-5(44)>AIMCM-41(22)>H-mordenite(20)>ZSM-5(60). Moreover, the kinetics of the AIKIT-5(10) catalyst in the acetylation of veratrole has been investigated in detail and the results are clearly discussed.

*Keywords:* Mesoporous, aluminosilicates, Brønsted acidity, acetylation, veratrole and acetic anhydride

## 1. Introduction

Ordered mesoporous materials with tunable pore size in the range of 2 to 50 nm have attracted a great deal of attention in the recent years owing to their unique structures with organized porosity, high surface area, and pore volume, and impending applications mainly in the field of catalysis, adsorption, separation, sensors, and fuel cells [1-19]. Among the porous materials, mesoporous silica materials consisting of interconnected large pore cage type mesoporous system with three-dimensional porous network are highly interesting and believed to be more advantageous than the porous materials having hexagonal pore structure with an uni-dimensional array of pores. SBA-16, SBA-1, and KIT-5 are a few examples of the porous materials possessing three dimensional cage type porous structures [9,12,13].

Among these materials, KIT-5, which was reported by Kleitz et al., is an interesting material and possesses highly ordered cage type mesoporous structure with cubic  $Fm\bar{3}m$  close packed symmetry, high surface area, large cage type tunable pores, and high specific pore volume [20]. These exciting properties stimulate the researchers to utilize them as the adsorbents for the adsorption and separation of large biomolecules.

KIT-5 materials have been also employed as the template for fabricating various non-siliceous mesoporous materials. Very recently, Vinu et al. have successfully used the KIT-5 materials with various pore diameters as the sacrificial inorganic templates for the preparation of large pore cage type mesoporous carbon materials with tunable textural parameters, carbon nanocages [21-22]. However, despite these interesting features, the KIT-5 silica materials have a few disadvantages such as neutral framework, poor stability, weak acidity, and low ion exchange capacity, which have restricted their application potential in many areas including catalysis, adsorption, and nanotechnology. These problems can be circumvented by introducing hetero-atoms in the silica framework of KIT-5 materials, which can provide the acidic surface and metallocate frameworks, which are much stronger than the pure silica framework. However, the incorporation of heteroatoms in KIT-5 silica framework, which require highly acidic medium for the formation, is very difficult and highly challenging task. Recently, Vinu et al. have introduced several techniques such as the controlled water to HCl addition and the controlled addition of HCl to silica methods to incorporate hetero atoms in the silica materials in a highly acidic medium. Al, Fe, and Ti in mesoporous SBA-15 and SBA-1 materials with high metal atom content has been successfully prepared using the above techniques [23-25]. The same synthetic strategy has been extended for the introduction of hetero-atoms in the KIT-5 silica framework as well, and we succeeded in the preparation of AIKIT-5 materials with a high content of Al in the tetrahedral coordination, tunable pore diameters, and different morphology [26].

Friedel-Crafts acetylation of aromatic compounds is one of the industrially important reactions for the production of several value-added aromatic ketones [27-36]. Several solid oxide heterogeneous catalysts such as zeolites and zeotype materials, and homogeneous catalysts have been employed for the acetylation of aromatic reactions, which are highly efficient, sustainable, recyclable, and ecofriendly [27-36]. However, these catalysts pose several disadvantages such as low surface area and small pore diameter, which would limit their application for treating heavier molecules and for the production of more bulky value-added organic intermediates.

Here, we report on the preparation and the characterization of AIKIT-5 materials with different Al contents and their catalytic activity in the acetylation of veratrole using AA as an acylating agent. The influence of reaction temperature, reaction time, the amount and the silica to aluminium ratios of the catalysts, and the reactant mole ratios has been studied in detail. The reaction conditions were optimized to get more conversion of acetic anhydride and the activity of these catalysts has been compared with zeolite catalysts namely HY, H $\beta$ , H-mordenite, and HZSM-5 zeolites, and the results are discussed in detail. The AIKIT-5 catalysts was found to be more effective and showed much higher performance in the acetylation of veratrole as compared with zeolites and other mesoporous catalysts used in the study.

## **2. Experimental section**

### **2.1 Preparation of the catalysts**

The AIKIT-5 materials with different  $n_{\text{Si}}/n_{\text{Al}}$  ratios were synthesized using Pluronic F127 as the template in an acidic medium. In a typical synthesis, 5.0 g of F127 was dissolved in 3 g of HCl (35 wt %) and 240 g of distilled water. To this mixture, 24.0 g of TEOS and the required amount of the aluminium isopropoxide were added, and the resulting mixture was stirred for 24 h at 100 °C. Subsequently, the reaction mixture was heated for 24 h at 100 °C under static condition for hydrothermal treatment. After hydrothermal treatment, the final solid product was filtered off and then dried at 100 °C without washing. The product was calcined at 540 °C for 10 h. The samples are denoted as AIKIT-5(x) where x denotes the  $n_{\text{Si}}/n_{\text{Al}}$  ratio in the final product. The molar gel composition of the reaction mixture was 1.0:0.041-0.071:0.0035:0.25:116.6 SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub>:F127: HCl: H<sub>2</sub>O

## 2.2 Characterization of catalysts

The powder X-ray diffraction patterns of AIKIT-5 samples were collected on a Rigaku diffractometer using CuK $\alpha$  ( $\lambda = 0.154$  nm) radiation. Nitrogen adsorption and desorption isotherms were measured at -196 °C on a Quantachrome Autosorb 1 sorption analyzer. The diameter of the cages in AIKIT-5 materials is calculated using equation (1) which was recently proposed by Ravikovitch et al. [37].

$$D_{\text{me}} = a \cdot (6\epsilon_{\text{me}}/\pi v)^{1/3} \quad (1)$$

In equation (1),  $D_{\text{me}}$  is the diameter of the cavity of a cubic unit cell of length  $a$ ,  $\epsilon_{\text{me}}$  is the volume fraction of a regular cavity and  $v$  is the number of cavities present in the unit cell (for  $Fm3m$  space group,  $v = 4$ ). The temperature-programmed desorption (NH<sub>3</sub>-TPD) was carried out on a Micromeritics Autochem 2910 instrument.

## 2.3 Catalytic reactions

Acetylation of veratrole with AA has been carried out in liquid phase (Scheme 1). The reaction was carried out in a 50 ml round-bottomed flask equipped with condenser and an additional port to withdraw samples at regular intervals under continuous stirring. The temperature of the above assembly was maintained by placing in a thermostatted oil bath. In a typical reaction, 0.15 g catalyst (5 wt% of total reaction mixture), 2.61 g of veratrole, (18.89 mmol), and 0.39 g AA (3.82 mmol) were mixed and heated between 55 and 75 °C for a period of 1 to 3 h. The collected samples were analyzed periodically by a Shimadzu gas chromatograph GC-2010 with TCD detector.

# 3. Results and discussion

## 3.1 Characterization of the catalysts

The textural parameters of the catalysts were given in Table 1. The complete characterization of the catalysts can be found elsewhere [26]. Table 1 shows the elemental compositions of AIKIT-5 materials synthesized with different  $n_{\text{Si}}/n_{\text{Al}}$  ratios. The  $n_{\text{Si}}/n_{\text{Al}}$  ratio of AIKIT-5 increases with increasing the amount of Al source in the synthesis mixture. The  $n_{\text{Si}}/n_{\text{Al}}$  ratio of the AIKIT-5 materials decreases from 44 to 10 with decreasing the  $n_{\text{Si}}/n_{\text{Al}}$  ratio in the synthesis gel from 12 to 7. It must be noted that in all the cases the  $n_{\text{Si}}/n_{\text{Al}}$  ratio of the final product is much higher than that used in the synthesis gel. This is probably a consequence of either higher solubility of aluminum isopropoxide or repulsion between the positively charged Al hydroxo species in the acidic medium. The specific surface area increases from 713 to 989 m<sup>2</sup>/g and the specific pore volume increases from 0.45 to 0.68 cm<sup>3</sup>/g (Table 2) with increasing the Al content in the AIKIT-5 samples. The capillary condensation is shifted towards higher relative pressure when the amount of Al in the silica

framework of KIT-5 is increased. Moreover, the pore diameter of the materials increases from 5.2 to 6.0 nm whereas the cage diameter of the materials increases from 10.3 to 12.0 nm with decreasing the  $n_{Si}/n_{Al}$  ratio from 44 to 10.

### 3.2. Catalytic activity

In order to evaluate the catalytic activity, the reaction has been carried out with various molar ratios of veratrole and AA ( $n_{VR}/n_{AA}$ ) such as 1.5, 2.5, 5, 7.5, and 10, and the results are shown in Figure 1. The acetylation of veratrole with AA generates acetic acid in the products, which resulted from the AA consumption. Only one product is obtained which is 3, 4-dimethoxyacetophenone (DMAP), due to the fact that both the ortho positions of veratrole are sterically crowded for electrophilic reaction, acetylation preferentially occurs at the fourth position which is the most favoured and para to one of the methoxy substituents. No products other than DMAP were found in the product mixture. The reaction was carried out at the reaction temperature of 60 °C and the catalysts weight of 5wt% of the total reaction mixture (0.15 g). The samples were taken from the reaction mixture at regular time intervals and analyzed by GC. AIKIT-5(10) catalyst, which exhibits excellent textural parameters and higher acidity and Al content as compared with those of other AIKIT-5 catalysts, was used for this study. No solvent used for the reaction as the veratrole itself acts as the self-solvent in the reaction.

It is interesting to note from the kinetic curve that the rate of the reaction is very slow when the  $n_{VR}/n_{AA}$  ratio of 1.5 is used. Moreover, a significant increase in the conversion of AA is observed when the  $n_{VR}/n_{AA}$  ratio in the reactant mixture is increased from 1.5 to 10. At a reaction time of 2 h, the conversion of AA is increased from 24.3 to 100% with increasing the  $n_{VR}/n_{AA}$  from 1.5 to 10, while the selectivity to DMAP is almost constant in all the cases. The increase of conversion of AA with increasing the amount of veratrole is mainly due to the adsorption of more amount of veratrole on the catalysts surface compared to AA molecules. This can avoid the possible catalytic poison effect expected from the adsorption of the acetic acid molecules, which are generated during the reaction by the consumption of AA, leading to high conversion of AA. The increase of the AA conversion at high  $n_{VR}/n_{AA}$  ratio may also be attributed by the fact that the higher amount of veratrole enhances the diffusion of the reactants and the discharge of the products from the cage type porous structure, which also reduces the inhibition effect generated by the adsorption of the products on the surface of the AIKIT-5 catalyst surface, leading to a high conversion of AA. As  $n_{VR}/n_{AA}$  ratio of 5 gives the AA conversion of AA more than 70% within the reaction time of 1h, we have chosen the  $n_{VR}/n_{AA}$  ratio of 5 is the optimum feed ratio for further studies.

To study the efficiency of AIKIT-5(10) with respect to the reaction temperature, the reactions have been carried out over AIKIT-5(10) at various reaction temperatures of 50, 60, 65, 70 and 75 °C, the  $n_{VR}/n_{AA}$  ratio of 5, catalyst weight of 0.15 g (5wt% of the total reaction mixture), and different reaction time, and the kinetic curves are shown in Figure 2. As expected, the conversion of AA increases with increasing the reaction temperature, indicating that the catalyst was quite stable and the reaction was free from diffusion limitation at higher temperature. At 50 °C, the conversion of AA was 55% even after 3 h. But for the temperature of 60 °C and above, 100% conversion of AA was obtained after 3 h of reaction. The complete conversion of AA with 100% selectivity to DMAP was achieved at the reaction temperature of 75 °C for a reaction time of 1 h. From these results it is found that the rate of the reaction at lower temperature is rather slow whereas the reaction is very fast at the reaction temperature above 60 °C. The more and quick conversion at higher temperatures clearly shows that this reaction is high activation energy demanding and also the Al sites are activated more at higher elevated temperature than at lower temperatures, leading to the

formation of rapid acetyl cations, a naked electrophile through the interaction of AA. Consequently, the conversion of acetic anhydride increased with increasing temperatures. The catalyst was tested for reusability where the used catalyst was reused more than three times. No major change in both the conversion and the selectivity of the product was observed, indicating that the catalyst is highly stable and can be recycled.

The apparent rate constant of the reaction at different reaction temperature was calculated using the pseudo-first order rate law:

$$\log (1/1 - x) = (k_a/2.303) (t - t_0)$$

where  $k_a$  is the apparent rate constant,  $x$  the fractional conversion of AA,  $t$  the reaction time and  $t_0$  the induction period corresponding to the time required for reaching equilibrium temperature. A plot of  $\log [1/1 - x]$  versus  $(t - t_0)$  gives a linear plot over a range from 10 to 90%. As expected, the apparent rate constant for the acetylation reaction was increased from  $43.87 \times 10^{-4} \text{ min}^{-1}$  to  $324.31 \times 10^{-4} \text{ min}^{-1}$  with increasing the reaction temperature from 50 to 75 °C. The activation energy for the AIKIT-5(10) calculated from an Arrhenius plot, which is shown in Figure 3, was found to be  $68.9 \text{ KJ mol}^{-1}$ . From the above kinetic results at different temperature, we have decided to choose the reaction temperature of 60 °C for investigating the effect of structure,  $n_{\text{Si}}/n_{\text{Al}}$  ratio, and the weight of the catalysts in the activity of AIKIT-5 in the acetylation of veratrole.

The influence of catalyst weight on conversion of AA over AIKIT-5(10) was studied at the  $n_{\text{VR}}/n_{\text{AA}}$  ratio of 5, and the reaction temperature at 60 °C and the results are shown in Figure 4. As expected, the conversion of AA increases with increasing the weight of the catalyst in the reaction mixture. It was obvious that as the amount of catalyst increases, the interaction of the reactant molecules with the catalytic active sites, which are significantly increased when higher amount of the catalyst is used, may be enhanced due to the larger availability of the active surface sites. This triggers the faster and efficient electrophilic reaction, consequently, the conversion of AA increases with increasing the concentration of the catalyst.

The effect of  $n_{\text{Si}}/n_{\text{Al}}$  ratios on the activity of AIKIT-5 catalysts in the acetylation of veratrole was also studied at  $n_{\text{VR}}/n_{\text{AA}}$  ratio of 5, the catalyst amount of 0.15 g (5 wt% of total reaction mixture) and the reaction temperature of 60 °C (Figure 9). As can be seen in Figure 5, the AA conversion is decreased with increasing the  $n_{\text{Si}}/n_{\text{Al}}$  ratios. The conversion was almost 100 % for AIKIT-5(10) and 76.5% for AIKIT-5(44) after the 3 h of reaction time. This trend can be easily interpreted in terms of the increase of the Al atoms in the AIKIT-5(10) matrix, where the reaction is believed to occur, which are responsible for the formation of Brönsted acid sites, leading to a higher activity in the acetylation of veratrole, as compared with other AIKIT-5 samples. The higher acidity in the AIKIT-5(10) was also confirmed by the data obtained from the acidity measurements. Moreover, the high specific surface area and the pore volume, and the large pore diameter of the AIKIT-5(10), which can provide the enough active sites and easy access for the reactant molecules, are also responsible for the higher activity.

The catalytic activities of AIKIT-5 materials synthesized at diverse  $n_{\text{Si}}/n_{\text{Al}}$  ratios in the acetylation of veratrole using AA under the optimized reaction conditions were compared with the zeolite catalysts such as H-β(30), H-Y(13.5), H-mordenite(20), and H-ZSM-5(60). The activity of the catalysts under the optimized reaction conditions at the reaction time of 2 h is presented in Table 2. As mentioned previously, among the AIKIT-5 catalysts studied, the catalyst with the high Al content, AIKIT-5(10) was found to be more efficient and active catalyst in the acetylation of veratrole. When the conversion of the AIKIT-5 catalysts is

compared with the zeolite catalysts under the optimized reaction conditions, as shown in Table 2, it is found that the conversion of AA decreases in the following order: AIKIT-5(10)>AIKIT-5(28)>HY(13.5)>H $\beta$ (30)>AIKIT-5(44)>AIMCM-41(22)>H-mordenite(20)>ZSM-5(60). It is quite surprising to see that the catalytic activity of AIKIT-5(10) is much higher as compared to that of highly acidic zeolite catalysts used in this study under the optimized reaction conditions. At the reaction time of 2 h, AIKIT-5(10) registers almost 69.1% conversion of AA where as the H-Y, which is the most active catalysts among the zeolites catalysts studied, displays AA conversion of 63%, under the same reaction conditions. The superior performance of AIKIT-5(10) is mainly attributed to the fact that the accessibility of the active sites by the reactant molecules is higher in AIKIT-5(10) than the zeolite catalysts, with a large number of Brønsted acid sites, which is supported by their huge specific surface area and the specific pore volume, and large pore diameter with well-ordered pore structure. These remarkable textural characteristics of the AIKIT-5(10) in combination with the huge acidity and three dimensional cage type porous structure, which can offer large number of active sites and easy access for the reactant molecules, are responsible for its higher catalytic activity. To the best of our knowledge, such a high catalytic activity in the acetylation reaction over mesoporous catalyst has never been reported in the open literature so far.

The acetylation of other aromatic substrates such as anisole, isobutyl benzene, and 2-methoxy naphthalene under the optimized reaction conditions was also carried out over AIKIT-5(10) and the results are given in Table 3. For anisole, p-isomer is formed exclusively with traces of o-isomer. The AA conversion of almost 83.4% was observed at the reaction time of 3h whereas selectivities to p-methoxy acetophenone and o-methoxy acetophenone of 97.5 and 2.5%, respectively, were observed for AIKIT-5(10). In the case of isobutylbenzene as the substrate, AIKIT-5(10) displayed 78% selectivity to 4-isobutylacetophenone with the AA conversion of 43.5%. The higher selectivity of p-isomer might be attributed to the faster diffusion of the p-products as compared to that of the o-products, and less steric hindrance due to the bulky groups in the aromatic ring. When 2-methoxy naphthalene was used as the aromatic substrate, the catalyst gave 66% conversion of AA and 96 and 4% selectivities to 1-acetyl-2-methoxynaphthalene and 6-acetyl-2-methoxynaphthalene, respectively. The preferential formation of 1-acetyl-2-methoxynaphthalene over AIKIT-5 catalysts could be mainly due to the fact that the catalysts possess very high surface area and pore volume which promotes the higher selectivity of the bulky product. Similar results have been also observed for the zeolites with a huge external surface area. Based on these results, it can be concluded that AIKIT-5(10) is the best catalyst, exhibits three dimensional cage type porous networks with a high surface area and comparable acidity which enhance the diffusion of the reactant molecules and allow the easy access to all the active sites. The novel catalyst could replace the existing zeolite catalysts which suffer from a lot of limitation such as low surface area and small pore size, in the acetylation of aromatics.

#### 4. Conclusion

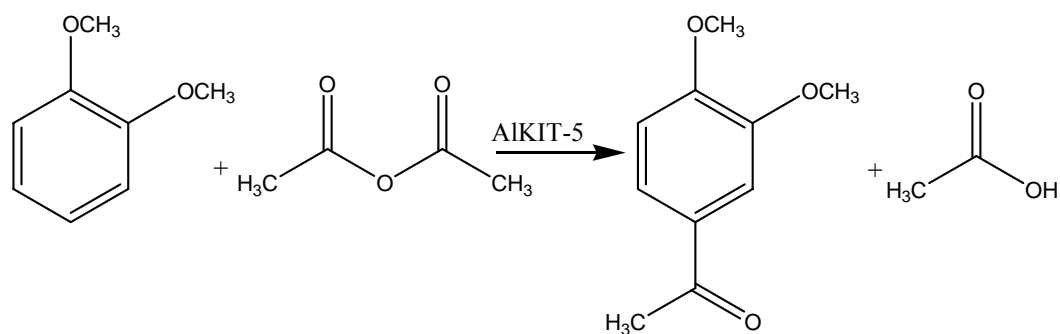
Highly ordered three dimensional cage type aluminosilicates (AIKIT-5) with cubic structure and high aluminium loading have been prepared using pluronic F127 as a surfactant in a highly acidic medium. The obtained materials have been characterized by sophisticated techniques such as XRD, N<sub>2</sub> adsorption, and NH<sub>3</sub>-TPD. The catalytic activity of the AIKIT-5 catalysts has been investigated on the acetylation of aromatics including veratrole, anisole, isobutylbenzene and 2-methoxynaphthalene and the results were compared with zeolites and unidimensional mesoporous catalysts. It has been found that AIKIT-5(10) was highly active and showed a remarkable catalytic performance in the acetylation of veratrole with high AA conversion. The conversion of AA in the acetylation of veratrole decreases in the following

order: AlKIT-5(10)>AlKIT-5(28)>HY(13.5)>H $\beta$ (30)>AlKIT-5(44)>H-mordenite(20)>ZSM-5(60). The high activity of AlKIT-5 over other catalysts used in the study could be related to its three dimensional structure with high surface area, high acidity and well-ordered pore structure. We strongly believe that the novel highly acidic AlKIT-5 catalyst could make a revolution in the heterogeneous catalysis field, and replace the conventional zeolites used for various acid catalyzed transformations, which suffer from various disadvantages such as low surface area and pore volume, and offer potential applications in the field of adsorption and separation of toxic bulky molecules.

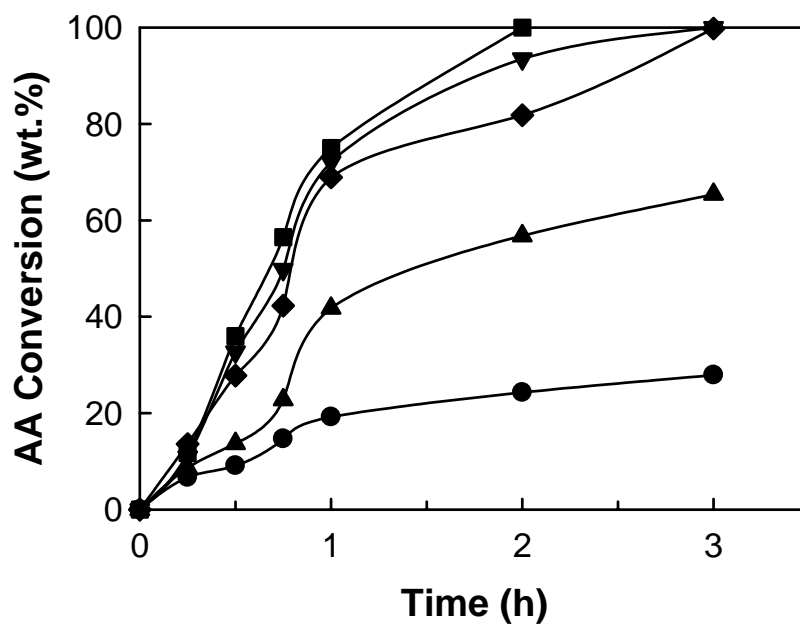
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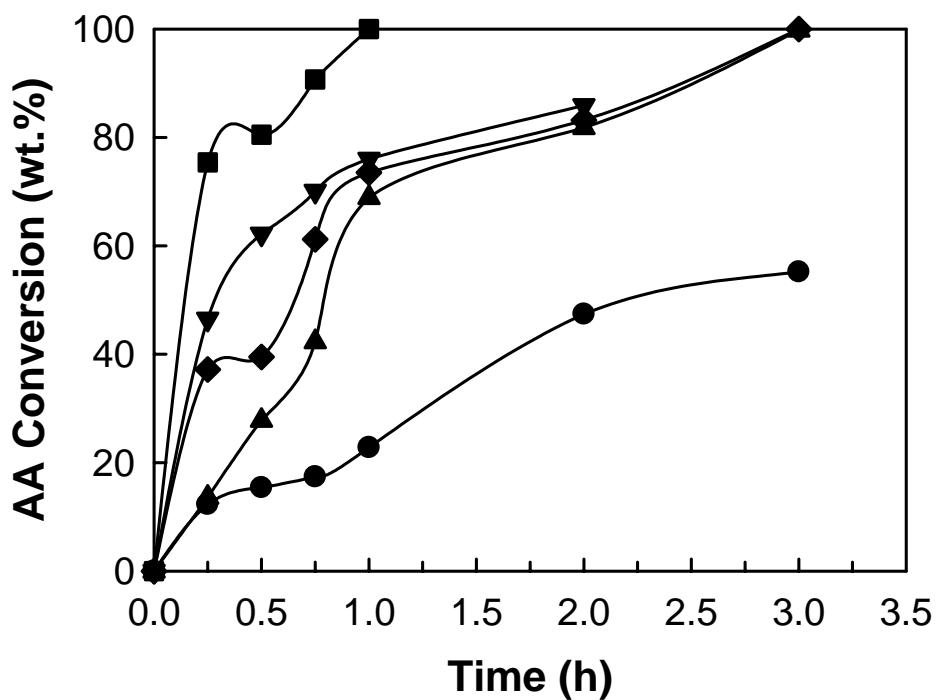
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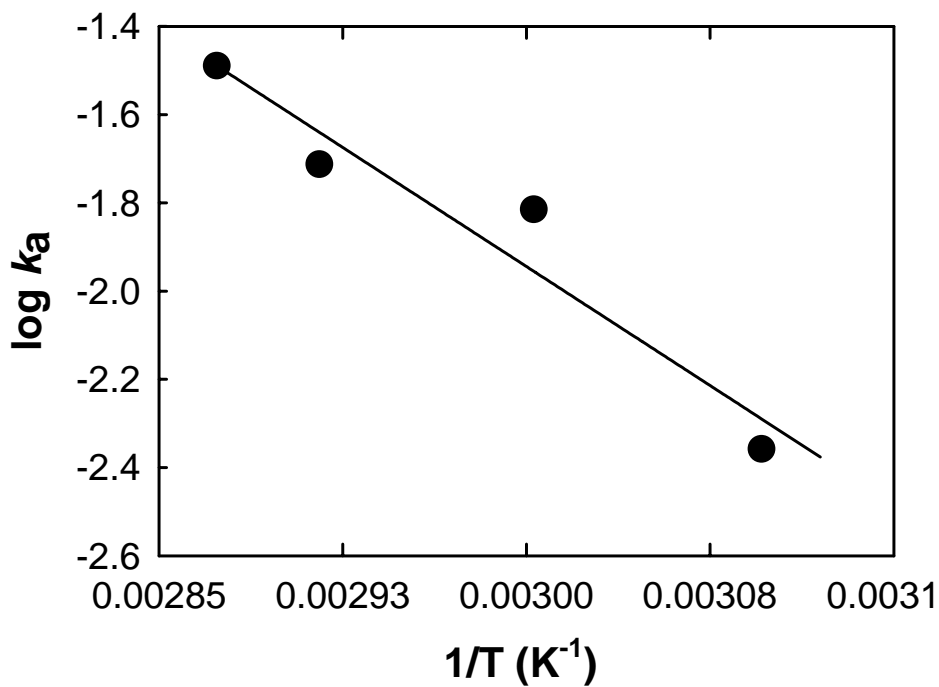
Scheme 1. Acetylation of veratrole with acetic anhydride by AIKIT-5(10) catalyst



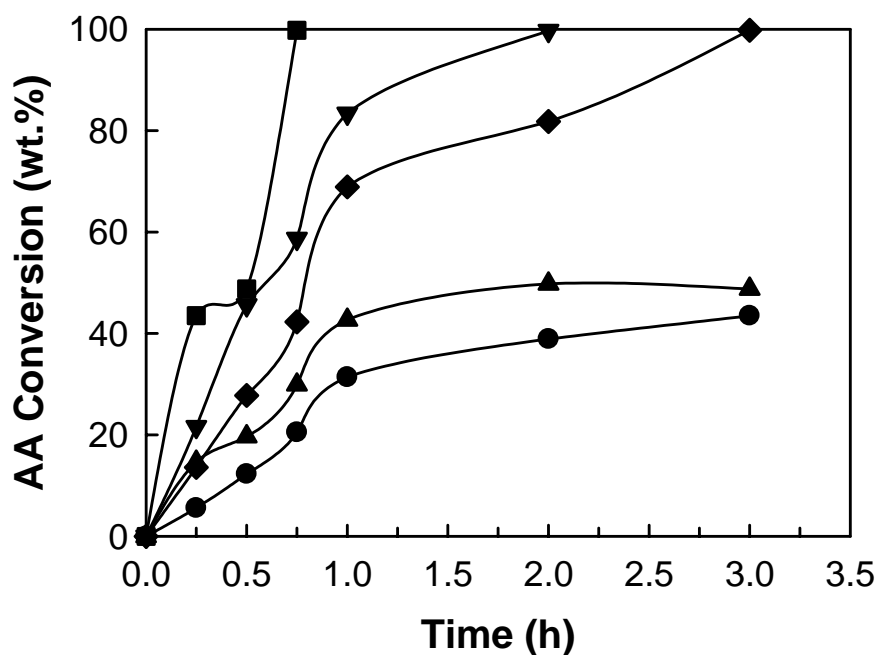
**Figure 1:** Effect of  $n_{VR}/n_{AA}$  ratio on the AA conversion in the acetylation of veratrole over AIKIT-5(10) (catalyst weight 0.15 g; reaction temperature 60 °C): (●) 1.5, (▲) 2.5, (◆) 5, (▼) 7.5, and (■) 10.



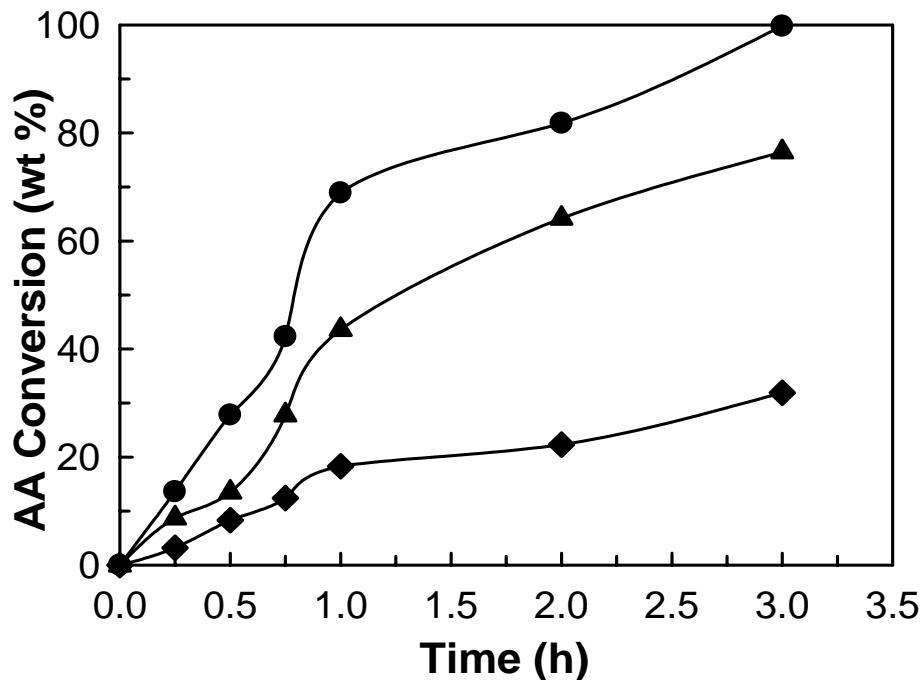
**Figure 2:** Effect of temperature ( $^{\circ}\text{C}$ ) on AA conversion in the acetylation of veratrole over AlKIT-5(10) ( $n_{\text{VR}}/n_{\text{AA}} = 5$ ; catalyst weight 0.15 g): (●) 50, (▲) 60, (◆) 65, (▼) 70, and (■) 75.



**Figure 3:** Arrhenius plot of  $\log k_a$  as a function of  $(1/T)$  for AlKIT-5(10) catalyst



**Figure 4:** Effect of catalyst weight on AA conversion in the acetylation of veratrole over AIKIT-5(10) ( $n_{VR}/n_{AA} = 5$ ; reaction temperature 60 °C): (●) 0.2, (▲) 2.5, (◆) 5, (▼) 7.5, and (■) 10.



**Figure 5:** Effect of  $n_{Si}/n_{Al}$  on AA conversion in the acetylation of veratrole over AIKIT-5 with different  $n_{Si}/n_{Al}$  ratios ( $n_{VR}/n_{AA} = 5$ ; reaction temperature 60 °C, catalyst weight 0.15 g): (●) 10, (▲) 28, and (◆) 44.

**Table 1:** Textural parameters of AIKIT-5 samples prepared at different  $n_{Si}/n_{Al}$  ratio.

Sample	$a_0$ (nm)	$n_{Si}/n_{Al}$		$A_{BET}$ (m <sup>2</sup> /g)	$V_p$ (cm <sup>3</sup> /g)	$dp_{ads}$ , BJH (nm)	Cage diameter (nm)	Wall thickness (nm)
		Gel	Product					
AIKIT-5(10)	18.44	7	10	989	0.68	6.0	12.0	3.0
AIKIT-5(28)	17.76	10	28	815	0.56	5.6	11.2	3.4
AIKIT-5(44)	16.97	12	44	713	0.45	5.2	10.3	4.0
KIT-5	16.61	-	-	622	0.41	5.0	9.9	4.2
AIMCM-41(22)	3.63	23	22	1210	0.8	2.43	-	1.2

where  $a_0$  = unit cell constant;  $A_{BET}$  = surface area;  $V_p$  = specific pore volume;  $dp_{ads}$  = pore diameter calculated from the adsorption branch of the isotherms.

**Table 2:** Comparison of the acidity and the catalytic activity of the AIKIT-5 materials with different  $n_{Si}/n_{Al}$  ratio with zeolites catalysts

catalysts	$A_{BET}$ ( $\pm 5$ m <sup>2</sup> /g)	acidity (mmol/g)	AA conversion ( $\pm 1$ %)	Product selectivity ( %)
AIKIT-5(10)	989	0.50	69.1	100
AIKIT-5(28)	815	0.32	63.2	100
AIKIT-5(44)	713	0.14	50.1	100
H $\beta$ (30)	540	0.94	53	100
HY (13.5)	530	2.25	63	100
H-mordenite(20)	490	0.72	12	100
H-ZSM-5(60)	364	0.82	9	100
AIMCM-41(22)	1210	0.36	30	100

**Reaction conditions:** temperature=60 °C,  $n_{VR}/n_{AA}$ ratio=5, catalyst weight=0.15g (5wt.% of total reaction mixture), time=2 h

**Table 3:** Comparison of catalytic activity of AI-KIT-5(10) materials with various substrates

Substrates	Mole ratio	Temp (° C)	Catalyst weight (g)	Time (h)	AA Conv. (wt%)	Product distribution	
						<b>A</b>	<b>B</b>
Anisole	10:1	90	0.15	3	83.4	97.4 <sup>a</sup>	2.6 <sup>b</sup>
Isobutyl benzene	10:1	100	0.15	3	43.5	77.3 <sup>c</sup>	23.7 <sup>d</sup>
2-Methoxy naphthalene	2:1	100	0.15	3	65.7	96.3 <sup>e</sup>	4.7 <sup>f</sup>

Where a = p-methoxyacetophenone, b = o-methoxyacetophenone, c = 4-isobutyl acetophenone, d = not identified, e = 1-acyl-2-methoxynaphthalene, f = 6-acyl-2-methoxynaphthalene