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PHOSPHOTUNGSTIC ACID SUPPORTED ON ACID-LEACHED POROUS KAOLIN FOR FRIEDEL-CRAFTS ACYLATION OF ANISOLE

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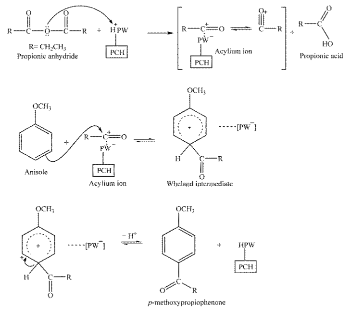

Abstract

Porous clay heterostructures (PCH) was derived from natural kaolin through intercalation with cationic potato starch as the template. Leaching of PCH was performed in concentrated acid solutions consisting of HCl and H_2SO_4. Phosphotungstic acid (HPW) supported on PCH and modified PCH were synthesized by wet impregnation method. The resulting PCH showed remarkable increase in surface area starting from 15 m^2g^{-1} for the parent kaolin to maximium value of 725 m^2g^{-1} for PCH. Acidity studies by pyridine adsorption and FTIR spectra showed that both natural kaolin and PCH possessed strong Lewis acid sites. In contrast, the surface acidity of HPW supported on PCH was significantly enhanced and comprising mainly Brönsted acid sites. The correlation between the Brönsted to Lewis acid ratios (B/L) and either conversion or selectivity of the catalysts has been studied in Friedel-Crafts acylation of anisole. The PCH/30HPW catalyst with the highest number of Brönsted acid sites showed excellent catalytic activity giving 86% conversion of anisole and high selectivity of 95% toward *p*-methoxypropiophenone.

Keywords: Porous clay heterostructure (PCH), phosphotungstic acid, Lewis and Brönsted acids, acylation of anisole

Abstrak

Heterostruktur tanah liat berliang (PCH) telah diperoleh daripada kaolin semula jadi melalui interkalasi dengan kation kanji kentang sebagai templat. Pelarutan lesap PCH telah dilakukan dalam larutan pekat asid HCl and H_2SO_4. Asid fosfotungstik (HPW) tersokong pada PCH dan PCH terubahsuai telah disintesis secara kaedah pengisitepuan basah. PCH yang terhasil menunjukkan peningkatan luas permukaan amat ketara bermula dengan nilai serendah 15 m^2g^{-1} untuk kaolin semulajadi meningkat kepada nilai maksimum 756 m^2g^{-1} untuk PCH. Kajian keasidan secara penjerapan piridina dan spektrum FTIR menunjukkan kedua-dua kaolin dan PCH mempunyai tapak asid Lewis kuat. Sebaliknya, keasidan permukaan HPW yang disokong pada PCH telah meningkat dengan ketara dan mengandungi banyak tapak asid Brönsted. Korelasi antara nisbah tapak asid Brönsted terhadap Lewis (B/L) dengan pertukaran atau kepilihan mangkin telah dikaji dalam tindak balas pengasilan Friedel-Crafts anisol. Mangkin PCH/30HPW yang mengandungi tapak asid Brönsted terbanyak menunjukkan aktiviti pemangkinan sangat baik dengan penukaran anisol 86% dan kepilihan tinggi sebanyak 95% terhadap *p*-metoksipropiofenon.

Kata kunci: Heterostruktur tanah liat berliang (PCH), asid fosfotungstik, asid Lewis dan Brönsted, pengasilan anisol

1.0 INTRODUCTION

Friedel-crafts acylation reactions are of great importance in the industrial manufacture of substituted aromatic ketones, valuable intermediates in the production of pharmaceuticals, cosmetics and fine chemicals [1]. One of the most widely studied model reactions is the acylation of anisole. Conventionally, the present industrial method applies liquid acids or Lewis acid-type catalysts such as $AlCl_3$, $FeCl_3$ and acyl halides as acylating agents for the reaction [2]. The overall process produces a significant amount of hazardous waste, undesirable product and difficulty in separation. Due to the environmental disadvantages of homogeneous catalysts, many efforts are necessary to develop solid acids, using more clean technologies, minimizing economical and environmental problems.

Heterogeneous catalysts have been given much attention for application in Friedel-Crafts acylation reaction, since they can be easily separated from any reaction mixture. Zeolites, modified clays, sulphated zirconia, silica-alumina and heteropoly acids containing either Lewis, Brönsted or both acid sites are among solid acid catalysts that have been applied in Friedel-Crafts acylation [3-6]. However, the use of sulphated zirconia, the well-known super acid catalyst suffers from experimental problems due to the lack of long term stability leading to rapid deactivation of the active sites. Zeolites have high initial activity but unfortunately, the slow diffusion of large, bulky reactant/product molecules within the microporous channels and coke formation makes them relatively poor catalysts in liquid phase reactions [7]. The exact nature of the acid site in these materials and a comprehensive approach to the acid strength remains an area of controversy [8].

Heteropoly acids (HPA) have received the most attention due to the strong acidity, simple preparation and environmental benignity. Phosphotungstic acid (HPW) is one of the HPA materials and possesses strong Brönsted acid sites. However, pure HPW have limitations in bulk form because of the low surface area, rapid deactivation and poor stability [9]. In an attempt to improve the efficiency and stability, the use of supported HPW is therefore preferable. HPW has been supported on SiO_2 (in the form of cesium salt), carbon, montmorillonite, zirconia, mesoporous materials such as MCM-41 and SBA-15 [10-11]. Impregnating the HPW on suitable supports may significantly increase the surface area, which is very important for heterogeneous catalytic processes. The acidity of supported HPW depends mainly on the type of support, and mesoporous silica was the most widely examined support material due to its inertness towards the HPW. However, the HPW acidity at low loadings is weaker and less uniform than for the bulk solid, and some decomposition of the HPW has been observed [12-13]. On the other hand, alumina and zirconia tend to decompose HPAs because of their basic properties, resulting in a deformation of the parent Keggin structure, thus reduction in the overall efficiency [10].

To date, the role of Brönsted and Lewis acid sites in the acylation reaction remains unclear since few studies have been focused on the approach for controlling the Brönsted and Lewis acid ratio in this reaction. Although the catalytic performances of various solid acid catalysts in the acylation reaction have been investigated, the role of Brönsted and Lewis acids sites have yet to be understood thoroughly [9, 14-15]. In this work, kaolin, a naturally occurring aluminosilicate mineral was chemically modified to produce porous clay heterostructures (PCH) by intercalation of cationic potato starch as a template with neutral amine as co-template and silica pillars. The approach is favoured to increase surface area and surface acid properties of kaolin. Then, the PCH was modified by acid leaching treatments to remove octahedral aluminium species from the framework. The treatment of natural clay with mineral acids such as HCl and H_2SO_4 resulted in dissolution of clay layers and the formation of amorphous materials [16]. HPW that possesses strong Brönsted acid sites was supported on PCH and acid treated-PCH. The effect of Lewis and Brönsted acid sites on Friedel-Crafts acylation of anisole using kaolin, PCH, acid-treated PCH, and HPW supported on PCH and acid treated-PCH is examined.

2.0 EXPERIMENTAL

2.1 Preparation of Kaolin Derived PCH and Mesoporous Alumina

Natural kaolin was functionalized using 3-aminopropyltrimethoxysilane (APTMS) according to a previously reported method [17]. The cationic starch was prepared as described elsewhere [18]. The kaolin derived PCH was prepared according to the literature methods [19-20]. Typically, 3 g of functionalized kaolin was mixed with 30 mL of ethanol, 30 µL of HCl (2M) and 20 mL of distilled water in a round bottom flask and stirred for 15 min. The mixture was refluxed and regularly stirred at 60 °C for 4 h. Subsequently, the mixture was added to the readily prepared cationic starch and left in the oven at 80 °C for 2 days. The product was separated by centrifugation and washed until pH 7 was obtained. In the next step, the modified kaolin was added to the natural amine (dodecylamine) and a silica source (TEOS) with a ratio of modified kaolin/dodecylamine/ TEOS of 1 : 10 : 75. The mixture was left at room temperature under continuous stirring condition for 4 h. Then, the product was filtered and dried at 60 °C. The modified kaolin was calcined at 500 °C for 6 h to remove the cationic starch template. The final product was designated as PCH. For comparison purposes, mesoporous alumina was prepared according to the published procedure and designated as MA [21].

2.2 Modification of PCH by Acid Treatment

The PCH (1 g) was refluxed with 5 mL of HCl and H_2SO_4 (2 M) at 80 °C for 12 h. The slurry was cooled and washed thoroughly with hot distilled water. It was dried initially at room temperature followed at 100 °C for 6 h and calcined at 400 °C for 2 h. The samples were designated as PCH-HCl and PCH-H_2SO_4 with to the mineral acids used during the process of digestion.

2.3 Preparation of the Catalysts

PCH, PCH-HCl and PCH-H_2SO_4 were dried in an oven at 100 °C for 2 h. A 30 wt.% amount of HPW was dissolved in 5 mL of methanol and added drop wise to the samples with continuous stirring. Then, it was stirred overnight at room temperature. The product was collected and dried in the oven. The prepared catalysts were denoted by the percentage loading of HPW and type of support. The samples containing 30 wt.% HPW on the PCH, PCH-HCl and PCH-H_2SO_4 supports were denoted as PCH/30HPW, PCH-HCl/30HPW and PCH-H_2SO_4/30HPW.

2.4 Characterization

All the materials obtained were characterized by means of Fourier Transform Infrared Spectroscopy (FTIR), X-Ray Diffraction (XRD) and Brunauer–Emmett–Teller (BET) surface area in order to determine their physicochemical properties. The acidity properties of the catalysts were studied by pyridine adsorption followed by FTIR spectroscopy analysis.

2.5 Catalytic Experiment

The acylation reaction was carried out in the liquid phase in a batch reactor consisting of a 50 mL round bottle flask equipped with magnetic stir bar and reflux condenser. A mixture of 30 mmol anisole and 30 mmol propionic anhydride was then placed in the reactor. The catalyst was added to the solution mixture at 100 °C and refluxed under vigorous stirring for 3 h. The liquid samples were withdrawn at regular intervals and analyzed by gas chromatography (GC) equipped with a FID detector and the Agilent Ultra-2 (100% dimethylposlysiloxane, 25 x 0.20 mm I.D) column.

3.0 RESULTS AND DISCUSSION

The FTIR spectra of natural kaolin, PCH, acid treated-PCH, HPW and PCH/30HPW are shown in Figure 1. The FTIR peaks of kaolin in the low wavenumber region (1600-450 cm^{-1}) are attributed to the Si–O–Si in plane at 1008 and 1032 cm^{-1}, the OH bending at 913 and 938 cm^{-1} and the Si–O–Al vibrations at 755 and 796 cm^{-1} [22]. Intercalation of kaolin with starch template has significantly changed the intensity of the bands at 1115 and 1032 cm^{-1} (Figure 1(b)). These bands were shifted to 1086 cm^{-1} after intercalation, which could be assigned to the Si–O vibrations of amorphous silica. A strong absorption band centred at 1086 cm^{-1} is assigned to asymmetric Si–O–Si stretching vibrations, the 801 cm^{-1} band is assigned as the symmetric Si-O–Si stretching while the 471 cm^{-1} band is assigned to Si–O–Si bending modes.

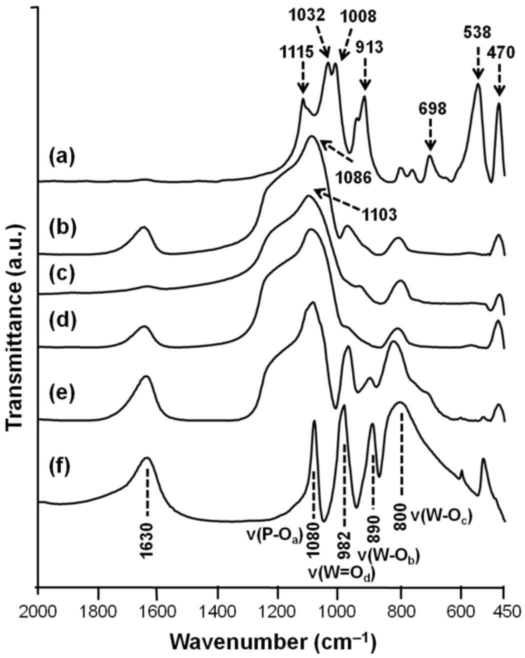

Figure 1 FTIR spectra of (a) kaolin, (b) PCH, (c) PCH-HCl, (d) PCH-H_2SO_4, (e) PCH/30HPW, and (f) HPW

The FTIR spectra of PCH treated with HCl and H_2SO_4 showed the band at 1086 cm^{-1} shifted to a higher wavenumber (1103 cm^{-1}) suggesting that the amorphous silica content in the PCH was increased after the acid treatment. The band at 1103 cm^{-1} is assigned to asymmetric Si–O–Si stretching. The spectrum of pure HPW showed characteristic asymmetric vibrations for P–O_a–W (1080 cm^{-1}), W=O_d terminal (982 cm^{-1}), W–O_b–W inter bridges between corner-sharing, WO_6 octahedra (890 cm^{-1}) and W–O_c–W intra bridges between edge-sharing WO_6 octahedra (800 cm^{-1}) [23]. For Figure 1(e), the spectrum of PCH/30HPW showed two bands of HPW at 981 and 894 cm^{-1} which may be attributed to the W=O_d and W–O_b–W, respectively. However, the bands at 1084 and 804 cm^{-1} are overlapping with the strong bands of silica in the PCH support. The HPW supported on PCH showed bands with much reduced intensity than pure HPW due to the overlapping bands of the support. The FTIR analysis confirmed that the HPW was impregnated onto PCH with the Keggin anion structure still intact.

Figure 2 presents the X-ray diffractograms of kaolin, PCH, acid treated-PCH, and PCH/30HPW. The XRD pattern of kaolin is matched with the JCPDS database file (JCPDS card 80-0886) with triclinic lattice structure [24]. The figure shows that kaolin is highly crystalline material based on the characteristic intense and narrow diffraction peak d_{001} at 12.35° with 7.16 Å basal spacing. After calcination at 500 °C, the intensity of the main d_{001} peak decreased in the PCH sample

(Figure 2(b)). The intercalation of cationic starch and neutral amine as well as the formation of the silica pillars in the interlayer spaces of functionalized kaolin breaks the hydrogen bonds between adjacent layers, leading to dealumination of the material. Therefore, decrease of the intensity of d_{001} peak could be due to the insufficient formation of silica pillars between the galleries which causes the layers to collapse after removal of starch template.

Figure 2(c) and Figure 2(d) show the XRD patterns of acid treated-PCH. After acid treatment, the d_{001} peak intensity of PCH-HCl and PCH-H_2SO_4 samples significantly decreased. This could be due to some disruptions in the structure owing to the acid treatment, which affected the long-range order of the PCH structure. The d_{001} peak is almost disappeared and broadened, which could be associated to formation of amorphous materials. Part of the layered structure of PCH may have collapsed and produced an amorphous phase as a result of the partial dissolution of the silica framework structure. Moreover, new peaks appeared in the spectrum of PCH/30HPW sample suggesting that HPW was successfully incorporated in PCH. Again, disappearance of the d_{001} peak is an indication that the layered structure of PCH was substantially destroyed. Besides, the low resolution peaks observed in the XRD pattern of PCH/30HPW clearly demonstrated that HPW particles are highly dispersed in the PCH support.

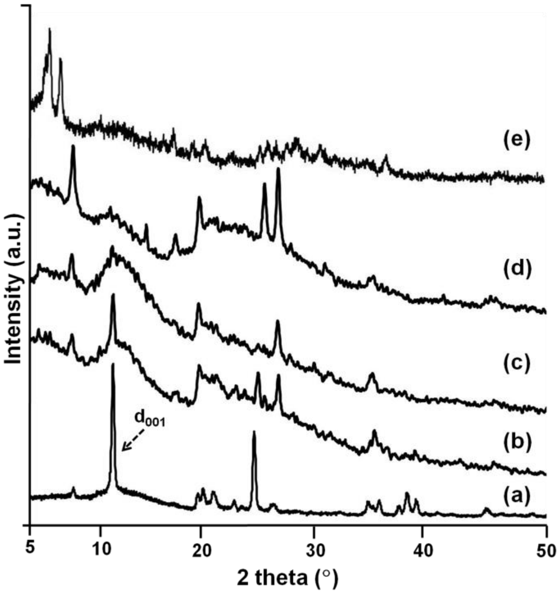

Figure 2 XRD diffractograms of (a) kaolin, (b) PCH, (c) PCH-HCl, (d) PCH- H_2SO_4, and (e) PCH/30HPW

The BET surface areas of all samples are presented in Figure 3. The surface area of the parent kaolin is found to be 15 m^2g^{-1}. In contrast, removal of the cationic starch template by calcination to give PCH produces a remarkable increase in the surface area (725 m^2g^{-1}) due to the contribution of micropores and mesopores. Intercalation of the desired amounts of cationic starch, neutral amine and silica pillars with kaolin was found to result in pore formation between successive kaolin layers and consequently, significantly higher BET surface area. After treatment with HCl and H_2SO_4, the surface area of PCH was severely decreased to 372 and 403 m^2g^{-1}, respectively. In addition, the PCH/30HPW sample showed decrease of the surface area (375 m^2g^{-1}) with respect to the parent PCH illustrating that HPW was well dispersed on the porous structure of the support. Even so, the surface area was very much higher when comparing with the pure HPW (10 m^2g^{-1}).

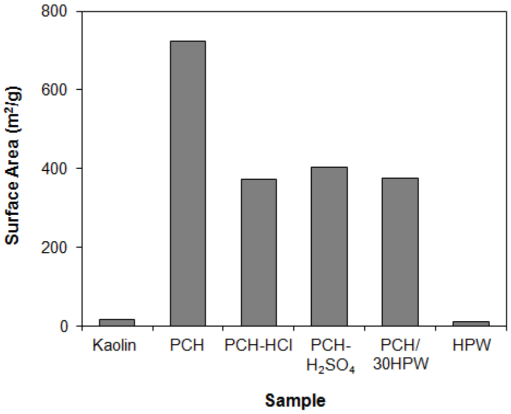

Figure 3 BET surface areas of kaolin and modified PCH catalysts

In this study the correlation between the Brönsted to Lewis ratios (B/L) and either conversion or selectivity of the acylation reaction of anisole has been studied. The concentration of the Brönsted (B) and Lewis (L) acid sites and the calculated B/L ratios are shown in Table 1. Concentrations of the surface acid sites (μmol g^{-1}) have been quantitatively determined from the integrated peak areas of the FTIR spectra shown in Figure 4 after pyridine desorption at 250 °C. The FTIR spectra of the samples show typical bands that are assigned to Lewis acid sites at 1450 cm^{-1}, Brönsted acid sites at 1540 cm^{-1} and a band at approximately 1490 cm^{-1} attributed to pyridine molecules associated with both Lewis and Brönsted acid sites.

The parent kaolin has a lower acidity than PCH which is in agreement with a previous study [25]. This is in line with the presence of octahedrally coordinated aluminium cations, a natural component of kaolin that can act as Lewis acid centres under anhydrous conditions. The unexpected increase in the number of Brönsted acid sites after formation of PCH could mean that protons were being released in order to balance the excess negative charge of the kaolin lattice after removal of the starch template. Lewis acid sites are more abundant in the kaolin-derived PCH as evidenced by the B/L ratio.

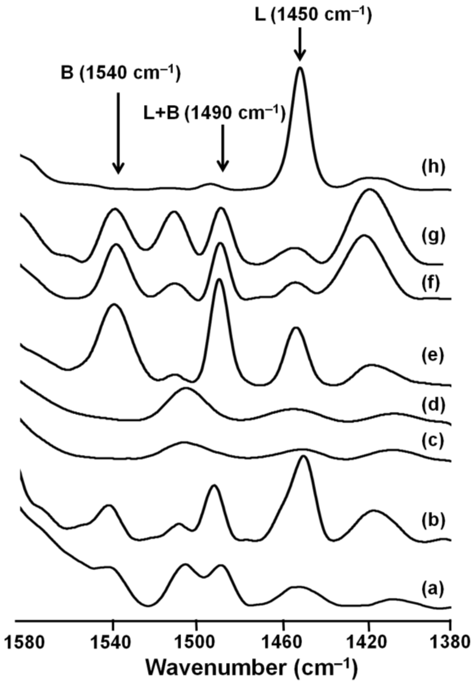

Figure 4 Pyridine adsorption of (a) kaolin, (b) PCH, (c) PCH-HCl, (d) PCH-H_2SO_4, (e) PCH/30HPW, (f) PCH-HCl/30HPW, (g) PCH-H_2SO_4/30HPW, and (h) MA evacuated at 250 °C

The FTIR spectra of the acid-leached samples PCH-HCl and PCH-H_2SO_4 are depicted in Figure 4(c) and 4(d). After acid treatment of PCH with HCl and H_2SO_4, the intensity of the band of Lewis acid site is markedly diminished, whereas those associated with Brönsted acid sites are completely removed. It may have occurred due to relocation of some aluminium cations from the framework lattice of PCH to the newly created pore surfaces. The acid treatments preferentially attack protons that penetrate into clay mineral layers and the structural OH groups. The dehydroxylation is connected with successive release of the central atoms from the octahedral as well as with removal of the aluminium from tetrahedral sheets [26]. Therefore, the acid treatment produced amorphous silica phase in PCH-HCl and PCH-H_2SO_4 samples thus reducing their acidic properties. The pyridine adsorption studies of the acid treated samples are fully consistent with their FTIR and XRD data. The spectrum of PCH/30HPW confirms that both the Brönsted and Lewis acid sites are of high strength (Figure 4(e)). In contrast, the spectra of PCH-HCl/30HPW and PCH-H_2SO_4/30HPW exhibit relatively lower density of Lewis acid sites but having high content of Brönsted acid sites. During acid treatment, the octahedral aluminium species extracted from the PCH structure are responsible for the marked decrease of the Lewis acid sites, as evidenced by the B/L value observed for the sample. HPW is known as a material with Brönsted acid properties. Based on the findings of the FTIR analysis, controlled impregnation of HPW onto the support has generated strong Brönsted acid sites on its surface. The marked increase of the Brönsted acidity could be related to the formation of monolayer coverage of HPW on the support. Therefore, B/L ratio increased after incorporation of HPW on PCH, PCH-HCl and PCH-H_2SO_4 samples. On the other hand, the surface acidity of MA sample only consists of Lewis acid sites.

All the catalysts were tested in the Friedel-Crafts acylation of anisole with propionic anhydride as acylating agent. The acylation of anisole with propionic anhydride gave *p*-methoxypropiophenone (*p*-MPP) as major product and propionic acid (PA) as the main side product. The conversion, product yield (mmol) and selectivity of *p*-MPP and other products as a function of B/L ratio are summarized in Table 1. It can be seen that the conversion of anisole using kaolin is lower (15%) than that of PCH with 62% selectivity for *p*-MPP. Although kaolin surfaces are known to have strongly acidic properties, the relatively low surface area appears to have affected its catalytic activity. The conversion of anisole using PCH catalyst was improved at 28% and the selectivity increased to 72%. As PCH has high amount of Lewis acid sites and enhanced Brönsted acid sites upon modification, the high conversion of anisole obtained when using PCH instead of kaolin could be due to differences in their pore structures and preferred blocking of pores in the case of kaolin.

The acid treated-PCH catalysts prepared using HCl and H_2SO_4 showed very low anisole conversions, with only propionic acid obtained as the main side product. Acid treatment of the PCH, led to removal of Al^{3+} ions from the octahedral sheets, and consequently leading to substantial amorphization of the layered silicate structure. This conclusion is supported by the results of the acidity studies in which insignificant surface acid properties were observed in all acid-leached samples. Furthermore, MA which contains only Lewis acid sites is not active in the acylation of anisole.

HPW was incorporated in PCH and acid treated-PCH as supports in order to create enhanced Brönsted acidity. The correlation between concentration of Brönsted acid sites and activity of the catalysts in acylation of anisole is presented in Figure 5. The activities of PCH/30HPW, PCH-HCl/30HPW and PCH-H_2SO_4/30HPW were compared so as to examine the synergism of the Brönsted and Lewis acid sites. The highest conversion of anisole (86%) and selectivity of *p*-MPP (95%), as well as the maximum yield of 25.8 mmol were achieved with the PCH/30HPW catalyst. In the reactions using PCH-HCl/30HPW and PCH-H_2SO_4/30HPW catalysts, the conversion of anisole was relatively lower (78% and 72%) giving 88% and 86% of selectivity, respectively. The conversion of anisole increased remarkably upon impregnation of HPW onto the support indicative of the influence of Brönsted acid sites on the catalytic activity.

PCH/30HPW exhibited the highest amounts of both Lewis and Brönsted acid sites among the catalysts studied. It is seen that the dispersion of HPW over the PCH surface has generated the Brönsted acid sites, while cationic aluminium species in PCH contributes to the Lewis acidic properties. On the other hand, both PCH-HCl/30HPW and PCH-H_2SO_4/30HPW exhibit high amounts of Brönsted acids and very low amount of Lewis acid sites as consequence of the removal of aluminium in the PCH structures. Although HPW supported on acid treated-PCH shows high B/L ratio, the amount of Brönsted acid sites is lower than that of PCH/30HPW sample. However, PCH/30HPW shows higher anisole conversion than other catalysts due to the higher amount of Bronsted acidity which is required for electrophilic substitution involving acylium ion [27]. Moreover, the high amount of Lewis acids in PCH/30HPW possibly increased the selectivity of *p*-MPP. It is assumed that anisole may interact with the Lewis acid sites of the catalyst which makes the reaction prefer to attack on the *para* position [9]. From studies that have been carried out using different catalysts with different acid type and acid strength, it was revealed that strong Brönsted acid sites play an important role in producing high amount of the desire ed product. Moreover, the presence of Lewis acid sites could facilitate the formation of *p*-MPP as the main product.

Table 1 Surface acidity of all samples after desorption of pyridine at 250 °C and catalytic acylation of anisole to *p*-methoxypropiophenone (*p*-MPP)

Catalysts	**Acidity (μmol g^{-1})**		**Ratio B/L**	**Conversion (%)**	**Product yield/ mmol**	**Selectivity (%)**		
	Brönsted	**Lewis**				***p*-MPP**	**PA**	**Other Products**
Kaolin	5	14	0.4	15	4.5	62	38	0
PCH	13	89	0.1	28	8.4	72	27	1
PCH-HCl	0	12	0	2	0.6	0	100	0
PCH-H_2SO_4	0	10	0	3	0.9	0	100	0
PCH/30HPW	109	23	4.7	86	25.8	95	4	1
PCH-HCl/30HPW	60	5	12.0	78	23.4	88	8	4
PCH-H_2SO_4/30HPW	51	6	8.5	72	21.6	86	10	4
MA	0	187	0	0	0	0	0	0

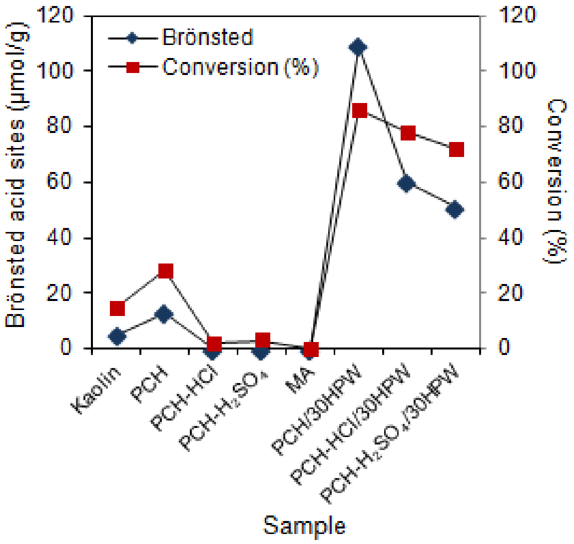

Figure 5 The effects of Brönsted acid sites concentration in different catalysts to the conversion of anisole

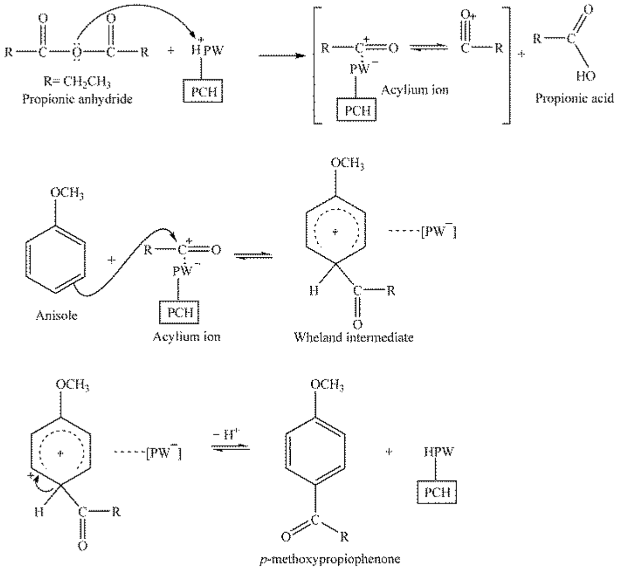

Figure 6 Proposed mechanism for the acylation of anisole with propionic anhydride using HPW supported on PCH catalyst

The possible mechanism for the production of methoxypropiophenone in the Friedel-Crafts acylation of anisole with propionic anhydride catalyzed by supported HPW is shown in Figure 6. The strong Brönsted acid sites on the acid HPW are able to generate acylium ions. The nucleophilic oxygen of propionic anhydride attacks the proton of strong Brönsted acid sites on the acid HPW to generate acylium ions and form propionic acid as side product. This acylium ion is the active intermediate in the acylation of aromatic substrates through the electrophilic attack at the π-electron system of the aromatic substrates. The acylium ion as electrophilic species is attacked by the pair of electrons from the π- cloud aromatic anisole at the *ortho*, *meta* and *para* positions. A Wheland type transition state acts as intermediate in the formation of aromatic ketones. The negative charge of PW^- then attacks the proton of the positive charge distribution of Wheland intermediate to form *ortho*, *meta* and *para*-methoxypropiophenone. Since *p*-MPP is the main product of the reaction, it is shown that the large number of Brönsted acid sites from HPW as well as the porous structure and acidic properties of PCH render the catalysts highly active in the acylation reaction.

4.0 CONCLUSION

High surface area PCH was successfully obtained from natural kaolin by using cationic starch as template. The synthesis of HPW (30 wt.%) supported on PCH and modified PCH was achieved with their Keggin-type structure retained successfully. The FTIR spectra analysis showed that Lewis acid sites are predominantly located on silica pillars of the PCH structure. Acid-leached PCH did not show either Brönsted or Lewis acid properties whereas HPW supported on PCH and acid-leached PCH showed enhancement of acid strength and concentration of Brönsted acid sites. Among the catalysts, PCH/30HPW was the most active in the conversion of anisole (86%) and selective towards formation of *p*-methoxypropiophenone (95%). Acid treatment of the PCH and incorporation of HPW in PCH has resulted in modification of the active sites, acidity properties and acid strength, thus affecting the reactivity and selectivity of the catalysts. In this work, it is established that high density of Brönsted acid sites of high strength is required for the Friedel-Crafts acylation of anisole.

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