

ACIDITY AND CATALYTIC ACTIVITY OF PHOSPHOMOLYBDIC ACID SUPPORTED ON MCM-41 MOLECULAR SIEVE

Shawky M. Hassan, Sohier A. Al-Hakam, Yathreb A. Salama
Chemistry Department, Faculty of Science, Mansoura University, Mansoura, Egypt

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ABSTRACT

A series of $H_3PMO_{12}O_{40}$ / MCM-41 (PMA/MCM-41) catalysts with different phosphomolybdic acid content of 30–70 wt. % PMA was prepared by impregnation method. The prepared catalysts were calcined at 350°C. The acidity examined by monitoring the adsorption of pyridine by FT-IR spectroscopy. Catalytic performance was examined in the liquid phase condensation of resorcinol and ethyl acetoacetate. 7-Hydroxy- 4-methylcoumarin was the only product observed in this reaction. The results revealed that 40 wt. % PMA/ MCM-41 is found to be the most active catalyst. Its also has the highest acidity examined by FT-IR spectroscopy of pyridine adsorption.

Keywords: Phosphomolybdic acid, MCM-41, FT-IR spectroscopy, Pechmann reaction, Coumarins.

INTRODUCTION

The catalytic function of heteropolyoxometalates (HPOMs) has attracted much attention particularly in the last two decades; these compounds provide a good basis for the molecular design of mixed oxide catalysts and have high capabilities in practical uses [C.W. Hu *et al.*,(1993); Y.H. Guo *et al.*,(2000); T. Okuhara *et al.*,(1996); M. Misono (1987) and M. Misono (1988)] . Due to their unique combination of acid-base and redox properties the heteropolyoxometalates have been used successfully as catalysts in their acidic form or in their cationic exchanged or substituted form for acid and redox catalyzed reactions in both homogeneous and heterogeneous media [C.L. Hill *et al.*,(1995) and N. Mizuno and M. Misono ,(1998)]. Their success in the catalysis field is associated to their redox character and strong Brønsted -type acidity, and these properties are easily tunable by varying their compositions [I.V. Kozhevnikov (1998); T. Okuhara *et al.*,(2000); S. Damyanova and J.L.G. Fierro (1998)].

These compounds exhibit very low-specific surfaces areas (1–10 m²/g) [I.V. Kozhevnikov (1995)] and moderate thermal stability, which limit their applications in processes at high temperature. Aiming to overcome these handicaps, HPAs have been supported over different solid matrices. Several conventional supports have been used

for dispersing HPAs, namely, silica [S. Damyanova *et al.*,(1999) and A. Rives *et al.*,(2001)], zirconia [E. Lo'pez-Salinas *et al.*,(2000) and A. De Angelis *et al.*,(1999)], activated carbon [Y. Izumi (1981)], etc. Among them, Beck *et al.* [J.S. Beck *et al.*,(1992)] discovered the mesoporous silica of MCM-41 type, then this type of materials have played an important role in catalysts, catalyst-precursors or catalyst supports [J. Mayerov *et al.*,(2005); L.R. Pizzio *et al.*,(2005); G. Kamalakar *et al.*,(2006); Q.-H. Xia *et al.*,(2003) and J.C. Juan *et al.*,(2007)] due to their high thermal stability, large internal surface area ($>1000 \text{ m}^2 \text{ g}^{-1}$), uniform and controllable pore size. In the last decade, various acid-catalyzed processes based on HPA supported on MCM-41 had been investigated by several groups [G. Kamalakar *et al.*,(2006); J.C. Juan *et al.*,(2007) and J. Kaur *et al.*,(2002)].

However, solids with high specific surface area such as mesoporous silica (MCM-41) [J.S. Beck *et al.*,(1992) and A. Corma (1997)], are excellent support for acid catalysts, allowing a better dispersion of the active phase, even for very large HPA-loading contents. The dispersion increases the concentration of active sites and as a consequence their catalytic activity. The differences between the performances of the supported catalysts were explained on the basis of heteropoly-acid-support interaction and the effect of the loading on the dispersion of the acid and in turn on the catalyst performance. The point of the heteropoly-acid-support interaction was discussed by Kozhevnikov *et al.* [I.V. Kozhevnikov *et al.*, (1996)].

EXPERIMENTAL

1. Materials:

Commercially available $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$ (PMo) was used. MCM-41 used for the preparation of supported HPAs was purchased from Aldrich.

2. Catalyst Preparation:

2.1. Preparation of MCM-41 supported phosphomolybdic acid catalysts:

MCM-41 supported phosphomolybdic acid (PMA) catalysts $\text{H}_3\text{PMo}_{12}\text{O}_{40}/\text{MCM-41}$ abbreviated as PMAS, containing 30, 40, 50, 60 and 70 wt. %PMA were prepared by the impregnation method. The $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ was incorporated onto the support by shaking the support with an aqueous solution containing the required amount of PMA at room temperature for 12 hrs to achieve different acid loading. The catalyst was dried in rotary evaporator at 50°C and calcined at 350°C for about 3 hrs, the product (PMAS), was stored and kept dry in a desiccator before being used for characterization.

3. Nitrogen adsorption measurements:

The Surface areas of all investigated samples as well as other textural parameters were determined via conventional volumetric apparatus. Prior to the adsorption measurements, the samples were thermally activated in situ at 200°C for about six hours using electrical furnace under a reduced pressure of 10^{-5} . The adsorption isotherm of nitrogen gas was determined at its boiling point (-196°C).

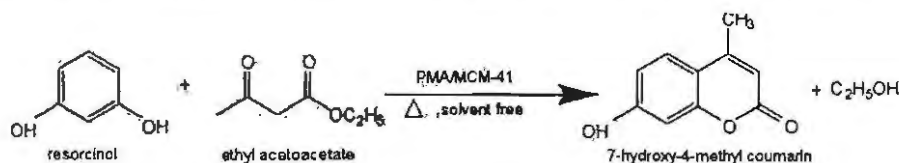
4. Surface acidity measurements:

The type of acid sites (Lewis and Brønsted) present on the surface of the catalysts was determined with FT-IR spectra of adsorbed pyridine. Prior to Pyridine adsorption, the samples were degassed at 200°C for about 3hrs under high vacuum followed by suspending in a desiccator containing dried pyridine in its bottom. For complete adsorption the samples were presented in a desiccator for about 3 weeks. Then, the excess Pyridine was removed by evaporation at 120°C for about 1hrs. The FT-IR spectra of the samples were carried out at room temperature using jasco FT/IR-420 spectrophotometer; by mixing 0.005 g of the sample with 0.1 g KBr in 30 mm diameter self supporting discs were used.

5. Catalytic study:

The liquid phase reaction was carried out in a batch reactor consisting of a three-necked round bottom flask fitted with a condenser, resorcinol (10 mmol), ethyl acetoacetate (20 mmol) the phenol and ethyl acetoacetate were taken in 1:2 molar ratio, and catalyst (0.1 g) (phenol to catalyst weight ratio = 10) was taken in the reactor and heated in an oil bath to the requisite temperature (120°C) with simultaneous stirring using a magnetic stirrer for 2h. After the reaction, the hot reaction mixture was filtered to separate the catalyst and the product was crystallized after cooling the reaction mixture. The yield of 7-hydroxy 4-methyl coumarin was obtained as follows:

Yield (wt %) = (obtained weight of product / theoretical weight of product) X 100



Scheme1. Schematic synthesis of 7-hydroxy- 4-methyl coumarin.

RESULTS AND DISCUSSION

1. Nitrogen adsorption-desorption isotherms:

The isotherms recorded for all solids prepared are included in Fig. (1). According to the IUPAC classification [K.S.W. Sing *et al.*, (1985)] they correspond to type IV, typical of mesoporous materials. In all of these isotherms up to five regions, characteristic of this sort of isotherms can be clearly distinguished: (1) monolayer adsorption on the surface, (2) multilayer adsorption, (3) capillary condensation inside mesopores, (4) multilayer adsorption on the external surface and (5) condensation of nitrogen within the interstitial voids between the MCM-41 particles. The capillary

condensation of nitrogen inside the mesopores occurs in the P/P^0 range 0.3–0.4 in all cases. [Daniel Carriazo]

All pore size distribution curves Fig.(2) show decrease in pore volume for PMA-loaded catalysts compared to pure MCM-41, as evident from reduce of the height of the distribution maxima evidently proved the formation of PMo Keggin phase within the pores of MCM-41. The gradual decrease in pore volume with increase of PMo loading from 30-70 wt % also confirmed the formation of Keggin phase within the pores of MCM-41 [K. Usha Nandhini *et al.*,(2006)].

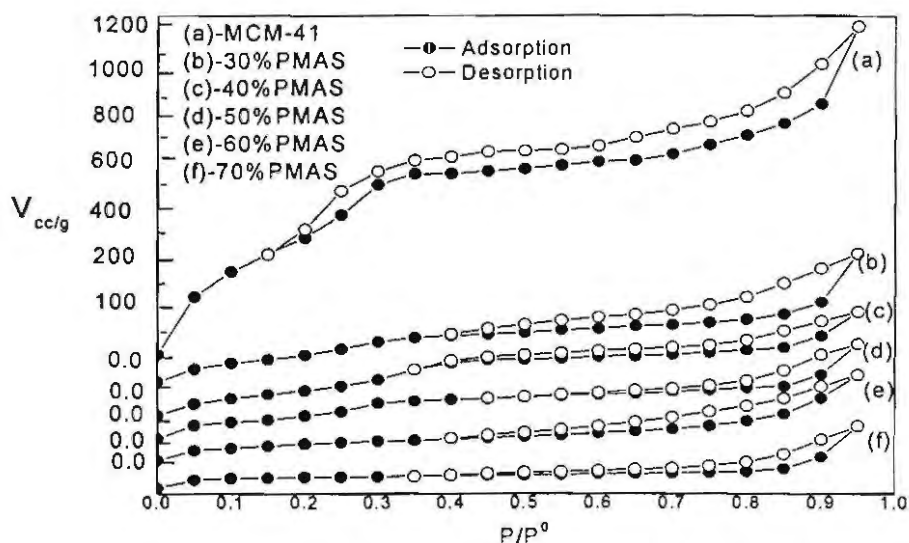


Fig.(1): Adsorption-desorption isotherms of nitrogen at -196°C on MCM-41 and MCM-41 supported PMA (PMAS).

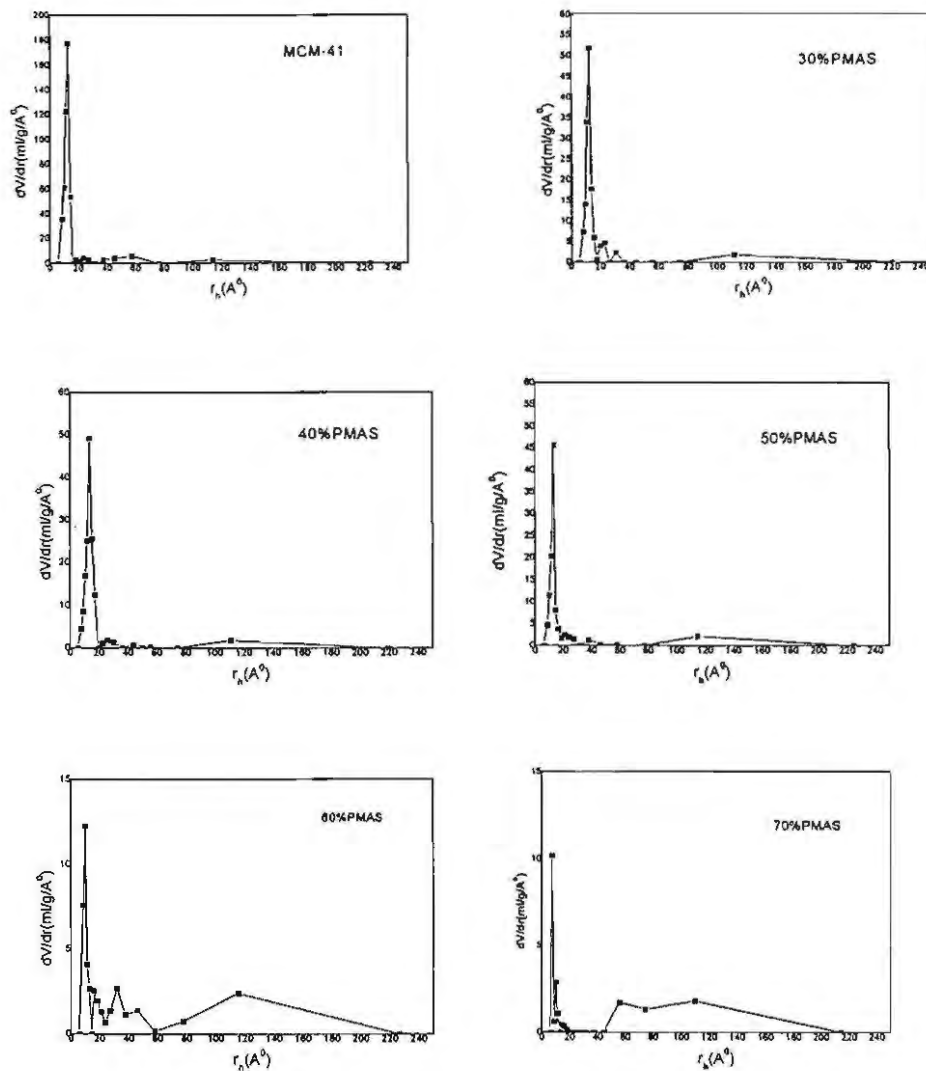


Fig.(2): Pore size distribution curves of MCM-41 and MCM-41 supported PMA (PMAS) samples.

From these results it can be thought that the HPAs units, with a diameter close to 1.2 nm, are preferentially located inside the MCM-41 pores, which do not become completely filled for low loading percentages, rather than on the external surface by increasing the wt. % of PMA may cause the blockage of the narrow pores and precipitate on the walls of relatively wider one, causing thus a decrease in their surface area and porosity Table(1).

Table (1): Textural properties of pure MCM-41 and PMA/ MCM-41 catalysts.

Sample	S _{BET}	V _T
MCM-41	1255.7	1.283
30%PMAS	379.01	0.506
40%PMAS	351.85	0.402
50%PMAS	265.67	0.354
60%PMAS	122.49	0.311
70%PMAS	41.48	0.218

3.2. Surface acidity measurements:

The FT-IR spectra of PMA / MCM-41 show, after adsorption of pyridine, all samples display both Brönsted and Lewis acidity. The acidity of the samples was determined by calculating the integral absorption of bands at 1635 cm⁻¹ characteristic of Brönsted acidity and that at 1487 cm⁻¹ assigned as pyridine bonded to Lewis acid sites. The position of the characteristic IR band is very important in study; where if the shift in the band wave number to higher values indicates that the strength of the acid sites increases and vice versa. The FT-IR spectra of PMA / MCM-41 catalysts are shown in Fig. (3).

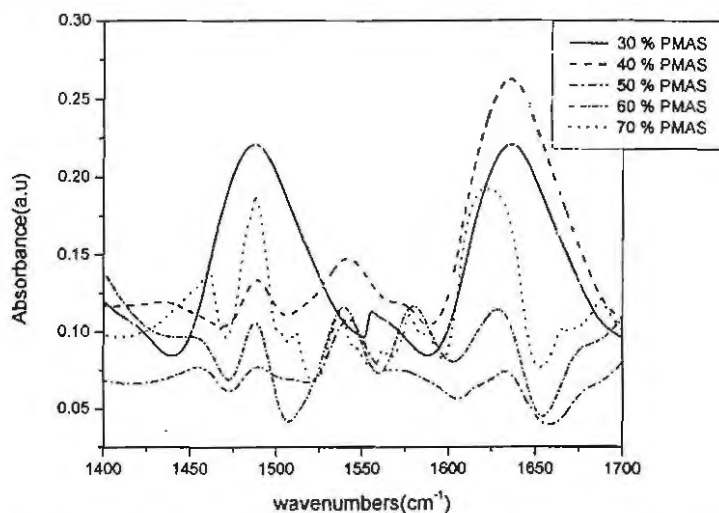


Fig.(3): FT-IR spectra of pyridine adsorbed on PMA / MCM-41 catalysts calcined at 350 °C.

The bands of Lewis acid sites have fixed positions but their intensity or area are changed with the change in catalyst composition. This indicates that the difference in the acid strengths between samples depend on the number of acid sites. Where the bands of Brönsted acid sites don't have fixed positions indicates that the strength of the acid sites was changed, also their intensity or area are changed with the change in

catalyst composition. This indicates that the difference in the acid strengths between samples depend on the number of acid sites as well as the strength of the acid sites.

The data in Table (2) show the Brønsted and Lewis acidities are quantified into integrated areas of the absorbance at 1635 and 1487 cm^{-1} , respectively. It is found that by increasing the loading of PMA on MCM-41 from 30% to 50% the band intensity of the Lewis acid sites decreases indicating a decrease in the number of acid Lewis sites, but for the band intensity of the Brønsted acid sites we found that it increase till 40% loading of PMA on MCM-41 and then decrease. We can explain the decrease in band intensity with increasing the loading of PMA on MCM-41 as low PMA loading allow a better dispersion of the active phase, The dispersion increases the concentration of active sites and by increasing PMA loading till 50% this lead to decrease the dispersion of active sites on the surface of MCM-41 which lead to decrease in the band intensity, by increasing the loading of PMA on MCM-41 to 70% it is found that the band intensity increase as the ratio of PMA:MCM-41 increase more than 1:1 so the acidic properties increase.

Table (2): pyridine adsorption data for the catalysts calcined at 350 °C

^b Brønsted and Lewis acidities are quantified into integrated areas of the absorbance at 1635 and 1487 cm^{-1} , respectively.

Sample	B acid ^b (at 1635 cm^{-1})	L acid ^b (at 1487 cm^{-1})
30%PMAS	0.222	0.222
40%PMAS	0.263	0.134
50%PMAS	0.076(at 1632)	0.078
60%PMAS	0.115 (at 1628)	0.106
70%PMAS	0.193 (at 1620)	0.188

3. Catalytic study:

Intermolecular condensation of resorcinol and ethyl acetoacetate was carried over MCM-41 supported phosphomolybdic acid (PMA) catalysts $\text{H}_3\text{PMO}_{12}\text{O}_{40}$ /MCM-41 in the liquid phase. The intermolecular condensation and subsequent intramolecular cyclisation led to the formation of 7-hydroxy-4- methyl coumarin.

2.1. Effect of phosphomolybdic acid content:

Effect of phosphomolybdic acid content was investigated over MCM-41 supported phosphomolybdic acid sample at 120° C; keeping the molar ratio of resorcinol / ethyl acetoacetate 2:1. The results are illustrated in Fig 4.

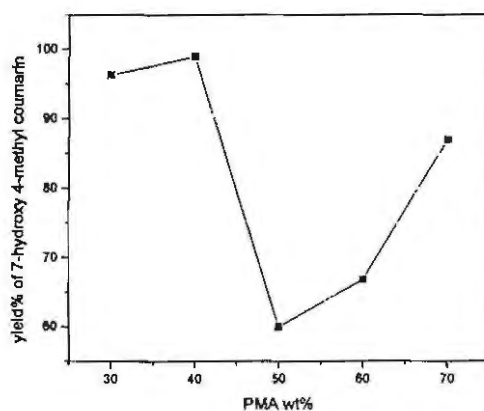
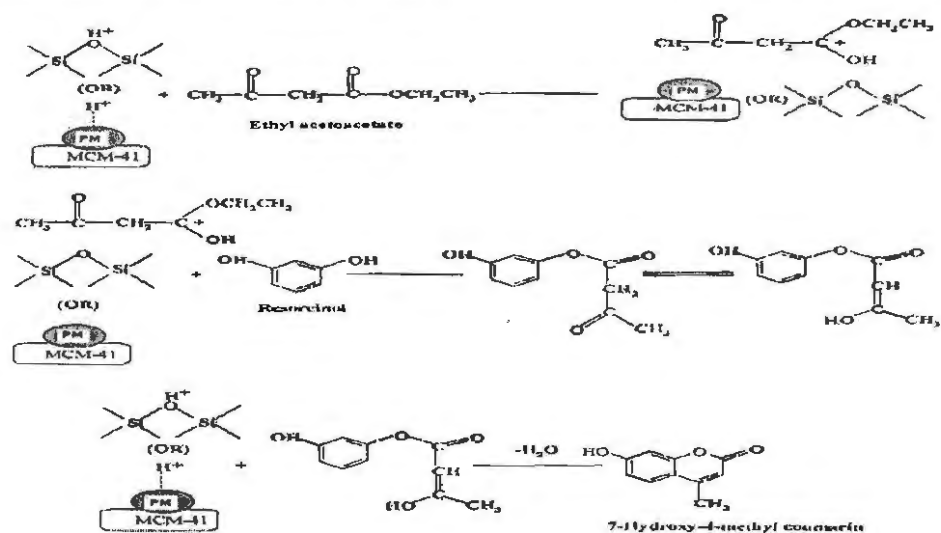


Fig.(4): Relation between PMA content and yield% of 7-hydroxy 4-methyl coumarin.

40 wt% PMA/ MCM-41 gave higher resorcinol conversion than other catalysts as low PMA loading allow a better dispersion of the active phase; the dispersion increases the concentration of active sites. Higher wt% PW/Al-MCM-41 gave less conversion than 40 wt% PMA/MCM-41 catalysts as high dense Keggin structure could offer diffusional constrain. Such a diffusional constrain was reported by previous workers [R. Maheswari *et al.*, (2003) and K. Usha Nandhini *et al.*, (2004)].

According to the above results the mechanism for the formation of 7-hydroxy-4-methylcoumarin is carried out through the chemisorption of carbonyl group of ethyl acetoacetate on the Brønsted acid sites of the catalyst. The resorcinol makes a nucleophilic attack on it to give the intermediate which rapidly undergoes cyclisation through intramolecular condensation yielding 7-hydroxy-4-methylcoumarin. This reaction is also catalyzed by Brønsted acid sites of the catalysts.



CONCLUSIONS

The results of present investigation concluded that 40 wt. % PMA/MCM-41 is a convenient substitute for conventional hazardous catalysts for the preparation of 7-hydroxy-4-methyl coumarin reactions with high selectivity at maximum resorcinol conversion. In conclusion, it has been demonstrated that PMA/MCM-41 catalyzed Pechmann reaction under solvent-free condition is an efficient alternative for the preparation of coumarin derivatives.

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الملخص العربي

الحامضية والنشاط الحفزي لحامض الفوسفوموليبيديك المحمل على (MCM-41) المنخل الجزيئي

شوقي محمد حسن - سهير عبد الحكم - يثرب امين سلامه

قسم الكيمياء - كلية العلوم - جامعه المنصورة - المنصورة- جمهوريه مصر العربيه

تم تحضير احماض الفوسفوموليبيديك المحمله على MCM-41 بطريقه التشرب وذلك بنسب ٣٠، ٤٠، ٥٠، ٦٠، ٧٠ نسبه وزيه وحمصت هذه العينات عند درجه حراره ٣٥٠ م. تم ايضا دراسه الخواص الحامضيه لهذه المجموعات من الحفازات الصلبه وذلك عن طريق امتزاز غاز البريدين. كما تم قياس النشاطيه الحفزيه تجاه تفاعل تحضير الكومارين في الحاله السائله. واتضح من ذلك MCM-41 المحمله بنسبه ٤٠ نسبه وزيه تكون أعلى العينات المحضره حامضيه كما أنها تعطى أعلى نسبه نشاط حفزي لتحضير الكومارين في الحاله السائله.