سیزدهمین کنگره ملی مهندسی شیمی ایران

و اولین کنفرانس بین المللی منطقه ای مهندسی شیمی و نفت

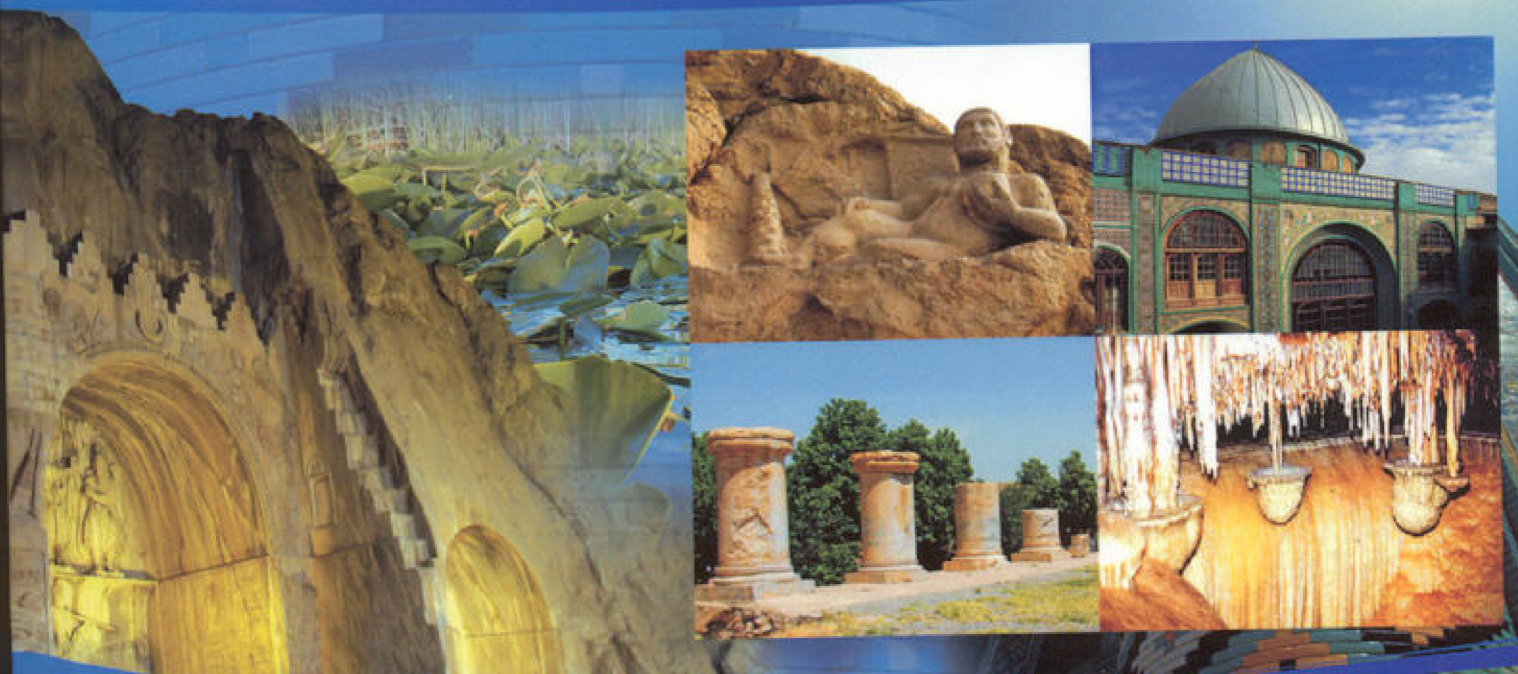
۳ - ۶ آبان ۸۹

کرمانشاه - دانشگاه رازی

13th National Iranian Chemical Engineering Congress
&
1st International Regional Chemical and Petroleum Engineering Conference

25-28 October 2010

Razi University - Kermanshah , Iran



برگزار کنندگان: دانشگاه رازی کرمانشاه • انجمن مهندسی شیمی ایران • دانشگاه بابل عراق

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Wednesday, 14:00-17:30 (Break: 15:30-15:50)		
Subject	**Code**	**Title**
Thermodynamics - Kinetics, Catalysis & Reator Design	06136	Optimization of Catalytic Carbon Monoxide Oxidation Reactor using Genetic Algorithm
	06138	Using Supported Heteropoly Acids as a Eco-Friendly and Recyclable Catalyst for Efficient Synthesis of Acetylsalicylic Acid
	06139	C2+ Production Optimization in Fischer-Tropsch Synthesis Using Genetic Algorithm
	06147	Comparative study on application of bimetallic Pt-based alloy electroctalysts in advanced chlor-alkali electrolysis
	06148	بررسی آزمایشگاهی اکسیداسیون حرارتی تولوئن به همراه گاز طبیعی در کورههای حرارتی
	06208	The Effect of External Magnetic Field on Performance of Ni/ γ-Al2O3 catalyst in Catalytic Partial Oxidation of Methane
	06209	A mathematical model for Hydrodesulfurization of Dibenzothiophene in a fixed-bed catalytic reactor
	06210	بررسی دو طراحی متفاوت از اختلاط گازهای واکنشی در واحد تولید اکسید اتیلن
	06212	A new reaction kinetic model for MTO process
	06213	سینتیک هیدروژناسیون CO روی کاتالیست آهن- منگنز سل- ژل
	06218	Synthesis and Characterization of CuO/ZSM-5 Nanostructured Catalyst Doped with ZnO via Impregnation Method
	06221	Synthesis of Ni-Co/MgAl2O4 Nanostructured Catalyst Using Ultrasound Energy
	06224	Synthesis and Characterization of CuO/CeO2-ZrO2 Nanostructured Catalyst via Co-precipitation-Impregnation Methods
	06225	A Comparative Synthesis and Characterization of Ni/Al2O3-CeO2 Nanostructured Catalyst from Al/Ce/Ni Nitrates via Impregnation and Sol-Gel Methods
	06226	Study on decontamination of Cr (VI) and tri-ethyl phosphate (TEP) stimulants via photacatalytic oxidation
	10123	Hydrothermal production of nano pyrite

Using Supported Heteropoly Acids as a Eco-Friendly and Recyclable Catalyst for Efficient Synthesis of Acetylsalicylic Acid

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Abstract
Catalytic performance of supported Preyssler and Keggin heteropolyacids on silica, $H_{14}[NaP_5W_{30}O_{110}]/SiO_2$ and $H_3[PW_{12}O_{40}]/SiO_2$, have been studied at room temperature for highly selective and rapid liquid-phase O-acetylation of salicylic acid in order to synthesize acetylsalicylic acid which is well-known century-old chemical pharmaceutical. The usual catalysts in acetylsalicylic acid synthesis are toxic liquid acids such as HNO_3 and H_2SO_4, which would cause serious corrosive and other environmental problems. The performance of silica-supported preyssler and Keggin with various loadings is compared with sulfuric acid method. The heteropolyacids show almost 25% more activity compared with H_2SO_4.

Keywords: *Acetylsalicylic acid, Green catalysts, Supported Heteropolyacids,* SiO_2

Introduction
The catalytic function of heteropolyacids (HPAs) and related polyoxometalate compounds have attracted much attention particularly in the last two decades [1]. HPAs has attracted much interest because of its potential of great economic rewards and green benefits [2]. They also have excellent activity and can be easily recovered from reaction mixtures and reused. Acidic or neutral substances, such as SiO_2, active carbon, acidic ion-exchange resin, etc., are all suitable supports, but SiO_2, which is relatively inert towards HPAs, is the one most often used [3].They are also of great interest as model systems for studying fundamental problems of catalysis [4]. Using HPA-based catalysts, it is frequently possible to obtain higher selectivity and successfully solve ecological problems [4]. HPAs are well-known to be strong Bronsted acids. All the HPAs are stronger than the usual inorganic acids (HCl, H_2SO_4, HNO_3, HBr) and even such strong acids as $HClO_4$ and CF_3SO_3H [4].
The application of Preyssler catalyst is mostly limited and only a few demonstrations of catalytic activity have been reported [12]. The important advantages of this heteropolyacid such as: strong Bronsted acidity with 14 acidic protons, high thermal stability, high hydrolytic stability (pH 0–12), reusability, safety, quantity of waste, separability, corrosiveness, high oxidation potential and greenness along with exclusive structure have attracted much attention on this catalyst [5]. The structure of this catalyst is shown in Fig. 1. On the other hand, Keggin

structure involves 4 three-foldM_3O_{13} groups. The total assemblage contains 40 close-packed oxygen atoms and has a tetrahedron pocket in its center for the heteroatom. The Keggin anions offer a limited hydrolytic and thermal stability compared to the Preyssler structure [5].

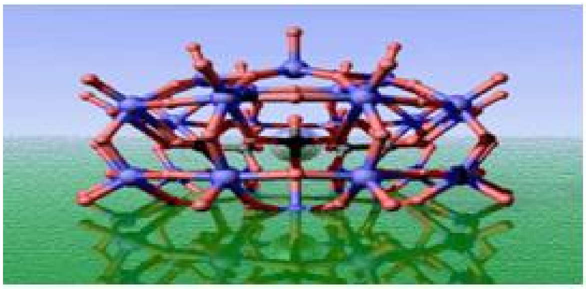

Fig.1. Preyssler structure [6]

The application of clean catalytic technologies, especially those with the use of heterogeneous catalysts, is becoming increasingly important for the development of environmentally benign chemical processes [7]. In the future, the number of such processes will undoubtedly increase because HPA-based catalysts have higher activity than known traditional catalysts.
In view of green chemistry, the substitution of harmful liquid acids by solid reusable HPAs as catalyst in organic synthesis is the most promising application of this acids [8]. In comparison with the liquid mineral acids, solid acids could be easily separated from the reaction mixture by simple filtration with high recovery. This advantage directly leads to a decrease in equipment cauterization and environment pollution [9].
The effect of various parameters such as catalyst type, loading, temperature, and reaction time on the yield of products were studied and compared with those obtained, using traditional acids. It is found that $H_{14}[NaP_5W_{30}O_{110}]/SiO_2$ is an eco-friendly catalyst for synthesize of *acetylsalicylic acid* [5].
Acetylsalicylic acid is both an organic ester and an organic acid. It is used extensively in medicine as a pain killer (analgesic) and as a fever-reducing drug (antipyretic). When ingested, acetylsalicylic acid remains intact in the acidic stomach, but in the basic medium of the upper intestinal tract, it hydrolyzes forming the salicylate and acetate ions. However, its additional physiological effects and biochemical reactions are still not thoroughly understood.
It is now reported the application of a green and recyclable solid acid catalyst, silica-supported preyssler and Keggin, for highly selective and rapid liquid-phase O-acetylation of salicylic acid in order to synthesize acetylsalicylic acid at room temperature. The usual catalyst in the synthesis of acetylsalicylic acid is toxic liquid acids such as HNO_3 and H_2SO_4, which would cause serious corrosive and other environmental problems.

Experimental

Materials

Acetic anhydride, salicylic acid, sodium tungstate dihydrate, molybdotungstate dihydrate, orthophosphoric acid, Tungstophosphoric acid, sulfuric acid, ethanol, potassium chloride and silica gel. All the chemicals were obtained from Merck Company and used as received.

Catalyst Preparation

Heteropolyacid preyssler was prepared according to the procedure reported before [10]. Supported heteropolyacid catalysts were prepared by impregnating a support in the form of powder (SiO_2) with an aqueous solution of the heteropolyacid with different concentrations. Samples were dried at 120-140°C, and the catalysts were calcined at 220°C for preyssler and 300°C for Keggin in a furnace prior to use.

General Procedure

The reactions were performed by mixing 2 g salicylic acid, 5 mL acetic anhydride with 0.05 g of 10-50Wt% $H_{14}P_5/SiO_2$ and $H_4[SiW_{12}O_{40}]/SiO_2$ at room temperature with intense stirring for the mentioned time. At the end of reaction, the mixture was diluted with 50 mL of water, and then the crude product was precipitated in an ice bath. The crude product was removed and the resulting solid was washed with cold water and recrystallized in ethanol. The product was characterized by comparison of its spectroscopic IR data, and melting point (using an Electro thermal IA 9100 Digital Melting Point apparatus) with those of an authentic sample. The product yield was determined quantitatively.

Results and Discussion

The performance of $H_{14}[NaP_5W_{30}O_{110}]/SiO_2$ and $[H_3PW_{12}O_{40}]/SiO_2$ in different loadings was compared with H_2SO_4. The heteropolyacids show higher activity compared with H_2SO_4. The reaction was carried out with different loadings. Catalyst loading was varied from 10 wt% to 50 wt%. As illustrated in Table 1, the yield of acetylsalicylic acid increased with an increase in catalyst loading from 10 wt% to 50 wt%. It can be seen from the figure that the activity of $H_{14}P_5/SiO_2$ (50wt%) is higher than sulfuric acid.

Table 1. Comparison of acetylsalicylic acid yields in two different processes at room temperature after 60 min

Entry	Catalyst	**Yield** (%)
1	$H_{14}[NaP_5W_{30}O_{110}]/SiO_2$(10wt%)	20
2	$H_{14}[NaP_5W_{30}O_{110}]/SiO_2$(20wt%)	35
3	$H_{14}[NaP_5W_{30}O_{110}]/SiO_2$(30wt%)	62
4	$H_{14}[NaP_5W_{30}O_{110}]/SiO_2$(40wt%)	68
5	$H_{14}[NaP_5W_{30}O_{110}]/SiO_2$(50wt%)	78
6	$H_4[PW_{12}O_{40}]/SiO_2$(20wt%)	30
7	$H_4[PW_{12}O40]/SiO_2$(30wt%)	55
8	$H_4[PW_{12}O_{40}]/SiO_2$(40wt%)	63
9	$H_4[PW_{12}O_{40}]/SiO_2$(50wt%)	69
10	H_2SO_4	53

Effect of the reaction time

Fig.2 gives the yield of acetylsalicylic acid as a function of time under the same conditions in the presence of $H_{14}P_5/SiO_2$(50wt%) and H_2SO_4. It can be seen from the Figure that the activity of $H_{14}P_5/SiO_2$(50wt%) is higher than that of sulfuric acid.

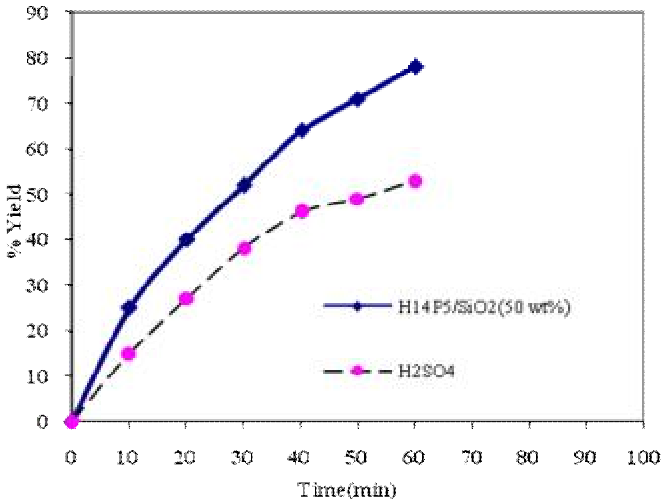

Fig.2. Yield of aspirin as a function of time with two different catalysts

Conclusions

silica-supported preyssler catalyst is an effective solid acid catalyst for preparation of acetylsalicylic acid. The results also indicate that the reaction time was an important factor. $H_{14}[NaP_5W_{30}O_{110}]$, $H_3[PW_{12}O_{40}]$ catalyst in heterogonous phase can be recovered and reused without loss of structures and appreciable activity.

Acknowledgements

The authors would like to acknowledge chemical Eng. Researcher lab. and organic research lab. for their helps.

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سنتز استیل سالیسیلیک اسید با استفاده از هتروپلی اسیدهای نهش یافته به عنوان کاتالیست های دوستدار محیط زیست و قابل بازیابی

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چکیده

سنتز استیل سالیسیلیک اسید در دمای اتاق از طریق استیلاسیون سالسیلیک اسید توسط استیک انیدرید در حضور پرایسلر و کگین نهش یافته بر روی سیلیکاژل که از انواع هتروپلی اسیدها است برای کمک کردن به داشتن تکنولوژی تمیز که نیاز اساسی جامعه می باشد مورد بررسی قرار گرفته است.کاتالیست های مورد استفاده در این جا همگی قابل استفاده مجدد می باشند.استیل سالیسیلیک اسید یک داروی مهم ماست که معمولا با فرایند کاتالیستی اسیدی تهیه می شود.کاتالیست هایی که بیشتر برای این واکنش مورد استفاده قرار می گیرند، اسید سولفوریک واسید فسفریک غلیظ می باشد.هر دوی این اسیدها بسیار خورنده هستند و باید با احتیاط زیادی مورد استفاده قرار گیرند. عملکرد پرایسلر و کگین نهش یافته در بارگذاری های مختلف با اسید سولفوریک مقایسه شده است.هتروپلی اسیدها فعالیت بالایی در مقایسه با اسید سولفوریک از خود نشان دادند.

واژه‌های کلیدی: استیل سالیسیلیک اسید، کاتالیست سبز، هتروپی اسید های نهش یافته، SiO_2

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