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SYNTHESIS OF TETRAHYDROFURAN OVER ALUMINOPHOSPHATE ALPO-11 CATALYSTS

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ABSTRACT

Crystalline AlPO-11 and its metal substituted CoAlPO-11 was prepared by the hydrothermal method and characterized by X-ray diffraction, scanning electron microscopy, Fourier transform infrared (FT-IR) spectroscopy and ICP-AAS. All the samples crystallized with the AFI structure. The catalytic properties of the catalysts in cyclodehydration of 1,4-butandiole to THF. CoAPO-11 with more Lewis acid sites, and stronger Bronsted acid sites gave better activity than AlPO-11.

1.1. INTRODUCTION

Microporous aluminophosphates (AlPO-*n*) have received considerable attention since the 1980s, and researchers have tried to develop new applications. After the aluminophosphate molecular sieve was firstly synthesized by Wilson et al. [1], numerous aluminophosphate type molecular sieves were developed. Aluminophosphate molecular sieves are made from corner-sharing AlO_4 and PO_4 tetrahedra. These tetrahedra form a three dimensional network containing channels and pores, which make them particularly attractive for adsorption and catalytic reaction. Among these aluminophosphate type molecular sieves, AlPO-5 (AFI) with one dimensional 12-ring channels (inner diameter 0.73 nm) has attracted the most attention.

MeAlPOs and SAPO family materials are produced when framework Al^{3+} and P^{5+} ions of the aluminophosphates molecular sieves are substituted by metal cations (Co, Mn, Cr, Mg, V, Ga, Fe, Zn, etc.) or silicon [2,3]. Metal substituted aluminophosphates molecular sieves have attracted great interest in recent years for their acid and redox properties [4–8], which have given remarkable catalytic performance in many reactions. FeAPO-5, CoAPO-5, and MnAPO-5 molecular sieves have exhibited good activity in many reactions, especially in cyclohexane oxidation to form cyclohexanone and cyclohexanol [9,10]. Raja and co-workers [11] found that these materials catalyzed the ammoximation of cyclohexanone to caprolactam with ammonia and H_2O_2. Recently, researchers have studied Beckmann rearrangements in the vapour phase using solid acid catalysts and molecular sieves [12,13]. Liquid phase Beckmann rearrangement using phosphotungstic acid has been carried out [14]. Tetrahydrofuran (THF) is a very important chemical from fuel synthesis point of view. Several other strategies have been adopted for its synthesis [15].

Cyclodehydration of butane-1,4-diol to tetrahydrofuran (THF) is industrially important reactions. These reactions are usually carried out by use of mineral and organic acids[16] solid acid catalysts such as clays [17] group(IV) metal halides [18] metallocenes [18] sulfated zirconia [19] zeolite [20] and calcium phosphate [21]. Tetravalent metal phosphates, to our knowledge, have not been used as catalysts for this reaction. These materials contain structural hydroxyl groups with labile protons and therefore are potential candidates as solid acid catalysts. These compounds can be prepared in both amorphous and crystalline forms. The amorphous forms possess a greater number of acid sites as compared to the crystalline materials [22] and thus are catalytically more active. These materials have been used as catalysts in a variety of reactions such as dehydration of alcohols [22] double bond isomerization of alkenes [23] Friedel–Crafts reactions [24] and reverse Prins reaction [25].

The present paper reports, for the first time, application of aluminophosphate as solid acid catalysts for cyclodehydration of 1,*4*-diols to the corresponding cyclic ethers in high yields and selectivity. In this paper, AlPO-11 and CoAPO-11 were synthesized by the hydrothermal method. The catalytic properties of these materials were studied for synthesis of THF.

1.2 Catalyst preparation

Pseudoboehmite (75% Al_2O_3), H_3PO_4 (85%), $Co(CH_3COO)_2 \cdot 4H_2O$ (99.5%), were used as the sources of aluminum, phosphorus, cobalt respectively. MeAlPO-5 was synthesized from a gel with the following molar composition: 0.06Me:0.94Al:1.0 P:0.75 Et_3N:20H_2O. Triethylamine (99%) was used as the template. A typical synthesis procedure is as follows. A solution of metal salts was prepared by dissolving the metal sources in deionised water. The calculated amount of pseudoboehmite was hydrolyzed for 30 min in a polypropylene beaker under stirring. Then the solution of metal salts was added into the alumina slurry at room temperature. After stirring for 1 h, diluted orthophosphoric acid was added dropwise into the gel solution and stirring was continued for another 2 h. Then, triethylamine was added into the mixed gel solution and stirred for 2 h. Finally, the mixture gel was sealed in a Teflon-lined stainless steel autoclave and heated to 180 °C under autogeneous pressure for 48 h. Afterwards, the gel was separated by filtration, washed with deionized water, dried at 120 °C overnight, and then calcined at 550 °C for 24 h in flowing air. AlPO-5 was synthesized according to the above method.

1.3. Catalyst characterization

The AlPO-11 structure and crystallinity of the samples were confirmed by X-ray diffraction (XRD) on a Japan Rigaku D/Max 2550 VB+ 18 kW X-ray diffractometer used under the conditions: 40 kV, 30 mA, Cu *K* radiation, with a scanning rate of 1°/min in the range of 2θ = 4°–65°. The morphology and dimensions of the samples were examined using scanning electron microscopy (SEM) with a JSM-6610LV spectrometer. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 380 spectrometer. The spectra of the samples were acquired in the wave number range of 400–4000 cm^{-1}.

1.4. Catalytic studies

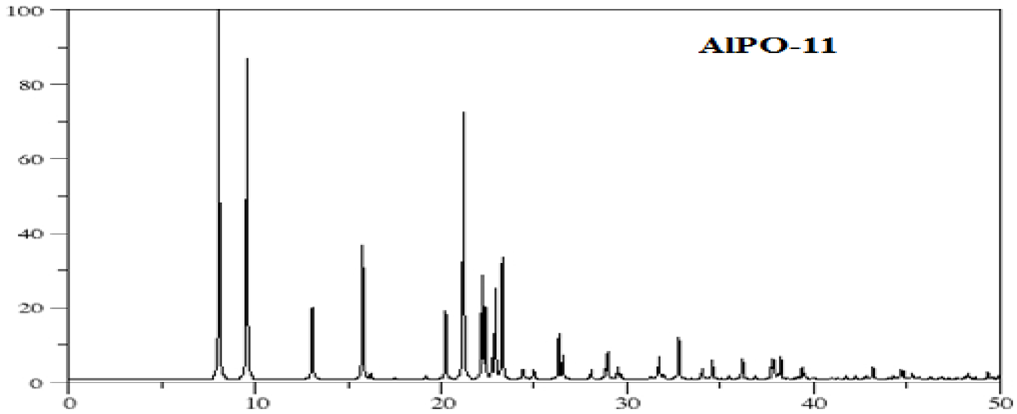
Catalytic reactions were performed in a 100 ml glass reactor. Typically, 5mL of dibutanol was taken a round bottom flask equipped with a condenser. Catalyst was added now and reaction temperature was increase. After completion of the reaction, reaction product was analysed by the GC chromatography to check the product yield and nature.

1.5. Characterization results

Fig. 1 shows the XRD patterns of AlPO-11 and CoAPO-11. The XRD patterns corresponded well to the patterns of the AFI structure. It has been observed that it can be converted into CHA because it has less thermodynamic stability than CHA [26, 27]. Except for the peaks due to AlPO-11, no other phase appeared in CoAPO-11 which indicated that these samples were highly crystallized in the AlPO-11 structure. The crystallinity of ALPO-11 was 88.48% and the crystallinity of AlPO-11 and CoAPO-11 were all above 90%. These values are larger than that of AlPO-5 (1.193 nm). The corresponding XRD peaks of the CoAlPO are shifted to the left with respect to AlPO-5, which may be because the lattice constants increased with metal substitution of Al atoms in the aluminophosphate network. These data indicated that the metals were incorporated into the framework of the AlPO-11. The SEM images of the synthesized AlPO-11 and CoAlPO-11 are shown in Fig. 2. Like the typical morphology of CoAlPO-11, the structures of AlPO-11 is mainly a hexagonal pillar structure with a middle collapse. The elemental composition ratio analyzed by ICP is shown in Table 1. The Me/P molar ratios ranged from 0.027 to 0.033 in CoAPO-5and AlPO-5 measured by ICP, which were less than that in the gel composition. This indicated that not all the metal ions in the gel were incorporated into the framework and the metal atom content did not depend directly on the gel composition. The (Me+Al)/P ratios were 1 for both the catalysts.

Table 1. Molar composition of elements of catalysts calculated by ICP-AAS

Sample	Molar composition of elements of catalysts		
	Metal	Al	P
AlPO-11	00	0.97	1
CoAPO-11	0.09	0.91	1.1



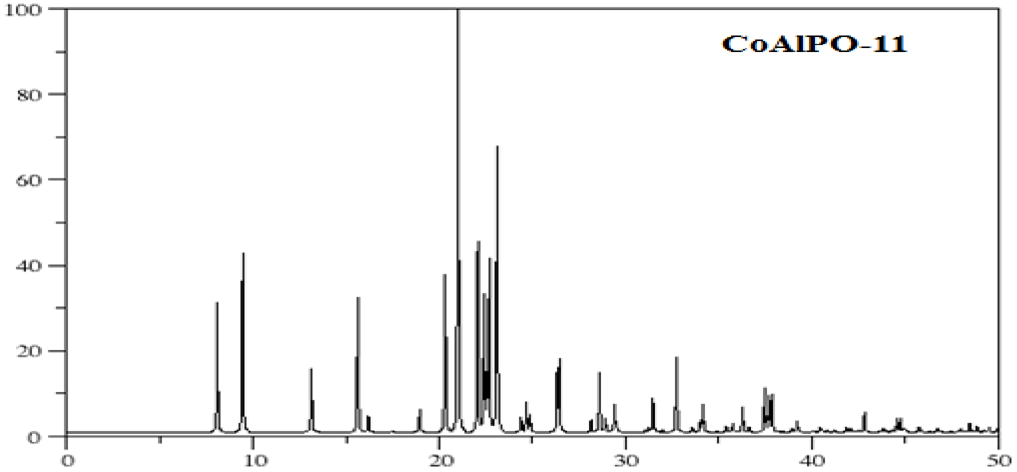


Fig. 1. XRD patterns of different samples. (Upper) APO-11; (Lower) CoAPO-11.

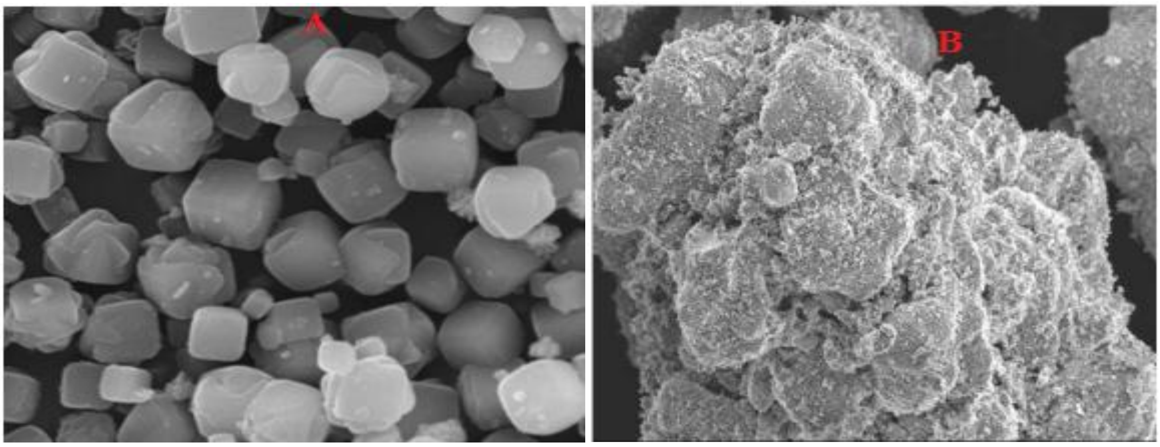


Fig.2. SEM images of AlPO-11(A) and CoAlPO-11(B).

The FT-IR spectra of AlPO-11, and the CoAPO-11 are presented in Fig. 3. The vibrations at 3478 and 1653 cm^{-1} were attributed to the bond stretching and bending vibrations of water molecules [28]. The peaks appearing at 1103 and 467 cm^{-1} were characteristic of aluminophosphates, and were attributed to the asymmetric stretching vibration of the P–O–Al unit and the P–O or Al–O bending vibrations in the AlPOs material [29]. With the introduction of Cobalt and metals, there was a slight change in the spectra of CoAlPO-11. The splitting of the peak at 467 cm^{-1} may be due to the presence of the metals. The reason may be that the Co–O bonds are longer than the Al–O bond. These data also confirmed that Co and the metals were incorporated into the framework of the AlPO-11. Stronger acid sites appeared when Si or metal was introduced into the framework of AlPO-11. When P^{5+} is replaced by Si^{4+}, or Al^{3+} is isomorphously replaced by a lower valence state metal atom such as Co^{2+}, Mn^{2+}, or Cr^{2+}, the framework is negatively charged and Bronsted acid sites are generated [30]. CoAlPO-11 exhibited most Lewis acid sites and strongest Bronsted acid sites.

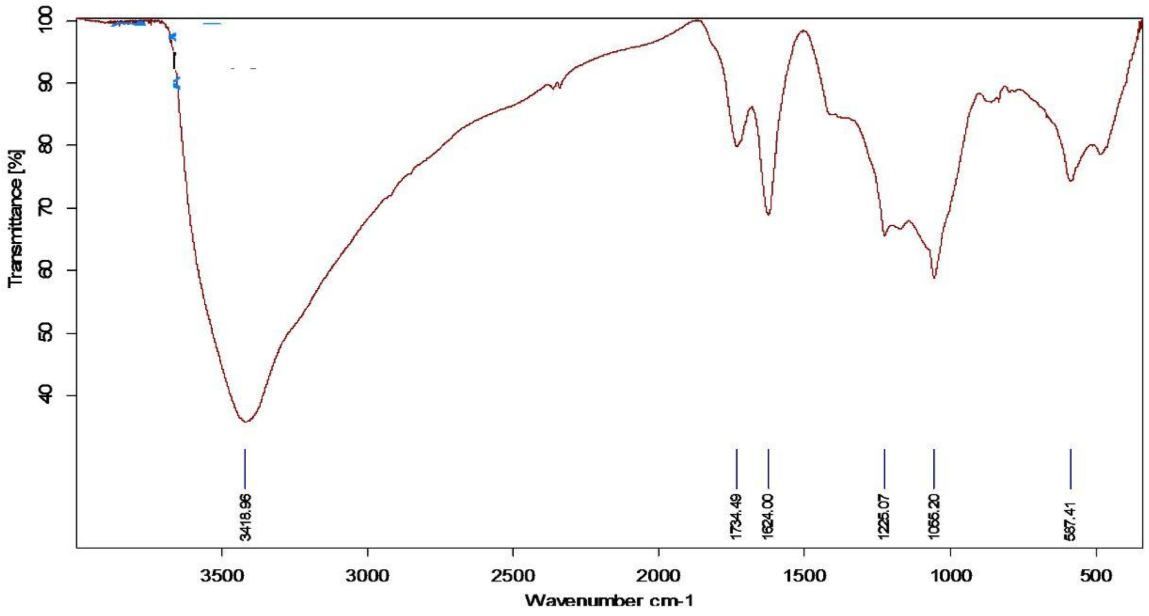
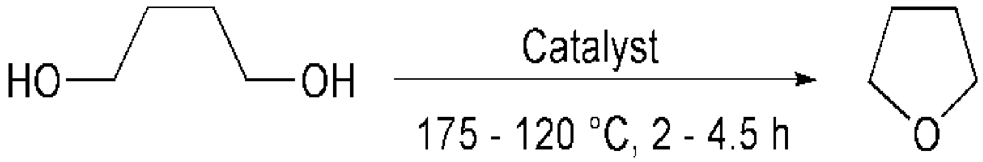


Fig. 3 FTIR Spectrum of CoAlPO-11

1.6. Catalytic tests

Representative results for the cyclodehydration over the AlPO-11 and the CoAlPO-11 catalysts are shown in Table 2. In the absence of a catalyst, the conversion of cyclohexane was very limited and it was converted to THF with very low selectivity for other side product, thus can be excluded. THF was efficiently obtained from 1,4-butanediole over the catalysts, which indicated that the catalysts played an important role in promoting the conversion of butanol and the formation of THF. From the results we can see that the catalytic activity increased when Cobalt was incorporated in the parent aluminophosphate AlPO-11.



It has been found that more Lewis acid sites and Bronsted acid sites are helpful in cyclodehydration of butanol to give better yield of THF, which was attributed to the efficient dehydration on the stronger Bronsted acid sites. Compared with AlPO-11, CoAPO-11 gave better activity, which may be due to its larger BET surface area, more Lewis acid sites, and stronger Bronsted acid sites.

Table 2. Representative results for the cyclodehydration over the AlPO-11 Catalysts

Yield(%) of THF over different catalysts*						
S.No.	**Temperature(℃)**	**AlPO-11**	**CoAPO-11**	**Time(h)**	**AlPO-11**	**CoAPO-11**
1	120	41	86	2	38	81
2	150	47	89	3	41	89
3	175	52	92	4.5	47	93

* Time and Temperature were constant (3h and 175 ℃) other variable was varied during the reaction

1.7. CONCLUSIONS

Crystalline AlPO-11 and CoAPO-11 were prepared by the hydrothermal method. The CoAlPO-11 had stronger Bronsted acid sites due to Si or metal introduced into the framework of AlPO-11 and the number of Lewis acid sites also increased. The catalytic properties of these materials were studied with cyclodehydration of butanol for the production of THF. The catalysts played an important role in promoting the conversion of but1anol and formation of THF. The catalytic activity increased with the BET surface area and Bronsted acid sites help give better activity for cyclodehdration. Among the both catalyst, with the larger BET surface area, more Lewis acid sites, and stronger Bronsted acid sites gave the better result with a conversion of 92 %

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