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## DEHYDRATION AND DEHYDROGENATION OF CYCLOHEXANOL OVER $\text{AlPO}_4\text{-5}$ BASED MOLECULAR SIEVES

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### Abstract

The role of incorporated divalent metal (Mn, Mg, Co and Zn) incorporated into the framework of  $\text{AlPO}_4\text{-5}$  in conversion of cyclohexanol has been examined. The influence of these metals to cyclohexene and cyclohexanone selectivities was correlated to the acidity and basicity properties of these molecular sieves. Possible mechanism for the dehydration and dehydrogenation for cyclohexanol was proposed.

*Keywords:*  $\text{AlPO}_4\text{-5}$ , acidity, basicity, cyclohexanol

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### INTRODUCTION

Solids exhibiting acidic and/or base sites on their surfaces play an important role in many catalytic reactions, either as catalysts or supports. Besides their acidic properties  $\text{AlPO}$  molecular sieves are known to have basic properties [1]. In addition, it was reported that oxygen atoms from the framework may act as basic sites in  $\text{AlPO}$  molecular sieves [2]. In this study, a series of divalent metal (Me) were incorporated into  $\text{AlPO}_4\text{-5}$  framework by direct synthesis in order to generate active acid and base sites. The following strategy has been applied to prove the role of active sites in metal-containing  $\text{AlPO}_4\text{-5}$ : Use conversion of cyclohexanol as a representative reaction model [2-4].

The conversion of cyclohexanol was chosen to explain the behavior of *both* the acid and base sites in  $\text{AlPO}_4\text{-5}$  molecular sieves by discovering the hidden relationship between acid and base sites.

## EXPERIMENTAL

Aluminophosphate ( $\text{AlPO}_4\text{-5}$ ) or metal-containing aluminophosphates (MeAPO-5) were synthesized by aluminum isopropoxide,  $\text{Al}[\text{OCH}(\text{CH}_3)_2]_3$ , as the aluminum source and tripropylamine ( $\text{Pr}_3\text{N}$ ) as the template following established procedure with some modifications [1].

MeAPO-5 was synthesized with a gel composition of 1.0  $\text{Al}_2\text{O}_3$  : 1.0  $\text{P}_2\text{O}_5$  : 0.13 MeO :  $y$   $\text{Pr}_3\text{N}$  : 40  $\text{H}_2\text{O}$ .  $\text{Al}[\text{OCH}(\text{CH}_3)_2]_3$  (Aldrich) was added to water; the mixture was kept for 12 h (hydrolysis) and was homogenized for 1 h. A separate solution of  $\text{H}_3\text{PO}_4$  (85% Ajax) with water and Me-acetate (BDH) was prepared and added to the above gel. Then  $\text{Pr}_3\text{N}$  (Aldrich) was added dropwise until the pH  $\sim 4.9$  was achieved. The gel was heated in a Teflon-lined stainless steel vessel at  $175^\circ\text{C}$  for 41 h. The product was washed and dried at  $110^\circ\text{C}$  overnight calcined at  $550^\circ\text{C}$  in air for 20 h in order to remove the entrapped organic molecules (template). The products were characterized by XRD, SEM, IR, TPD and MAS NMR as described previously [6].

The dehydration and dehydrogenation of cyclohexanol over the samples were carried out using a down-flow, fixed bed, Pyrex reactor of 8 mm internal diameter at atmospheric pressure. The reactor was heated by furnace. Oxygen was then passed through the catalytic bed. The reaction was carried out at  $300^\circ\text{C}$ , with a feed rate of  $6 \text{ mL h}^{-1}$  and 0.3 g of catalysts. The reaction mixture was fed from the top using a syringe pump. The water-cooled product was collected at the bottom. The unconverted cyclohexanol and the products were analyzed by a Hewlett Packard Model 5880A gas chromatograph using Flame Ionization Detector (FID). The products were analyzed on Carbowax 20 M column. The column temperature was raised from  $35$  to  $210^\circ\text{C}$  with a rate of  $6^\circ\text{C}/\text{min}$ .

## RESULTS AND DISCUSSION

Figure 1 shows the influence of metal-substituted MeAPO-5 molecular sieves on the selectivity of cyclohexene and cyclohexanone. The overall trend is that selectivity of cyclohexene increases with a decrease in selectivity of cyclohexanone. The detection of cyclohexene indicates the presence of acid sites, whereas cyclohexanone corresponds to the presence of negative charge on the oxygen atom. As shown in Table 1, the basicity increases when the negative charge on oxygen atom calculated, using Pauling's third rule [7], increases. Interestingly, it shows that the catalyst with the stronger acid strength exhibits a lower basicity, due to the fact that  $\text{H}^+$  can jump from one oxygen atom to its neighboring oxygen atom. Previously, it was found that the acidity and basicity of MeAPO-5 are structure dependent (T-O-P angle) [6]. Since the calculated trends in Table 1 do not correlate with the experimental data (Fig. 1), quantitatively demonstrates the correlation between the acid strength (at oxygen atom No. 1) with the basic strength (at oxygen atom No. 2) of MeAPO-5.

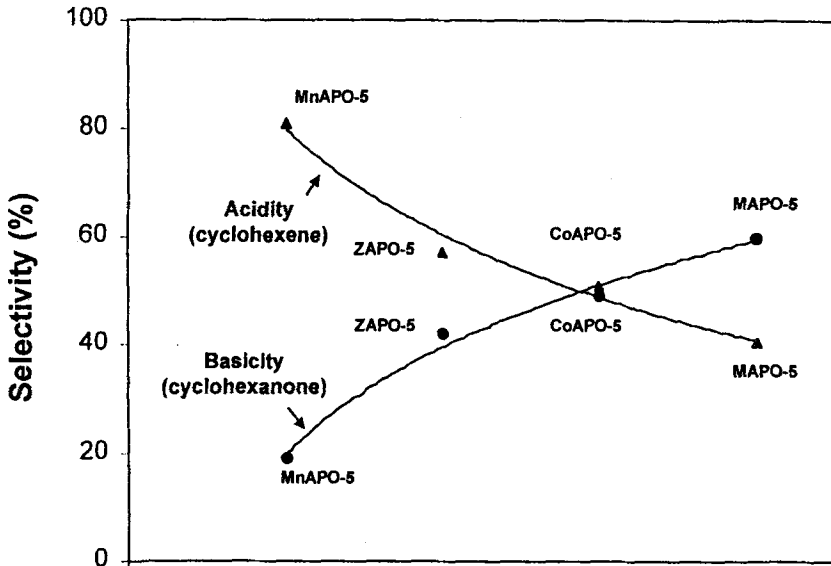


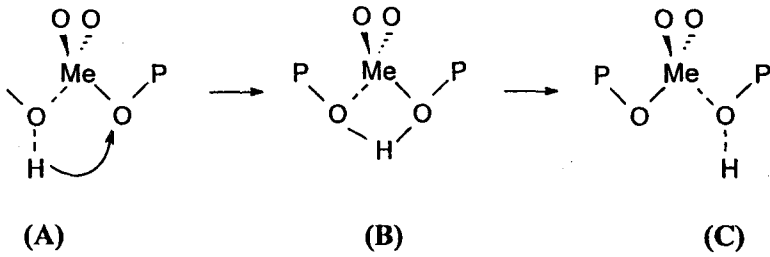
Fig. 1. Cyclohexanone and cyclohexene selectivities over MeAPO-5

Table 1

Relationship between effective charge of oxygen atom with the acid and base strength of MeAPO-5

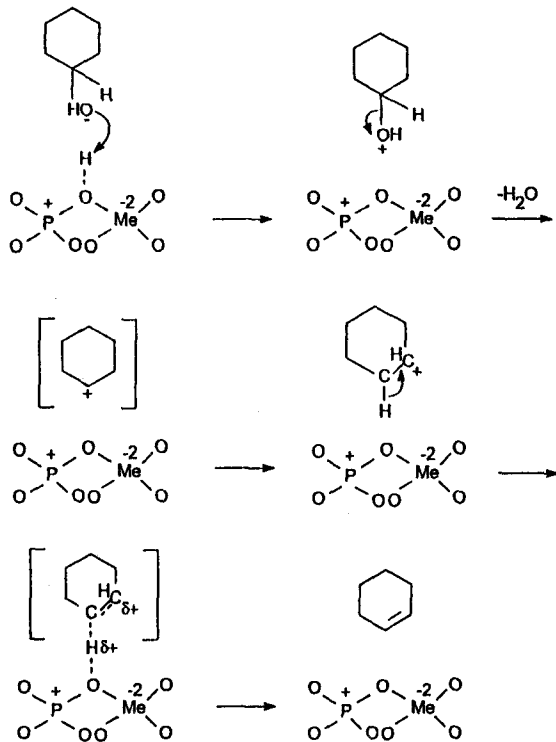
Effective charge of oxygen atom		
Me atom	(1) Acid site	(2) Base site
Co	-2.10	-1.78
Zn	-2.19	-1.87
Mn	-2.22	-1.91
Mg	-2.32	-2.00

↑ Acid strength increase      ↓ Base strength increase



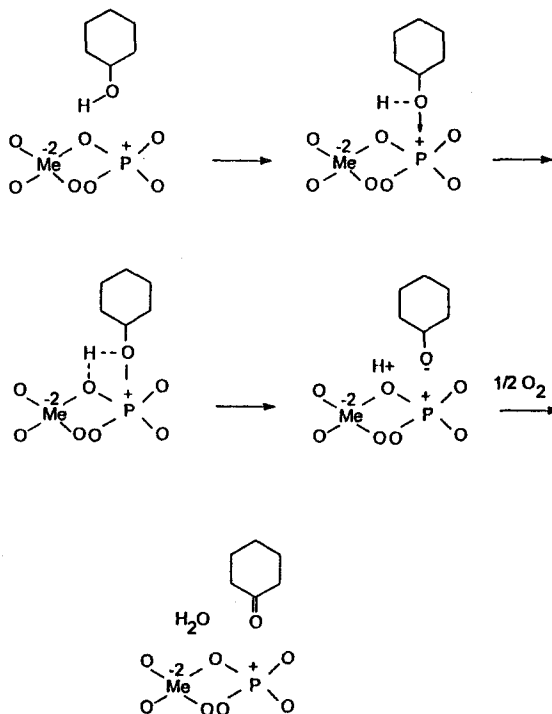
**Fig. 2.** Proton transfer in metal substituted aluminophosphate molecular sieves

(a) Dehydration of cyclohexanol



**Fig. 3a.**

## (b) Dehydrogenation of cyclohexanol

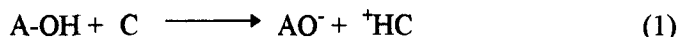


**Fig. 3.** Proposed mechanisms of (a) dehydration of cyclohexanol over an acid site, and (b) dehydrogenation of cyclohexanol over a base site in AlPO<sub>4</sub>-5

According to the scheme shown in Fig. 2, the proton attached to a given oxygen atom of an AlO<sub>4</sub> tetrahedron, (A), can jump to any other oxygen atom belonging to the same tetrahedron (C) *via* a transition structure (B). This suggests that the protons in AlPO molecular sieves are mobile, which may seem possible from theoretical consideration [8]. The effective charges on those oxygen atoms were calculated in order to explain acidity and basicity properties based on the neighboring oxygen atom. It shows that the stronger acid site is located next to the neighboring atom with a lower basic site.

Dehydration and dehydrogenation of alcohols are catalyzed by the acidic and the base sites, respectively [9]. These reactions provide a diagnostic means of determining the acid-base character of solid surfaces. It is known that

dehydrogenation occurs easily with cyclic alcohols [10]. Alcohols undergo elimination reactions to yield alkenes. Since water is lost in the elimination, this reaction is named dehydration. For secondary alcohols, dehydration follows an E<sub>1</sub> mechanism [11], whereby hydroxygroup is protonated, a carbocation is formed with loss of a water molecule, followed by the elimination of a proton to yield an alkene. The initial step of acid catalysis by a zeolitic Brønsted acid is proton



transfer, where A is AlPO molecular sieve and C is cyclohexanol. This reaction is also known as deprotonation of active sites. The next step of the reaction is the protonation of cyclohexanol, followed by desorption of the base from the active site. Dehydrogenation of cyclohexanol is a proven reaction that can be used to determine base sites in aluminophosphate molecular sieves. Dehydrogenation is a reaction in which hydrogen is eliminated when reacted with oxygen. This is called oxidative dehydrogenation. It has been accepted that the oxidative dehydrogenation involves lattice oxygen ion [12-15]. However, the mechanism of cyclohexanol with acid and base sites in the aluminophosphate molecular sieves is not yet clearly understood. Considering the possible role of acid and base sites in MeAPO-5, the mechanism of dehydration and dehydrogenation of cyclohexanol over these materials are proposed as depicted in Fig. 3.

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