

## Catalytic Properties of AlPO Molecular Sieve Derivatives

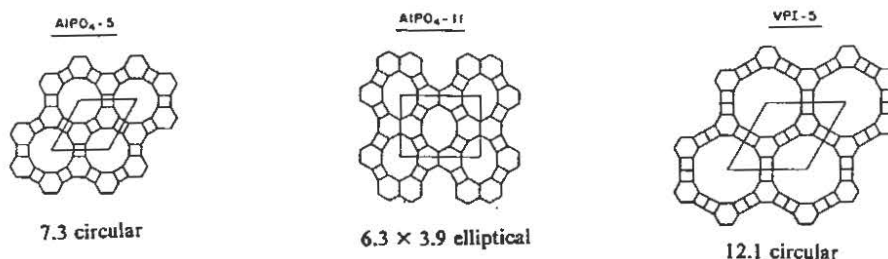
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Zeolites, made of tetrahedral  $\text{SiO}_4$  and  $\text{AlO}_4$  units, are widely used for their abilities as adsorbents, ion exchangers, catalyst supports, and shape selective catalysts [1]. A remarkable feature of zeolites is their uniform pore sizes. Typical pore sizes in zeolites range from 4 to 12 Å. The largest number of window atoms forming the pore is 12 for zeolites. To date, there are approximately 70 different structure types known for zeolites [1-6].

The announcement of aluminophosphate molecular sieves (AlPO) in 1982 revealed an entirely new family of zeolite-type materials [7]. The AlPO materials are made of tetrahedral  $\text{AlO}_4$  and  $\text{PO}_4$  units. At least 25 different AlPO's have been synthesized [8-9]. Although many of these AlPO's have the same structure types as those found in zeolites, over half of them have novel structures [10]. Of particular note are those designated AlPO-5, AlPO-11, and VPI-5. In fact, VPI-5, which was first reported in 1988, has 18 window atoms and a pore size of 12.1 Å, which is larger than the largest zeolite pore [11-12]. Large pore sizes are necessary for heavier molecular weight fuel stocks in Fluid Catalytic Cracking (FCC) processes. However, the largest pore size in molecular sieves does not belong to an AlPO but rather a recently discovered gallophosphate known as cloverite, announced in June, 1991 [13].



The AlPO molecular sieves are typically crystallized from a mixture of reactive aluminophosphate gel, templating amine, and water in a Teflon-lined stainless steel bomb between 150 and 200°C [9]. The crystalline material must then be calcined to remove the templating amine before it is functional.

Unlike zeolites, the AlPO framework is charge neutral, limiting its catalytic properties. In order to create reactive acidic sites such as those found in zeolites, elemental substitution into the AlPO framework must be made. In 1984, silicoaluminophosphates (SAPO) with AlPO structure-types were announced [14]. Specifically, SAPO-5 and SAPO-11 have the same structure types as AlPO-5 and AlPO-11, respectively. Silicon substitution is noteworthy because not only does silicon substitute for phosphorous, but two silicon atoms can substitute for aluminum plus phosphorous, leading to the undesired neutrally charged framework [15]. Substitution by other tetravalent elements such as Ti, Zr, and Ge is the same as that of Si: 1 atom for P or 2 atoms for (Al+P). Aluminum substitution is made by elements such as Be, B, Mg, Mn, Fe, Co, Zn, and Ga, which are mono-, di-, or trivalent [9-10]. All of the substitution modes discussed lead to neutral or negatively charged frameworks.

Once acidic sites are created, the nature of acidity can be characterized using several methods. First, the infrared hydroxyl stretching frequency of activated AlPO and SAPO wafers can be used to indicate the acidic strength of hydroxyl groups [8,16-18]. Lower frequencies indicate weaker O-H bonds, which means stronger acidity. Temperature Programmed Desorption (TPD) can be used to determine the strength of acidity: the higher the temperature at which ammonia desorbs, the stronger the acidity [16-18]. The number of acidic sites can also be probed by the TPD of n-propylamine [15]. Finally, the pseudo first-order rate

constant ( $k_a$ ) of n-butane cracking provides an overall indication of acidity from an empirical perspective [10,14,20].

A clear advantage of molecular sieve catalysts arises from their shape-selectivity [1,3,5]. The uniform pore size allows only molecules smaller than the pore to reach active sites. The exclusion of molecules larger than the pore size is known as reactant selectivity. Two other types of selectivity are transition state selectivity and product selectivity. The former refers to the restriction of transition states to those which fit inside the channels; the latter refers to the entrapment of products inside the channels which are too large to fit through the pore windows. Different structures have different selectivities because their pore sizes, shapes, and volumes will differ, allowing only molecules which fit to undergo reaction.

Three sample catalytic reactions will provide an indication of the novel catalytic abilities of the SAPO-5 and SAPO-11 materials over common zeolites such as zeolite Y and ZSM-5: cumene cracking, toluene methylation, and xylene isomerization [16-18,21-22]. Cumene cracking data show that the SAPO-5 molecular sieve favors rearrangement reactions over the cracking reactions which are favored by ZSM-5 [18]. In SAPO catalyzed reactions between toluene and methanol, SAPO-11 shows excellent selectivity for methylation of toluene to produce xylene, rather than disproportionation of two toluene molecules into benzene and xylene [22]. Finally, xylene isomerizations require higher temperatures than ZSM-5, but activity is higher than ZSM-5 at higher temperatures [16].

In conclusion, the SAPO molecular sieves are useful for catalytic transformations without the high degree of cracking which occurs in zeolites such as ZSM-5. In general, AlPO derivatives are not as active as common zeolites such as ZSM-5, but they show promise for unique catalytic applications due to their larger pore size and lower acidity.

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