

## TRITIUM STUDIES OF CATALYSIS OVER MICROPOROUS ALUMINOPHOSPHATE SURFACES.

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### SUMMARY

Microporous  $\text{AlPO}_4\text{-5}$  catalysts exhibit catalytic activity for tritium isotope exchange and other reactions but the activity of the catalyst may vary widely from one batch of catalyst to another although all catalyst samples appear to show pure  $\text{AlPO}_4\text{-5}$  phase. This catalytic activity appears to correlate with the presence of octahedral aluminium in the catalyst samples as revealed by solid state  $^{27}\text{Al}$  NMR spectroscopy and this is attributed to defect sites in the lattice. The exchange patterns may show high regional specificity. These patterns have some of the features of acid catalysis but are assumed to be modified by the constraints imposed by the micropore geometry.

**Keywords:** Tritium exchange, aluminophosphate catalyst,  $\text{AlPO}_4\text{-5}$ , tritium NMR

### INTRODUCTION

A tritium isotope exchange reaction is inherently one of the simplest chemical reactions that can be studied and therefore has appealed to the physical chemist as a mechanistic tool for many decades. The development of modern instrumentation has meant that tritium has replaced deuterium to a considerable extent as the isotope to be used in investigations of reaction mechanisms. The pioneering work with tritium NMR in the early to mid 70's at the University of Surrey, and in conjunction with the tritium group at Amersham, played a major part in this instrumental development (1).

Tritium has been used for probing many types of reaction system. The detritiation of compounds in solution, investigated by Elvidge, Jones, Evans and their colleagues (2) is well known. The studies of homogeneous phase metal catalysis of tritium exchange reactions, again at Surrey (3), and by Lockley (4) and other groups (3) is well known, and there is a wealth of published work on various forms of heterogeneous catalysis by metal surfaces, zeolites and related

catalytic systems by Williams et al. (5) and many other groups. While some of the above work was undertaken because of an interest in developing methods for producing tritium labelled compounds the prime reason for some of the studies was to explore the mechanisms of the catalytic processes.

We previously reported (6) the use of a relatively new type of heterogeneous catalyst, namely microporous aluminophosphates as catalysts for tritium exchange from either tritium gas or water into organic compounds. We now report further detailed studies of the ALPO systems carried out for the purpose of exploring the nature of ALPO catalysis rather than as the development of a labelling method, although these ALPO catalysts have interesting application as a method of labelling simple molecules.

Silica based microporous molecular sieves, or zeolites, are used extensively today throughout the petroleum refining and chemical process industries as selective adsorbents, catalysts, carriers of catalysts and ion exchange materials. It is about 10 years since the class of molecular sieves, based on aluminophosphates, was first reported in the literature (7). Since then, the synthesis of a wide variety of such microporous structures have been described and the possibility of including many metals in the structure continues to be explored (8).

An example of one of these widely studied structures is the so called  $\text{AlPO}_4\text{-5}$ . It has a three-dimensional structure with hexagonal symmetry and contains one dimensional channels (diameter 0.7 nm) oriented parallel to the c-axis and bounded by 12-membered rings composed of alternating  $\text{AlO}_4$  and  $\text{PO}_4$  tetrahedra. The Al/P ratio is about unity and so the framework positive charge on P is balanced by the corresponding negative charge on Al. The units which comprise the structure may be linked in a variety of ways and hence the large pores may vary widely in size and in shape (8). This type of structure provides two features of importance as far as catalysis is concerned: a large surface area and shape selectivity for molecules which may be able to enter the pore. The catalyst can be engineered to suit the particular molecular reaction it is required to promote. This shape selectivity in a reaction may be the result of selectivity towards reactant molecules, reaction transition state, or product molecules.

There is one fundamental difference between ALPO's and silica based zeolites. Silica based zeolites containing some Al have a charge imbalance which imparts a strong acidity to the zeolitic surface by virtue of the proton that compensates that negative charge imbalance to maintain overall neutrality. In contrast, ALPO's with their overall neutrality are expected to display virtually no ion exchange or acid-catalytic properties. It was therefore with some surprise that early studies (9) of

ALPO's as catalysts detected a reasonably high degree of catalytic activity in a variety of hydrocarbon isomerisation and related reactions. The present study was carried out in the hope that the tritium isotope exchange reactions might provide insight into the nature of this catalytic activity for a variety of reactions.

## EXPERIMENTAL

*Synthesis of ALPO's* - Appropriate ratios of alumina and phosphoric acid together with an organic template molecule in the form of a viscous gel are allowed to undergo hydrothermal crystallisation at a temperature around 200°C. The crystalline material is dried and calcined at about 700°C in air which removes the organic template and water which would otherwise fill the pores. Details of the procedure are described elsewhere (7).

*Characterisation of ALPO's* - The following techniques were routinely applied to confirm the ALPO structure: elemental analysis (to confirm the 1:1 AL:P structure); x-ray diffraction analysis on the powder (to confirm the crystalline phase on the basis of comparison with published XRD data);  $^{27}\text{Al}$  and  $^{31}\text{P}$  solid state NMR spectroscopy (to explore the atomic environment of Al and P in the structure); pore volume measurement (by standard BET type analysis).

*Tritium Exchange Procedure* - A variety of experimental procedures as described in detail elsewhere (10) were adopted. The catalyst was normally evacuated and the tritium source ( $\text{T}_2$  gas or HTO) added, followed by the organic substrate to be labelled (previously degassed). Analysis of the products was carried out by radio-gas chromatography and  $^3\text{H}$  NMR spectroscopy (300MHz).

## RESULTS

### *Exchange of various compounds with $\text{T}_2$ Gas over $\text{AlPO}_4\text{-5}$ catalyst*

A summary of the results of a variety of model compounds which were allowed to undergo exchange with tritium gas over  $\text{AlPO}_4\text{-5}$  catalyst is presented in Table 1. The results show that a wide range of simple model compounds can be labelled effectively, some requiring a higher temperature than others. These results were obtained for reactions performed with a limited reaction time selected so that the relative exchange rates of various compounds was apparent.

If the objective was to maximise the degree of tritium incorporation then the reaction time could be extended. Table 2 shows the dependency of the exchange of toluene on the reaction time. It is apparent that the tritium exchange reaction continues at a steady rate and will in time approach equilibrium. Alternatively the exchange rate can be increased by an increase in reaction temperature but this will lead to some loss in positional specificity. However, not all batches of  $\text{AlPO}_4\text{-5}$  catalyst synthesised showed the above catalytic activity. This anomaly between batches will be discussed below.

**Table 1.** Exchange of organic compounds with tritium gas catalysed by  $\text{AlPO}_4\text{-5}$ .

Compound	Temperature (°C)	Activity (mCi/g)	Incorporation (%)	Impurities (mCi/mL)
Toluene	100	92	9.0	n.d.
Ethylbenzene	100	27	2.6	n.d.
i-Propylbenzene	180	15	1.4	n.d.
n-Butylbenzene	180	43	3.6	n.d.
i-Butylbenzene	180	28	2.4	n.d.
t-Butylbenzene	100	54	5.3	n.d.
Naphthalene	100	31	3.0	n.d.
o-Xylene	100	24	2.4	n.d.
m-Xylene	100	83	8.1	n.d.
p-Xylene	150	11	1.0	n.d.
Mesitylene	100	41	4.0	n.d.
Durene	100	67	6.6	n.d.
m-Diethylbenzene	100	74	7.3	n.d.
Chlorobenzene	150	46	4.5	n.d.
Furan	100	36	3.5	n.d.
Thiophene	100	27	2.7	n.d.
Anisole	100	40	3.9	n.d.
2,3-Dimethylbutane	100	38	3.7	17
Methylcyclopentane	180	81	6.8	n.d.

0.3g substrate, 357mCi  $\text{T}_2$ , 75mg catalyst, reaction time: 72 hours

**Table 2.** Tritium exchange of toluene /  $\text{T}_2$  gas over  $\text{AlPO}_4\text{-5}$  at various reaction times.

Time (hours)	Activity (mCi/mL)	Incorporation (%)	%Tritium Distribution per Hydrogen			
			<i>Ortho</i>	<i>Meta</i>	<i>Para</i>	<i>Methyl</i>
6	48	4.7	3.3	2.3	88.8	<0.1
24	92	9.0	3.6	<0.1	92.8	<0.1
72	92	9.0	5.5	<0.1	89.0	<0.1
120	138	13.6	5.4	5.2	78.9	<0.1
168	153	15.0	4.8	3.1	84.3	<0.1
336	220	21.6	8.3	8.1	67.2	<0.1

reaction temperature 100°C, other conditions as in table 1.

*Comparison with other catalytic systems and isotope sources.* - Use may be made of tritium gas, tritiated water or tritiated benzene as isotope source with a variety of microporous catalyst systems.

Table 3 compares the exchange of toluene with these isotope sources and catalysts under similar

reaction conditions. It is noteworthy that  $\text{AlPO}_4\text{-5}$  has a remarkable activity for promoting exchange with tritium gas compared with other microporous catalyst systems.

*Specificity of Exchange* - Figure 1 shows the tritium distribution in a number of compounds labelled over  $\text{AlPO}_4\text{-5}$  catalysts with tritium gas. It is clear that remarkable specificity can be achieved in some compounds such as toluene. No other exchange catalyst will yield toluene specifically labelled in the single para position. It is necessary to adopt a synthetic process such as dehalogenation to achieve that specificity.

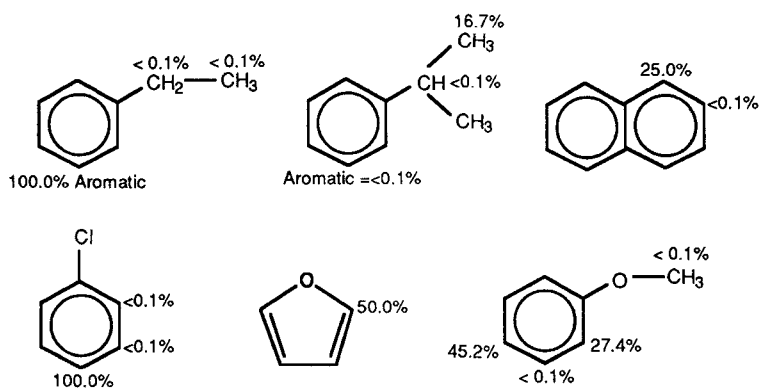


Figure 1. Distribution of tritium (per H atom) in compounds labelled by exchange with tritium gas.

**Table 3. Exchange of Toluene with various microporous catalysts and isotope sources.**

Isotope source	Catalyst	Temperature	Time (hours)	Incorporation (%)
T <sub>2</sub> gas	AlPO <sub>4</sub> -5	100°C	72	29.5
T <sub>2</sub> gas	HNaY	100°C	96	<2.0
T <sub>2</sub> gas	Mordenite	125°C	173	1.1
T <sub>2</sub> gas	ZSM-5	130°C	168	2.0
HTO	AlPO <sub>4</sub> -5	125°C	136	3.9
HTO	HY	175°C	7	100.0
HTO	Mordenite	125°C	24	76.0
HTO	ZSM-5	125°C	24	100.0
C <sub>6</sub> H <sub>5</sub> T	AlPO <sub>4</sub> -5	125°C	72	1.5
C <sub>6</sub> H <sub>5</sub> T	HY	100°C	24	58.0
C <sub>6</sub> H <sub>5</sub> T	ZSM-5	125°C	117	76.0

### *Methylation Reactions of Methane*

AlPO<sub>4</sub>-5 catalyses the methylation of aromatic alkanes by methane gas under high pressure. The results in Table 4 are illustrative of the results obtained.

**Table 4. Methylation of aromatics with methane gas over AlPO<sub>4</sub>-5 catalyst.**

Reactant	Products
Toluene	xylenes 30%, tri-me-benzenes 18%, others 52%
Naphthalene	me-naphthalenes 94%, di-me-naph.1%, dinaphthalene 6%
Biphenyl	alkylbenzenes 77%, phenanthrene 5%, others 18%

Typical reaction conditions: 400°C, 1hr, methane 6.8MPa, catalyst AlPO<sub>4</sub>-5

This reaction is of considerable interest as a possible utilisation of methane in the generation of appropriate liquid fuels.

### *Partial Oxidation of Methane*

The partial oxidation of methane to higher hydrocarbons is a subject which has received much study of recent years. The objective is to couple methane to ethylene or higher hydrocarbons with the minimum formation of the products of so called deep oxidation, CO and CO<sub>2</sub>. Alkaline earth oxide and rare earth oxide catalysts have been the most studied (11) and require temperatures around 900°C. We have tested a variety of ALPO catalysts and have measured surprisingly high yields of C<sub>2</sub>+ (up to 18%) products from methane at temperatures in the region of 700 - 800°C. This oxidative coupling of methane also has major significance in the production of liquid fuels from methane gas.

## DISCUSSION

### **Nature of the Catalytic Site in ALPO's**

The results quoted above have established that ALPO's do indeed exhibit catalytic activity for the exchange of tritium and other reactions. The question arises as to the nature of the catalytic site in structures which are not expected to have the catalytic activity of acidic solids such as silico-alumina zeolites. Evidence as to the nature of the catalytic activity has been obtained by a consideration of the variation in activity between different synthesis batches of AlPO<sub>4</sub>-5 catalyst.

Table 5 shows the results of the exchange of toluene with tritium gas over different synthesis batches of ALPO catalyst. These showed quite different catalytic activity. The reason for this was assumed to lie in the structure of the catalyst.

**Table 5. Exchange of toluene with tritium gas over different batches of AlPO<sub>4</sub>-5 catalyst**

Batch No.	Surface Area (m <sup>2</sup> /g)	Incorporation (%)	%Tritium Distribution per Hydrogen			
			<i>Ortho</i>	<i>Meta</i>	<i>Para</i>	<i>Methyl</i>
AlPO <sub>4</sub> -5-1	237	9.0	3.6	2.0	88.8	<0.1
AlPO <sub>4</sub> -5-2	320	29.7	6.9	2.3	81.8	<0.1
AlPO <sub>4</sub> -5-8	269	1.4	7.1	<0.1	85.7	<0.1
AlPO <sub>4</sub> -5-9	309	<1.0	-	-	-	-
AlPO <sub>4</sub> -5-10	398	<1.0	-	-	-	-

All catalyst batches listed in Table 5 showed similar XRD patterns and pore volumes. However, careful examination of their <sup>27</sup>Al NMR spectra showed the presence of varying amounts of octahedral Al. (Figures 2 and 3). Signals at chemical shifts of 37.42 and -13.40 are assigned to

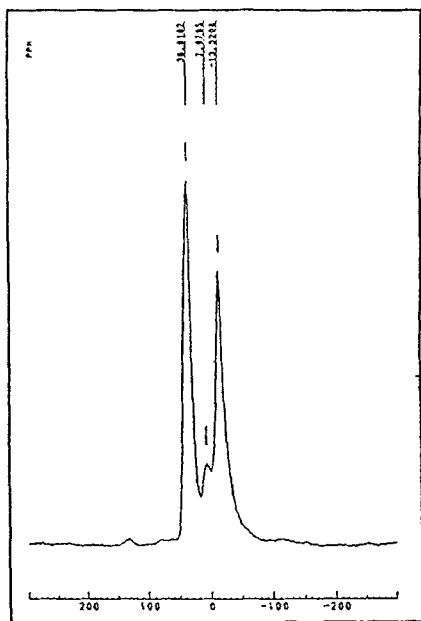


Figure 2. <sup>27</sup>Al NMR spectrum of AlPO<sub>4</sub>-5-2

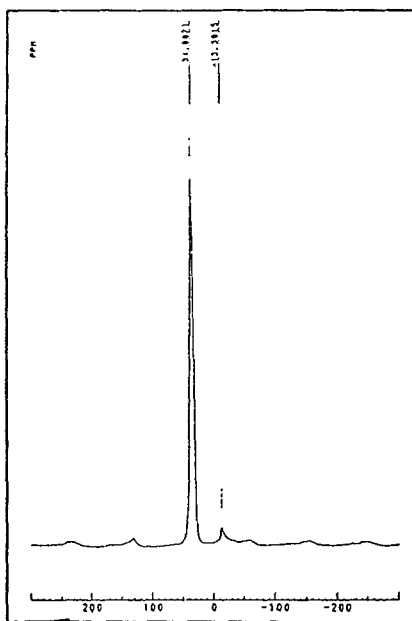


Figure 3. <sup>27</sup>Al NMR spectrum of AlPO<sub>4</sub>-5-9

tetrahedral and octahedral Al respectively. There is a notable absence of the latter peaks in the spectra of those catalysts which showed little exchange activity. It is concluded that the presence of octahedral Al in the  $\text{AlPO}_4\text{-5}$  framework is responsible for the catalytic activity towards tritium exchange.

In the structure of pure crystalline  $\text{AlPO}_4\text{-5}$  phase, all aluminium atoms should reside in a tetrahedral configuration. The presence of some octahedral Al indicates either the presence of a different Al phase (such as alumina) or the presence of defects in the ALPO lattice. The XRD patterns showed no significant amounts of amorphous material nor the presence of other crystalline phases. Hence the octahedral Al is assumed to be indicative of the concentration of lattice defects. The corollary of this is that the catalytic activity is associated with these lattice defects.

Other workers (12) studying the  $\text{AlPO}_4\text{-5}$  catalysis of hydrocarbon formation from methanol have also linked the catalytic activity to the presence of octahedral Al. Furthermore, in a study of  $^{18}\text{O}$  exchange of  $\text{CO}_2$  with the framework oxygen of  $\text{AlPO}_4\text{-5}$  it has been concluded (13) that the presence of defects of various types leads to the presence of -OH groups on the surface and hence possible acidic sites similar to the Si-OH groups of zeolites. Exchange may then resemble the electrophilic type substitution typical of acid surfaces such as the zeolites.

*Specificity of Exchange* - The exchange in molecules such as toluene was remarkably specific to the para position (Table 5). Electrophilic substitution would be expected to favour the ortho as well as the para position. High ortho deactivation, relative to other positions, was a frequently observed phenomenon of metal surface catalysed exchange (14). But the reaction mechanism in these ALPO systems is thought to be fundamentally different to that of metal systems. Enhancement of substitution at the para position is a phenomenon observed in the bromination of molecules such as toluene. The charge at the para position is considered to be delocalised by an interaction of the  $\pi$ -electron system with the C-H bonding orbitals of the methyl group. It has been surmised that the faster rate of electrophilic substitution at the para position is attributed to the operation of a resonance stabilisation favouring enhanced charge density at the para location.

A molecule of toluene confined by the pore geometry to lie along the pore axis would be expected to interact with the oxygen atoms which form the surface of the pore. The ortho and meta positions would be most intimately involved with the pore surface. The electronic interactions involved may thus lead to the preferential substitution at the para position.



## CONCLUSION

A variety of simple organic molecules may be labelled by exchange with tritium gas over microporous AlPO<sub>4</sub>-5 catalysts. The activity of these ALPO catalysts extends to other reactions but may vary widely from one batch of catalyst to another although all appear to show pure AlPO<sub>4</sub>-5 phase. This catalytic activity appears to correlate with the presence of octahedral aluminium in the catalyst samples as revealed by solid state <sup>27</sup>Al NMR spectroscopy and this may be attributed to defect sites in the lattice. The exchange patterns in molecules such as toluene have many of the features of acid catalysis. But the close interactions of molecules within the micropores with the surface of the pores and the geometrical constraints imposed on those molecules is assumed to influence the exchange patterns.

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