

TRITIUM GAS EXCHANGE STUDIES OF PLATINUM-LOADED MICROPOROUS ALUMINOPHOSPHATE MOLECULAR SIEVES

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SUMMARY

Platinum-loaded microporous aluminophosphate molecular sieves (Pt- $\text{AlPO}_4\text{-5}$) were synthesized and studied as catalysts for promoting tritium isotope labelling by exchange between tritium gas and aromatic, heteroaromatic and aliphatic hydrocarbons. The presence of the Pt metal considerably enhanced the activation of the tritium gas. Detailed isotope orientation patterns, as determined by ^3H nmr spectroscopy, showed that the $\text{AlPO}_4\text{-5}$ component of the catalyst dominated the exchange reactions, but some influence of the Pt metal was apparent with some substrates.

Keywords: Tritium exchange, aluminophosphate catalyst, platinum catalyst, $\text{AlPO}_4\text{-5}$, ^3H nmr

INTRODUCTION

The discovery of aluminophosphate type molecular sieves (*e.g.* $\text{AlPO}_4\text{-5}$) was first reported by Wilson *et al.*^{1,2} in 1982. Subsequently, various elements have been incorporated into the aluminophosphate frameworks, including Li, Be, B, Mg, Si, Ti, Mn, Fe, Co, Zn, Ga, Ge, As, Cu and Pb.³⁻⁶ Extensive publications exist on the conversion of organic compounds over different forms of $\text{AlPO}_4\text{-5}$ catalysts, with only three reports^{7,8,9} containing information on the catalysis of hydrogen isotope exchange over $\text{AlPO}_4\text{-5}$. These latter publications describe the use of both tritium gas and tritiated water as isotope source for exchange into various organic compounds but exchange with tritium gas was reported to be relatively inefficient. The regioselectivity of the exchange patterns in both aromatic and aliphatic compounds was studied.⁸

Silica based zeolites are also known to activate hydrogen gas,¹⁰ but the activation is slow at all but very high temperatures (250 - 300°C), and so the use of zeolites as a tritium labelling procedure is limited. It has been demonstrated¹¹ that the proximity of a noble metal in zeolites accelerates hydrogen activation at room temperature to a rate only observed over H-zeolites at the

much higher temperature of 300°C, and it has been proposed that the activated hydrogen migrates from a metal site to the zeolite surface *via* a spillover mechanism. Furthermore, the use of noble metal substituted zeolites as catalysts for activating tritium gas for isotope labelling purposes has been described.^{12,13} The awareness of this apparent spillover effect of hydrogen on metal-zeolites, provided the motivation to conduct the present study of tritium gas exchange over AlPO₄-5 in which Pt had been incorporated. The purpose of this study was to assess the extent to which the highly stable, microporous, Pt-AlPO₄-5 catalysts might be used for labelling purposes, using model organic compounds, and to establish the regioselectivity of exchange of different classes of compounds over these bifunctional catalysts. In particular, the intention was to determine whether the regioselectivity was characteristic of the platinum metal component of the bifunctional catalyst or of the AlPO₄-5 support itself.

Platinum was chosen as the metal to be introduced into the AlPO₄-5 catalyst because of its wide application in hydrogen activation. The use of platinum in various chemical forms as an isotope exchange catalyst has been widely investigated using a variety of substrates and isotope sources.¹⁴ Various methods have been used in the preparation of active Pt metal catalyst. For gaseous tritium exchange the self-activation technique and the sodium borohydride reduction methods are well established.¹⁵⁻¹⁸ For the self-activation method Pt was reported to be the most active metal when compared to Pd, Rh, Ru, Ir, Re and Ni.¹⁹ Similarly, platinum substituted zeolites, *viz.* Pt-Y, Pt-Mordenite and Pt-ZSM-5 have been reported¹² to be the most active of metal substituted zeolites in tritium exchange.

EXPERIMENTAL

Platinum-loaded microporous aluminophosphate catalysts (designated Pt-AlPO₄-5) were synthesised by the procedure described by Wilson *et al.*¹ for synthesis of AlPO₄-5. Platinum as PtO₂ (1.0 mole% relative to Al₂O₃) was introduced into the synthesis gel prior to hydrothermal crystallization at 200°C.⁶ Crystallised material was dried in air at 100°C and calcined at 700°C. The powder XRD pattern of the calcined Pt-AlPO₄-5 was similar to the established pattern²⁰ of AlPO₄-5 (*i.e.* AFI phase). Solid-state MAS nmr spectroscopy and pore volume measurements provided supporting evidence that AlPO₄-5 phase was the major component present in the crystalline material.

Exchange reactions were carried out using the procedure described in detail elsewhere.⁷ The catalyst (normally 75 mg) was placed in a glass reaction vessel with side-arm, evacuated to

0.13 Pa and the required amount of T₂ gas added by means of a Toepler pump. The vessel was flame sealed, and the previously degassed organic substrate was admitted by the rupture of a breakseal attached to the side-arm. The vessel was then heated in an oven for the required time.

Tritiated products were analysed with a gas-liquid chromatograph fitted with an ion chamber/electrometer for radioactivity detection. Proton-decoupled ³H nmr spectra of the tritiated products were obtained on a Bruker CXP 300 Fourier transform nmr spectrometer using ghost referencing to TMS.²¹

RESULTS AND DISCUSSION

A summary of the activity of a variety of compounds which were allowed to undergo exchange with tritium gas over Pt-AlPO₄-5 catalyst is presented in Table 1. The results show that a wide range of simple compounds can be labelled substantially, some requiring a higher temperature than others. The degree of incorporation of tritium into many of the substrates was much higher than that previously observed in tritium gas exchange with pure AlPO₄-5.⁹ Some compounds, such as pyridine and alkanes, which were extremely difficult to label over pure AlPO₄-5,⁸ were labelled with this present catalyst system. A likely reason for the enhancement of the labelling is that the incorporation of Pt into AlPO₄-5 catalyst substantially increased the activation of the tritium gas.

The radiochemical purities of the products were frequently very high with undetectable amounts of impurities. Exceptions to this were some branched chain alkylbenzenes, o-xylene and alkanes where some labelled isomerisation products were observed. The halobenzenes yielded some benzene from dehalogenation. In the case of the branched alkanes, isomerisation products constituted the major labelled species.

The orientation of tritium in the molecules, as derived from ³H nmr analysis, is shown in Figure 1. For most compounds, this exchange over Pt-AlPO₄-5 shows patterns dominantly characteristic of published data for exchange over AlPO₄-5 itself,^{7,8,9} rather than that over platinum.¹⁸ Thus aromatic positions were readily exchanged in compounds that would normally be expected to undergo exchange by electrophilic aromatic substitution, as was observed over AlPO₄-5. Compounds containing deactivating groups attached to the aromatic ring were deactivated towards exchange. Furthermore, the marked dominance of exchange at the single *para* position in toluene and bromobenzene is a phenomenon observed in AlPO₄-5 catalysis and not Pt catalysis. This unique characteristic of AlPO₄-5 appears to have been maintained although Pt was

included in the catalyst structure and although the Pt appears to have activated the exchange with tritium gas.

Table 1. Exchange of organic compounds with tritium gas catalysed by Pt-AlPO₄-5.

Compound (mCi/mL)	Activity (%)	Incorporation (mCi/mL)	Impurities (mCi/mL)
Toluene	1110	92.9	n.d.
Ethylbenzene	413	34.7	n.d.
n-Propylbenzene	426	35.8	n.d.
i-Propylbenzene	997	83.8	13
n-Butylbenzene	115	9.6	8
i-Butylbenzene	48	4.0	69
s-Butylbenzene	761	64.0	n.d.
t-Butylbenzene	644	54.1	16
Naphthalene	713	59.9	n.d.
o-Xylene	405	34.0	19
m-Xylene	1030	86.3	n.d.
p-Xylene	1160	97.8	n.d.
Hemimellitene	787	66.2	n.d.
Pseudocumene	781	65.6	n.d.
Mesitylene	870	73.1	n.d.
Durene	502	42.2	n.d.
m-Diethylbenzene	342	28.7	n.d.
Fluorobenzene ^{150°C}	809	68.0	19
Chlorobenzene ^{150°C}	831	69.8	27
Bromobenzene ^{150°C}	679	57.0	89
Furan	878	73.8	n.d.
Pyrrole	333	28.0	n.d.
Thiophene	215	18.1	n.d.
Anisole	767	64.5	n.d.
Pyridine ^{180°C}	1190	99.7	n.d.
n-Hexane ^{180°C}	552	46.4	91
2,3-Dimethylbutane	25	2.1	169
Methylcyclohexane	39	3.3	181

Reaction conditions: 0.3g substrate, 357mCi T₂, 75mg catalyst, temperature: 100°C, times: 72 hours. n.d. = not detected

The only evidence of Pt-catalysis character in the exchange of the alkylbenzenes was significant labelling in the alkyl groups of ethylbenzene, *normal*-propylbenzene, and *normal*-, *iso*-

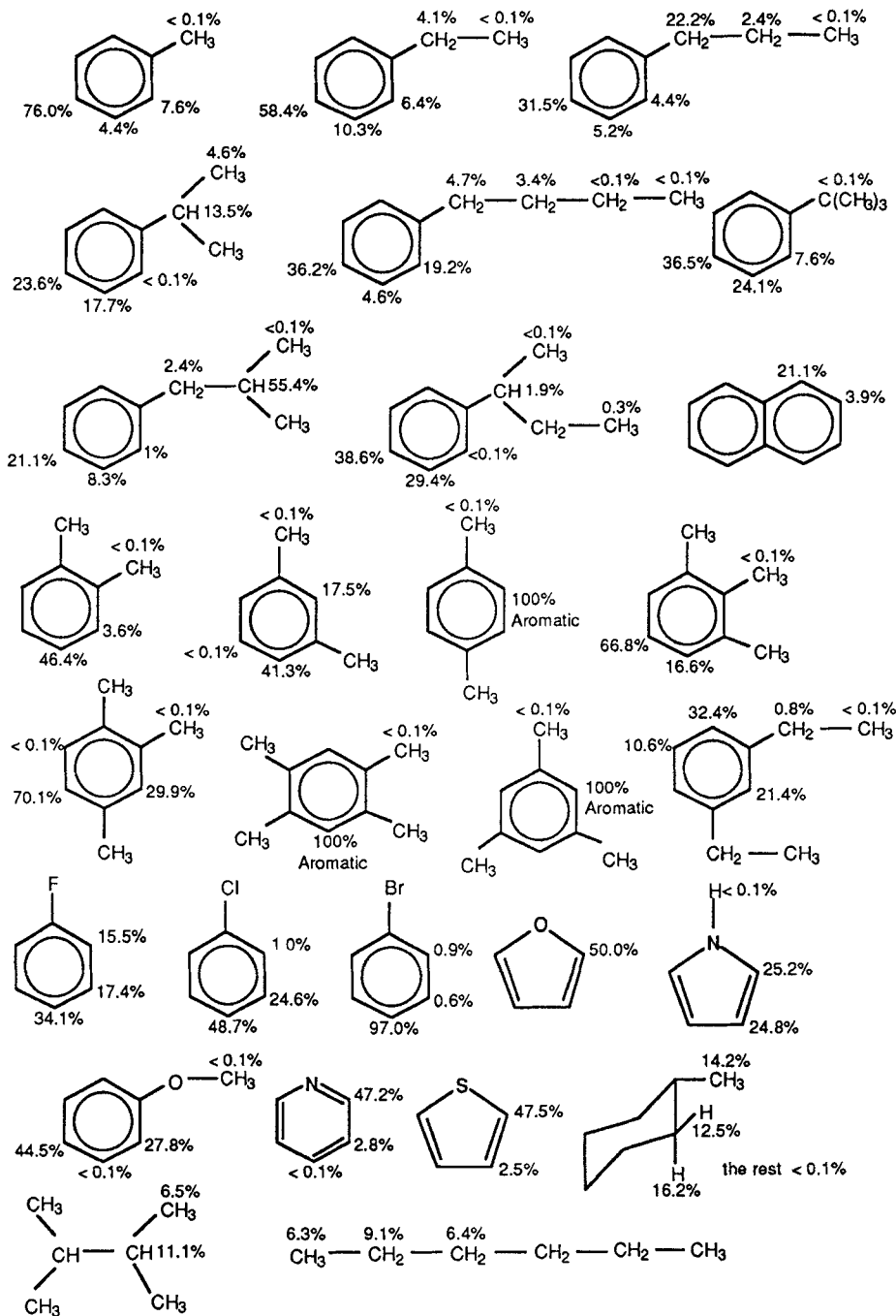


Figure 1. Distribution of tritium (per H atom) in compounds labelled by exchange with T₂ gas.

and *sec*-butylbenzene. One distinctive feature in the non-branched chain alkyl group tritiation was that the methylene groups closer to the aromatic ring obtained higher tritium than other methylene or methyl groups. This type of tritium orientation in alkyl groups is a characteristic feature of Pt metal catalysed exchange reactions as previously reported for exchange systems using pre-reduced bulk Pt catalyst.^{13,18} The same preference of exchange for hydrogen on carbon atoms of alkyl groups has also been observed over Pt-zeolites, viz. Pt-Y, Pt-Mordenite and Pt-ZSM-5.²²

For branched-alkyl exchange the incorporation of tritium in methine groups was found to be higher than in methylene or methyl groups. This exchange pattern of branched-alkyl groups (*e.g.* *iso*-propylbenzene) is similar to that normally obtained with pre-reduced bulk Pt catalyst,^{13,18} but it is in marked contrast to that found in exchange over $\text{AlPO}_4\text{-5}$,⁹ and Pt-Y²² catalysts where tritium was incorporated in the methyl group only.

In contrast to the mono-alkylbenzenes, the orientation of tritium in all poly-alkylbenzenes indicates predominant exchange in the aromatic rings, and no significant alkyl tritium. Within the aromatic positions, the distribution in poly-alkylbenzenes (with the exception of pseudocumene) was similar to that reported^{7,8} over $\text{AlPO}_4\text{-5}$ (*i.e.* positions *meta* to a substituent were deactivated, those *ortho* or *para* were activated). The positions *para* to one or two methyl groups had a noticeably higher incorporation, a result also in keeping with the *para* selective property of $\text{AlPO}_4\text{-5}$.⁷

The halobenzenes also showed high *para* orientation in their exchange, but this *para* dominance, previously noted⁸ over $\text{AlPO}_4\text{-5}$ was not as pronounced in fluorobenzene and chlorobenzene.

The pattern of naphthalene exchange with Pt- $\text{AlPO}_4\text{-5}$ as catalyst (>20% in a positions) is similar to that when $\text{AlPO}_4\text{-5}$ ⁷ was used.

The relative rates of exchange of methyl and methylene protons in *normal*-hexane followed the order previously reported²³ for exchange of alkanes with D_2 over Pt -film catalysts viz. $\text{CH}_2\text{CH}_2 > \text{CH}_3$. That same order for the relative rates of exchange in *normal*-hexane was observed with T_2 over Pt-Y and Pt-Mordenite catalysts.¹² However, the orientation observed in hexane exchange with T_2 over Pt-ZSM-5²² and heterogeneous Pt¹⁸ have been reported to be in contrast ($\text{CH}_3 > \text{CH}_2$) to the above results.

The tritium orientation in 2,3-dimethylbutane showed higher tritium in CH positions than in CH_3 positions, which is in agreement with that reported over $\text{AlPO}_4\text{-5}$,⁸ Pt-Mordenite and Pt-ZSM-5 catalysts.²²

It has been proposed⁹ that the catalytic sites for tritium gas exchange of organic compounds over $\text{AlPO}_4\text{-5}$ reside at crystal defects in its structure where the formation of -OH groups on the surface of the otherwise non acidic $\text{AlPO}_4\text{-5}$ may occur. A mechanism of isotope exchange between D_2 and the hydrogen from OH groups of metal loaded zeolites has also been reported elsewhere.²⁴ Since it appears that the orientations observed in the aromatic centres of organic compounds labelled with $\text{Pt-AlPO}_4\text{-5}$ in the present study are generally attributable to $\text{AlPO}_4\text{-5}$ catalysis, it is assumed that the exchange step in which the tritium is incorporated into the organic species occurs via an -OT species on the $\text{Pt-AlPO}_4\text{-5}$ catalyst surface. This mechanism is essentially an electrophilic substitution step, similar to that which is generally accepted for HNaY , *Mordenite* and *ZSM-5* exchange systems.^{12,13,25} However, the exchange step which leads to the formation of the -OT species is likely to have involved dissociation of the T_2 molecule on the Pt metal atoms with a spillover mechanism leading to the -OT formation on the microporous aluminophosphate surface.

It is assumed that relative exchange rates and distribution patterns within various molecules may also be influenced by molecular size constraints on the diffusion and orientation of species within the catalyst pores.

CONCLUSION

The results presented in this paper provide an example of the action of a bifunctional catalyst in the tritiation of organic substrates by exchange with T_2 gas. The Pt metal present within the $\text{AlPO}_4\text{-5}$ greatly enhances the activation of the T_2 , thereby increasing the specific activity attainable, but it has a relatively minor affect on the regiospecificity of aromatic exchange. Representatives of groups of compounds hitherto beyond the capabilities of $\text{AlPO}_4\text{-5}$ (such as the heterocycles and the alkanes) were labelled through the action of $\text{Pt-AlPO}_4\text{-5}$. Furthermore, the range of orientations possible from exchange of several compounds with $\text{AlPO}_4\text{-5}$ has been increased with the observation of exchange in alkyl chains of straight and branched-chain alkylbenzenes, and in some cases of *para* labelling in the benzene rings of substituted benzenoid compounds. These results illustrate that the applications of $\text{AlPO}_4\text{-5}$ as a labelling catalyst may be broadened by the introduction of platinum, so that it is possible to obtain labelling patterns not possible by the use of either pure unsubstituted $\text{AlPO}_4\text{-5}$ or platinum alone.

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