Asian Journal of Chemistry Vol. 10, No. 1 (1998), 109–116

Investigation of the Activity of $AlPO_4$ and $Al_2(HPO_4)_3$ as Support for Pt in the Hydrogenation of *o*-Xylene with Comparison to Pt/Al_2O_3

HASAN M. ASFOUR†, RIYADH. A. SAYMEH* and ISAM ARAFA‡
Department of Chemistry
Yarmouk University, Irbid, Jordan

The active forms of $AlPO_4$ and $Al_2(HPO_4)_3$ supported platinum have less activity than alumina supported platinum for the hydrogenation of *o*-xylene in the temperature range 30–250°C. This change is attributed to the strong metal support interaction. The activity of $Pt/Al_2(HPO_4)_3$ is exhibited after calcination at 530°C, while the activity of $Pt/AlPO_4$ is exhibited before calcination. The IR and thermal analysis of these two supports, before and after calcination at 530°C, show some changes in their crystal forms.

INTRODUCTION

The use of supported metal catalyst with metal-support interaction have different activity than when using inert supports as SiO_2 and Al_2O_3. TiO_2 and $AlPO_4$ supports are known to have interaction with metals such as Pt, Pd and Ir[1–8]. The difference of activity was ascribed to the electronic transfer from the metal to the acidic sites of the support. Also surface area of the support, pore size and pore size distribution have a role in the activity of the catalyst. $AlPO_4$ and $Al_2(HPO_4)_3$ enjoy a high surface area, because they are porous materials such as zeolite, and have high acidity compared to Al_2O_3[9–11]. Hence we used these materials as support since they are expected to exhibit a high activity in the hydrogenation of aromatic compounds such as *o*-xylene.

EXPERIMENTAL

Preparation of $AlPO_4$, $Al_2(HPO_4)_3$ Supports and Catalyst Preparation

The two supports $AlPO_4$ and $Al_2(HPO_4)_3$ were prepared by mixing solutions of $AlCl_3$ (high purity, Merck) and phosphoric acid 65% using the proper stoichiometric amounts. Ethylene oxide was used for jellification[5, 11]. The product was washed with ethanol, then dried at 120°C for 24 h. A portion of $AlPO_4$ was calcined by passing O_2 with flow rate of 30 mL/min at 530°C for 3 h, before preparing the catalyst. Also another portion of $Al_2(HPO_4)_3$ was calcined similarly.

---

†Dept. of Applied Chemistry, College of Science, Applied Science University, Amman, Jordan
‡Dept. of Applied Chemistry, Jordan University of Science and Technology, Irbid, Jordan.

Other catalysts were prepared by using uncalcined $AlPO_4$ and $Al_2(HPO_4)_3$. Al_2O_3 support was obtained from Merck (150 m^2/g).

All catalysts were prepared by the incipient wetness technique. Initially, the appropriate weight of $PtCl_4$ (Janssen Chimica, 99%) required to prepare a catalyst having a nominal weight loading of 1 w% Pt was dissolved in an amount of deionized water. The solution containing the Pt was added to the support in a dropwise manner to give a thick slurry. The resulting slurry was dried in air for 12 h at 120°C. Catalyst pretreatment schedules and chemisorption measurements were done as described earlier[12].

IR spectra for $AlPO_4$ and $Al_2(HPO_4)_3$ were done on FT-IR (PE-2000). Thermal analyses for these supports were done on STA 1500 + (rheometric scientfic) version V5.42.

Reaction

The hydrogenation reaction was performed in a continuous flow reactor at atmospheric pressure. The catalyst sample was put in the microreactor in a vertical furnace connected to temperature controller and a thermocouple to control the termperature of the reaction. The catalyst sample was treated *in-situ* before starting the reaction. Hydrogen (756.3 torr) saturated with vapour of *o*-xylene (Fluka, 99.9%) at 14°C and 3.7 torr was passed through the reactor. The total gas flow rate of H_2 and *o*-xylene was 15 mL/min. This rate was controlled by using Matheson flow controller (multiple flow controller model 8274).

The reaction products and the unreacted *o*-xylene were analysed by the gas chromatography with a column of 5% didecylphthalate plus 5% Beneton on chromosorb W-Hp, 80/100, SST, 4-meter.

Between runs, when changing reaction temperature, the catalyst was maintained under pure hydrogen flow for at least 15 min.

RESULTS AND DISCUSSION

From the GC-chromatogram it was found that the hydrogenation products of *o*-xylene over $Pt/AlPO_4$, $Pt/Al_2(HPO_4)_3$ and Pt/Al_2O_3 were *trans*- and *cis*-1,2-dimethylcyclohexane (1,2-DMCH). At 60°C, the activity of Pt/Al_2O_3 was greater than that over $Pt/AlPO_4$ and $Pt/Al_2(HPO_4)_3$ for the same metal loading and in cases of calcination and uncalcination. However, the conversion over the unclacined 3% $Pt/AlPO_4$ increased with temperature and reached 100% at 90°C. A decrease of metal loading caused a decrease of conversion, for all catalysts. At 60°C, while the conversion of *o*-xylene was zero over the uncalcined 1% $Pt/Al_2(HPO_4)_3$, the conversions of *o*-xylene were 28% and 2% over 1% Pt/Al_2O_3 and over the uncalcined 1% $Pt/AlPO_4$ respectivley, Fig. 1, 2 and Table-1. Initially, at a relatively low temperature, *cis*-1, 2-DMCH was the major product over the catalysts. This high conversion to *cis*-isomer at low temperature is expected since it is the kinetically favoured product[12, 13].

In contrast, for a work done by others[5, 11] on the hydrogenation of olefins, in the liquid phase, using $AlPO_4$ as support, the conversion of olefins was recorded to be greater than that over Ni/Al_2O_3. This is because $AlPO_4$, as a metal support,

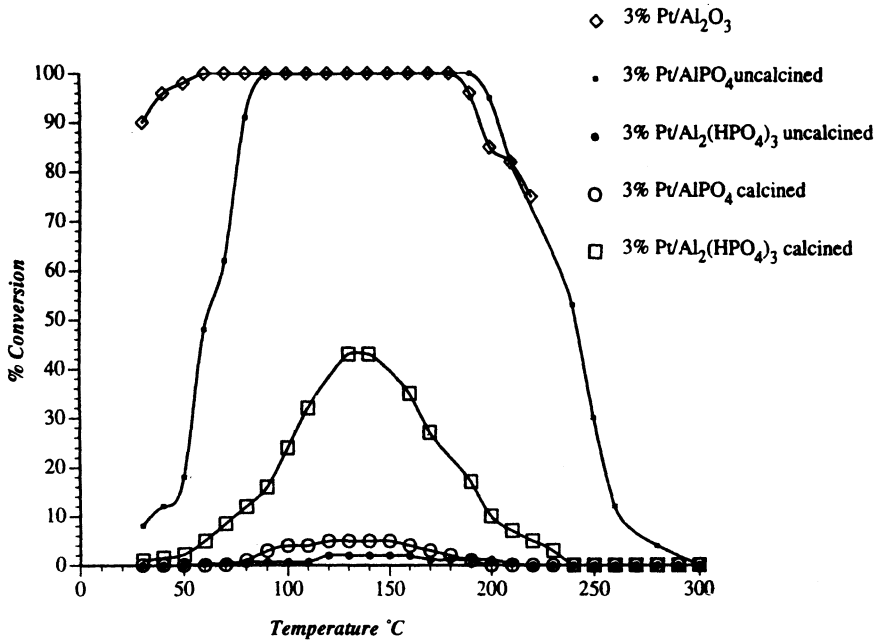


Fig. 1. Comparison between Pt/Al_2O_3, $Pt/AlPO_4$ and $Pt/Al_2(HPO_4)_3$ catalysts in case of calcined and uncalcined supports for the 3w% metal loading in the increasing temperature regime.

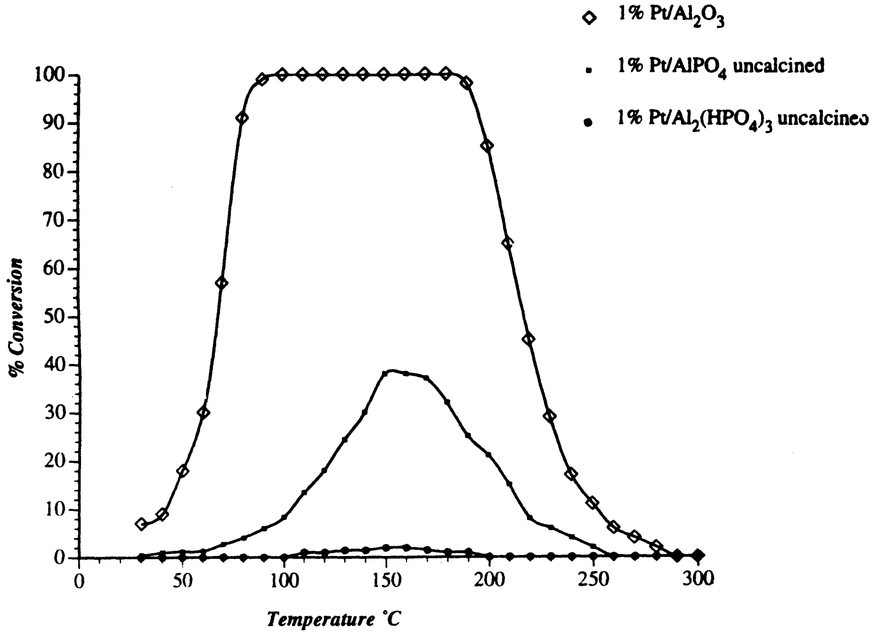


Fig. 2. Comparison between Pt/Al_2O_3, $Pt/AlPO_4$ and $Pt/Al_2(HPO_4)_3$ catalysts in case of calcined and uncalcined supports for the 1w% metal loading in the increasing temperature regime.

has higher surface area and of higher acidity (the condition for high activity) than Al_2O_3; yet in our study this behaviour is not exhibited.

The low activity, in case of $AlPO_4$, as a support for Pt, which was shown in our study, could be attributed to the low dispersion of Pt which is due to the effect of the strong metal-support interaction (Table-1). This effect is known to cause a decrease in metal dispersion in the case of $AlPO_4^2$.

When investigating the catalytic activity of the two forms of the supports, $Al_2(HPO_4)_3$ and $AlPO_4$ before and after calcination at 530°C, it was found that $AlPO_4$ was the active form before calcination, but when calcined its activity severely dropped. For example, at the reaction temperature of 150°C, the activity of the 3% metal loading of $Pt/AlPO_4$, the activity dropped from 100% to 4% when it was calcined. $Al_2(HPO_4)_3$ does not show any activity before calcination while after calcination at 530°C, the activity for the 3% metal loading of $Pt/Al_2(HPO_4)_3$ catalyst was 45% (Table-1).

TABLE-1
VARIATION OF ACTIVITY* WITH TEMPERATURE FOR THE DIFFERENT CATALYSTS

Catalyst	% Dispersion†	Reaction Temperature (°C)	% Conversion of *o*-xylene
3% Pt/Al_2O_3	43	60	100
		150	100
3% $Pt/AlPO_4$ uncalcined support	21	60	48
		150	100
3% $Pt/Al_2(HPO_4)_3$ uncalcined support	9	60	0.0
		150	~1
3% $Pt/AlPO_4$ calcined support	13	60	0.0
		150	~4
3% $Pt/Al_2(HPO_4)_3$ calcined support	16	60	~5.0
		150	42
1% Pt/Al_2O_3	36	60	~30
		150	100
1% $Pt/AlPO_4$ uncalcined support	11	60	~2.0
		150	38
1% $Pt/Al_2(HPO_4)_3$ uncalcined support	5	60	0.0
		150	~1

*Activity: measured as % conversion of *o*-xylene.
†Dispersion:
—measured by H_2 chemisorption at 25°C.
—All catalysts were reduced with H_2 at 400°C, and cooled with He to 25°C.
—All dispersions were measured before the hydrogenation reaction.

The IR study of $Al_2(HPO_4)_3$ showed a change of the frequency of the absorption bands before and after calcination. There were bands at 1650 cm^{-1} and 1130 cm^{-1} before calcination, but after calcination the band at 1650 cm^{-1}, which is characteristic of ν(H—O—H) of water of crystallization disappeared.

The band at 1130 cm^{-1} which is characteristic of ν(OH—P=O) disappeared and new two bands appeared at 1290 cm^{-1}, which is characteristic of ν(—O—P=O), and the other band appeared at 1120 cm^{-1}, which is characteristic of ν(P=O), in the crystals of the calcined form of the compound[14] (Fig 3).

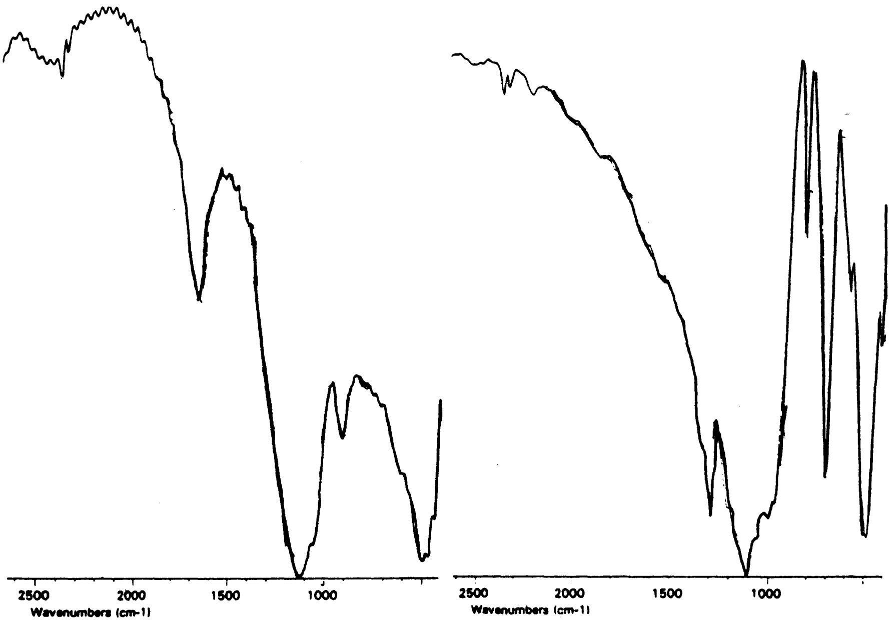
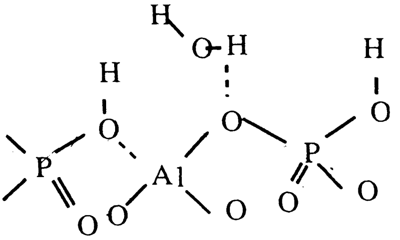


Fig. 3. I.R. spectra for uncalcined and calcined $Al_2(HPO_4)_3$.

The graph of the thermal analysis of $Al_2(HPO_4)_3$ showed a sharp change in the heat flow (loss in weight) at 240°C, denoting a loss of water of crystallization and confirming the disappearance of the band at 1650 cm^{-1} and the change in the frequency of the band (OH—P=O) at 1130 cm^{-1} (Fig. 4). The appearance of the band at 1290 cm^{-1} which is characteristic of the bond (—O—P=O) indicates the formation of the bonding (Al—O—P=O) instead of $(\mathrm{A}\ldots\overset{\overset{\mathrm{H}}{|}}{\mathrm{O}}\text{—}\mathrm{P{=}O})$ bond.

By analogy to the hydrogen form zeolite structure[15-17], the structure of $Al_2(HPO_4)_3$ before calcination could be:



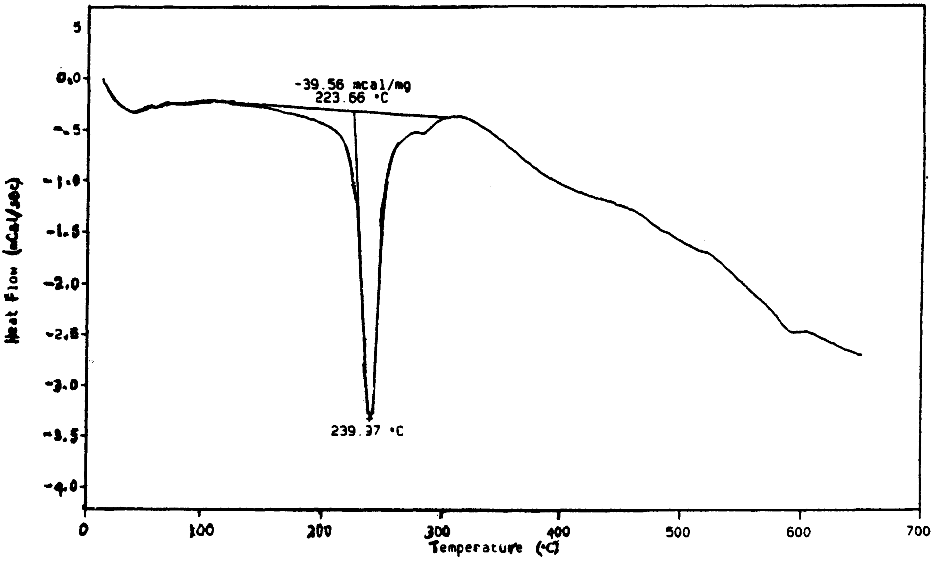
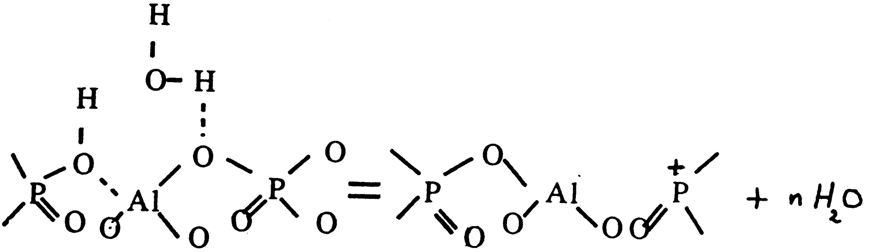


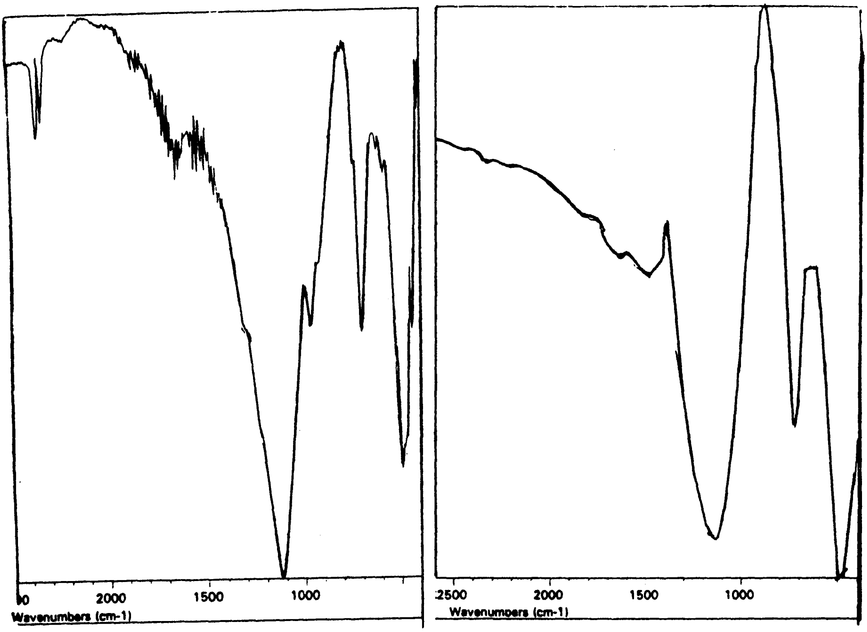
Fig. 4. Graph of thermal analysis for $Al_2(HPO_4)_3$.

Hence, the Al—O—P═O bonding which is formed as a result of calcination process can be considered as the Lewis acid site.



This result agrees with a previous work that the Lewis form of acidity is the effective form in the hydrogenation[11]. In this work the relatively low activity observed over $AlPO_4$ compared to Al_2O_3 can be explained by the strong metal support ineraction.

Concerning the IR study of $AlPO_4$, the absorption spectra at 1140 cm^{-1} of ν(P═O) before and after calcination had no change, denoting no change in the crystal form (Figure 5). This agrees with the thermal analysis having no loss in weight except that at 100°C which is due to hygroscopic water (Figure 6). The loss of activity in $AlPO_4$ after calcination could be attributed to the decrease of surface area due to the compacting of crystals on heating.



a. Calcined $AlPO_4$ b. Uncalined $AlPO_4$

Fig. 5. IR spectra for uncalcined and calcined $AlPO_4$.

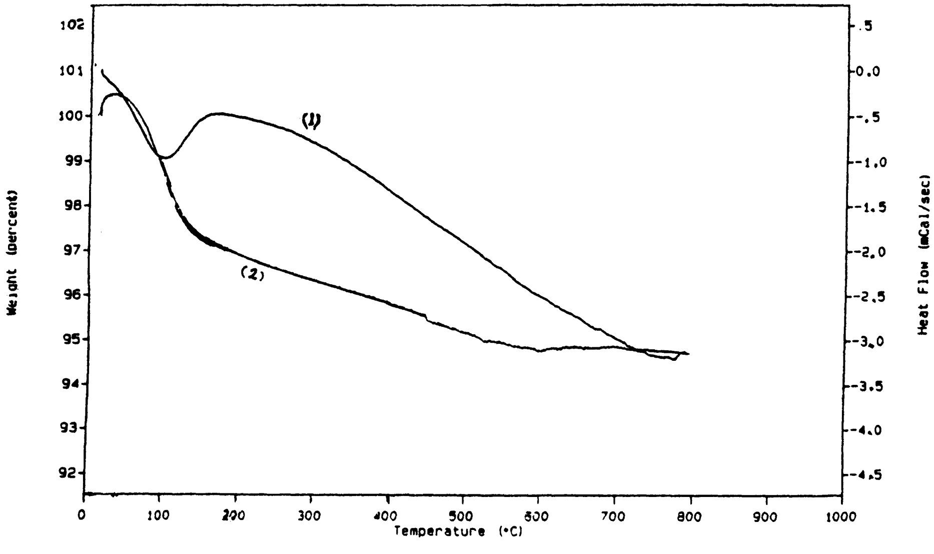


Fig. 6. Graph of thermal analysis for $AlPO_4$:
1. change of heat flow; 2. mass change.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the support by the deanship of Scientific Research and Graduate Studies at Yarmouk University under the project No. (14/97). Thanks are also due to the Applied Science University (A.S.U.) for the use of the chemistry lab. instruments in the Applied Chemistry Department.

REFERENCES

1. M. Vannice and R. Carten, *J. Catal.*, **56**, 236 (1979).
2. G. Marcelin and R. Vogel, *J. Catal.*, **82**, 482 (1983).
3. S. Tauster, S. Fung and R. Garten, *J. Am. Chem. Soc.*, **100**, 170 (1978).
4. S. Tauster, S. Fung, R. Baker and J. Horsley, *Science*, **211**, 1121 (1981).
5. J. Cabello, J. Campelo, A. Garcia, D. Luna and J. Marinas, *J. Catal.*, **94**, 1 (1985).
6. ________, *J. Chem. Soc., Faraday Trans.*, 1, **80**, 659 (1984).
7. ________, *Applied Catal.*, **3**, 315 (1982).
8. J. Campelo, A. Garcia, J. Gutierrez, J. Luna and J. Marinas, *App. Catal.*, **7**, 307 (1983).
9. G. Marcelin, R. Vogel and H. Swift, *J. Catal.*, 83, 42 (1983).
10. J. Campelo, A Garcia, D. Luna and *J. Marinas, Appl. Catal.*, **10**, 1 (1984).
11. L. Cerveny, Catalytic Hydrogenations, Elsevier, Amsterdam-New York-Tokyo, p. 425 (1986).
12. R. Saymeh, H. Asfour and W. Abu-Tuaimeh, *Asian J. Chem.*, **9**, 353 (1997).
13. M. Viniegra, G. Cordoba and R. Gomez, *J. Molec. Catal.*, **58**, 107 (1990).
14. R. Silverstein, G. Bassler and T. Morril, Spectroscopic Identification of Organic Compounds, 3rd ed., John Wiley, New York-London, pp., 151 (1974).
15. B.C. Gates, Catalytic Chemistry, John Wiley, New York, p. 271 (1992).
16. M.E. Davis, C. Montes, P.E. Hathaway, J.P. Arhancet, D.L. Hasha and J.M. Graces, *J, Am. Chem. Soc.*, **111**, 3919 (1989).

(*Received*: 23 June 1997; *Accepted*: 16 September 1997) AJC-1343