

# HYDRODENTROGENATION WITH NiMo SUPPORTED ON Al<sub>2</sub>O<sub>3</sub>-AlPO<sub>4</sub>

R. Menon, H.S. Joo, J.A. Guin, Department of Chemical Engineering  
Auburn University, Auburn, Alabama, 36849

P. J. Reucroft and J.Y. Kim, Department of Chemical and Materials Engineering  
University of Kentucky, Lexington, Kentucky, 40506

Aluminum phosphate - metal oxides can be used as nonconventional supports for NiMo hydrotreating catalysts. Several Al<sub>2</sub>O<sub>3</sub>-AlPO<sub>4</sub> (AAP) supports were prepared by coprecipitation. Effect of variations in Al/P atomic ratios, precipitation method, final pH, and washing agent on various support properties were examined. Catalysts containing 3 wt% Ni and 13 wt% Mo were prepared by incipient wetness and characterized by several methods. Hydrodenitrogenation (HDN) activities of the catalysts were examined in model compound and coal liquid reactions.

Keywords : catalyst support, aluminum phosphate, solid acid catalyst, HDN

## INTRODUCTION

New and more stringent environmental regulations are expected to have a major impact on the refining industry. To achieve future government specifications for fuels, significant changes will likely be required in refinery operations to produce products with good combustion characteristics and reduced emissions. Emphasis in this research is on the development of new and improved catalysts for upgrading coal-liquids and coal/waste liquefaction liquids (CWL) to clean transportation fuels. Because coal liquids contain significant quantities of heteroatoms, (S, O, and N) and have higher aromaticity than their petroleum based counterparts, hydroprocessing operations will form the nucleus of technology for their upgrading.

One of the latest studies in catalysis (Catalytica, 1994) suggests solid acids (metal oxides, heteropoly acids, metal sulphates, *metal phosphates* etc) as important industrial catalysts. The incentive for developing new solid acid and base catalysts to replace hazardous or corrosive liquid ones is again environmental considerations (Tanabe., 1994; Catalytica, 1994). The use of phosphorous as a promoter element for Co-Mo and Ni-Mo/ Al<sub>2</sub>O<sub>3</sub> catalysts has received significant attention in coal-liquids upgrading (Tischer et al., 1987), with varying degrees of success; however, actual metal phosphate supports have received little attention as upgrading catalyst supports. There is considerable evidence of their utility as a possible catalyst support material in light of their high stable surface area, pore geometry, surface acidity properties and surface chemistry (Marcelin et al., 1983; Moffat, J.B., 1978; Rebenstorf et al., 1991). Chen et al (1990) studied hydrodesulfurization reactions of residual oils over CoMo/Alumina-Aluminum phosphate catalysts. They reported that larger surface area, smaller acid amount and weaker interaction of AAP supports made the metal more highly dispersed, produced more active sites and resulted in high initial HDS activity. In this study we explored the performance of metal phosphates of aluminum, zirconium and titanium as potential new supports for HDN upgrading catalysts. Preparation of cogels of AlPO<sub>4</sub> and Al<sub>2</sub>O<sub>3</sub> by coprecipitation of an aluminum salt and H<sub>3</sub>PO<sub>4</sub> has been discussed in the literature ( Kearby, K., 1961; Mitchell et al., 1987; Vogel et al., 1982; Campelo et al., 1986 ).

## EXPERIMENTAL SECTION

### PREPARATION OF ALUMINA-ALUMINUM PHOSPHATES (AAP)

The experimental procedures used here in were based on earlier works ( Chen et al., 1990; Cheung et al., 1986; Marcelin et al., 1983). Various factors taken into consideration were an appropriate aluminum compound, precipitating agent, gelation conditions, washing agent, drying and calcination temperatures. Three methods were examined.

**METHOD A:** Supports were prepared by a coprecipitation method. Phosphoric acid solution (H<sub>3</sub>PO<sub>4</sub>, 85 wt%) was added to an aqueous solution of aluminum nitrate nona hydrate Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, slowly in an amount to give the desired Al/P ratio. After the addition, the acidic solution was well stirred for at least 10 minutes. A basic solution was prepared by mixing ammonium hydroxide(NH<sub>4</sub>OH, 28-30%) and distilled water with a volume ratio 1:1. Both the acidic and basic solutions were added slowly to a third well stirred vessel containing 1L of distilled water. The pH value in the third vessel was maintained at 8.0 throughout the precipitation process by adding small amounts of the acidic and basic solutions. This process was continued until the acidic solution was consumed. The resulting precipitates were centrifuged, washed three times with distilled water, dried overnight at 393K in a vacuum oven, and calcined in a muffle furnace for 12h at 773K. Varying the Al/P ratio allowed various AAP composites to be obtained. Each support is designated based on the Al/P mole ratio.

**METHOD B:** Certain modifications were made in Method A. [1] Coprecipitation was done at 273K; not at room temperature, [2] A ripening period of 12h was allowed at room temperature, [3] The washing agent was chosen as isopropanol and [4] pH =5.0 instead of 8.0 during precipitation.

H<sub>3</sub>PO<sub>4</sub> (85wt%) was added to a solution of Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O. The acidic solution was well-stirred and cooled to 0°C. A basic solution was prepared by mixing ammonium hydroxide and distilled water with a volume ratio 1:1. Both the acidic and basic solutions were added slowly to a third vessel of distilled water at 0°C. After standing overnight, the gel was thoroughly extracted with isopropanol three times, allowed to stand at room temperature overnight to evaporate residual isopropanol, dried at 106-110°C for 12h in a vacuum oven, and calcined at 500°C for 12h in a muffle furnace. Two sets of experiments were done to study the effects of pH on the textural properties of AAPs. The first set of experiments was done with varying Al/P ratio and keeping the pH constant at 5.0 during precipitation. In a second set of experiments, Al/P ratio was kept constant at 1.0 and constant values of pH 5.0, 6.0, 7.0, 8.8 and 9.2 were used during precipitation. Heat treatment was same as above.

**METHOD C:** The precipitation methods were modified. Solutions of Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and H<sub>3</sub>PO<sub>4</sub> were stirred together to form an acidic solution to which ammonium hydroxide solution (13%) was added rapidly. Precipitation occurred rapidly at 0°C. During precipitation pH was not held constant. As ammonia was added to the acidic solution, the pH rose from less than 1.0 to neutrality, and precipitation occurred during a 1-2 min interval. A ripening period of 12h was allowed. The gel was centrifuged and washed with isopropanol three times, followed by drying in the vacuum oven for 12h at 108°C and calcination in the muffle furnace at 649°C for 3h. The samples prepared were AAP1, AAP2, AAP3.5, AAP4, AAP5, AAP6 and AAP8. An Al<sub>2</sub>O<sub>3</sub> support also was prepared for comparison purposes.

#### PREPARATION OF NiMo/AAP CATALYSTS

Supports AAP1, AAP2, AAP4, AAP5, AAP8, and Al<sub>2</sub>O<sub>3</sub> prepared in the lab using Method C were chosen for final catalyst preparation. All were made by Method C. Three commercial materials were also used: Shell 424 NiMo/Al<sub>2</sub>O<sub>3</sub> as catalyst and AlPO<sub>4</sub>-G (Grace Davison), and Al<sub>2</sub>O<sub>3</sub>-H (Harshaw) as supports. The metal compounds chosen were ammonium molybdate tetrahydrate (NH<sub>4</sub>)<sub>2</sub>MoO<sub>24</sub>·4H<sub>2</sub>O and nickel nitrate hexahydrate, Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O. The compounds were dissolved in an exact amount of water to fill the pore volume of the support. The supports were impregnated with ammonium molybdate first, dried for 16h at 120°C in a vacuum oven, and calcined at 500°C for 5h in a muffle furnace. Then, they were impregnated with nickel nitrate solution, dried for 16h at 120°C and calcined again for 5h at 500°C.

#### CHARACTERIZATION OF CATALYSTS

**Surface area and pore volume measurements:** Surface area was determined by nitrogen adsorption (BET Method) using a Quantasorb adsorption unit manufactured by Quantachrome Corp. The samples were degassed for 4.5h at 350°C prior to the measurements. The pore volumes were measured by using water as a pore filling medium.

**XPS Studies:** X-Ray photoelectron spectroscopy was used for the surface (in the top 2-5 nm of the solid) elemental analysis of the catalysts.

**X-ray Diffraction studies:** Catalysts were characterized by X-ray diffraction to investigate their crystallographic properties. A powder diffractometer was used, at 40 kV and 40 mA with Cu K $\alpha$  radiation.

**ICAP:** Bulk metal analysis was done by a Jarrell Ash ICAP (Inductively Coupled Argon Plasma) 9000. The values are given in Table 1.

**MEASUREMENT OF HDN ACTIVITY:** All reactions were performed in 20cc 316 ss tubing bomb microreactors (TBMR) which were agitated in a fluidized sand bath and replicated at least twice. A reactant solution (5g) containing 2 wt% pyridine in hexadecane was used for model compound studies and coal liquid (3g) for upgrading. Experiments were charged with 1000 psig cold hydrogen pressure and performed at 350°C for 20 min using 0.1 g catalyst for model compound reactions and at 375°C for 1 hr using 0.4 g catalyst for upgrading coal liquid. Catalyst was sulfided *in situ* with dimethyl disulfide.

#### RESULTS AND DISCUSSION

**Elemental Analysis:** Bulk metal concentrations calculated, based on the amount of reagents used and the amount of the support formed (experimental) and actual analysis by ICAP is shown in Table 1. A comparison between the experimental and theoretical (based on weight of support expected) weights of the supports (Method C) are given in Table 3.

**XPS Studies:** The Al/P ratios were similar for both bulk and surface with a slight depletion of Al or enrichment of P on the surface compared to the bulk (Table 1). AAP4, AAP8 and Al<sub>2</sub>O<sub>3</sub>-H

showed lower Mo/Ni values on the surface compared to the bulk.

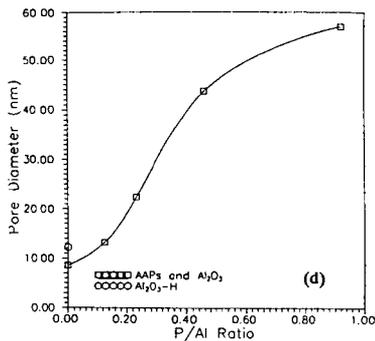
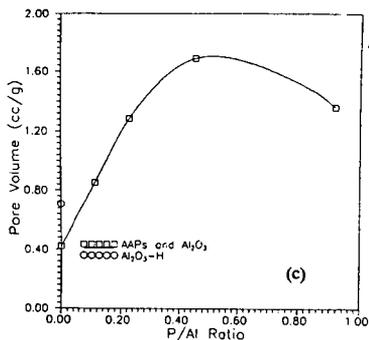
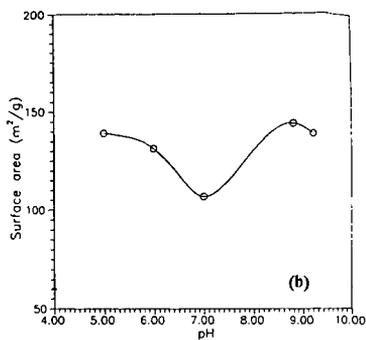
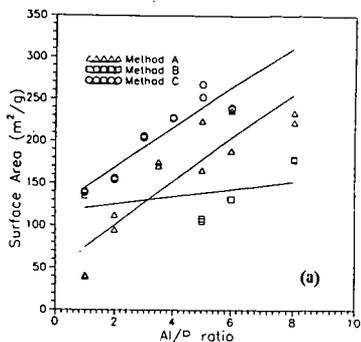
**Surface areas and pore volumes:** In METHOD A, the surface area of AAPs increased as the A/P ratio varied from 1.0 to 8.0 (Fig. 1a). The area of AAP1 was only 41 m<sup>2</sup>/g. The modifications done to Method A, in Method B, provided an AAP1 with much higher surface area (141 m<sup>2</sup>/g). However, the AAPs showed a different trend and the highest area did not exceed 200 m<sup>2</sup>/g. In Method C, the AAPs exhibited higher surface areas, the maximum being at 267 m<sup>2</sup>/g (AAP5). With increasing pH surface areas of AAPs declined (METHOD B), but above pH= 8 it showed a tendency to increase (Fig 1b). The pore volume and pore diameter (Method C) increased with increasing P/Al ratio (Fig 1c & Fig 1d). After impregnation with Mo and Ni, the catalyst surface areas (Fig 2) were reduced considerably (Table 2), possibly due to the plugging of small pores. By studying the effect of gelation condition, precipitating agent, washing agent etc, on the textural properties of AAPs, a systematic method of preparation for these catalysts can be recommended. Rapid precipitation at 273K, a ripening period before centrifuging the gel, choice of isopropanol as washing agent and an optimum calcination temperature can provide catalysts with desired pore size for hydrotreating reactions.

**X-Ray Diffraction Patterns:** For NiMo/AAP1 the position of the main peaks (at  $2\theta = 27.3$  and  $26.6$ ) suggested the presence of MoO<sub>3</sub> and Al(PO<sub>3</sub>)<sub>3</sub> phases. This also agrees partially with those of aluminophosphates with P/Al = 1.0 (Cheung et al., 1986) and with CoMo/AAP1 (Chen et al., 1990). For NiMo/AAP2, the peaks at  $2\theta = 23$  and  $26.4$  were in partial agreement as those of MoO<sub>3</sub> and AlPO<sub>4</sub>. No characteristic peaks of Al<sub>2</sub>O<sub>3</sub> was observed. This may be due to the formation of a mixture of crystalline bulk oxide and surface compounds and can be attributed to the metal oxide-support interaction. Reducing the phosphorous content (NiMo/AAP4 and NiMo/AAP8) demonstrated an amorphous (X-Ray indifferent) pattern, giving no hint of alumina, NiO or MoO<sub>3</sub>. The broad XRD pattern of NiMo/Al<sub>2</sub>O<sub>3</sub> (Method C) indicated a low order of crystallinity. Al<sub>2</sub>O<sub>3</sub>-H showed a more crystalline pattern than the above, but after impregnation with Ni and Mo, the catalyst gave an amorphous pattern. The AlPO<sub>4</sub>-G sample gave a broad peak around  $2\theta = 28$  which is characteristic of the tetrahedral structure in amorphous AlPO<sub>4</sub>. The main peaks ( $2\theta = 23, 27.0$ ) for NiMo impregnated AlPO<sub>4</sub>-G indicated the presence of an MoO<sub>3</sub> phase.

**HDN Activity:** Pyridine HDN occurs through a sequential pathway as shown in Fig. 3 in which pyridine is saturated to form piperidine followed by the formation of pentylamine through piperidine hydrogenolysis. Subsequent nitrogen removal from pentylamine results in pentane and ammonia as final products. Pentylpiperidine is formed in a side reaction from the alkyl-transfer reaction of piperidine and pentylamine. Di-n-pentylamine was also found to a minor extent in our experiments. In this experiment, a loss of N can be caused by the adsorption of N-containing compounds (pyridine, piperidine, pentylamine, and pentylpiperidine) on catalyst and the wall of reactor and evaporation (Joo et al., 1995). Because of these losses, in this paper, all values of pyridine HDN are considered as semi quantitative. Pyridine and coal liquid HDN activities of a series of catalysts which have different A/P atomic ratio and the same Ni/Mo content are in Fig. 4a. HDN activity generally increased with the increase of A/P ratio (or surface area of catalyst). As shown in Fig. 4b, generally HDN activity is linearly correlated with surface area of catalyst. The surface area is directly related to pore size. When the size of reactants are small enough in comparison with pore size, *hindered* internal diffusion is not the rate determining step. In this type of reactions, higher surface area of catalyst can give higher catalytic activity due to higher metal dispersion (Ni and Mo). However, *hindered* diffusion may take place with very heavy feeds. It has been reported that an optimum pore diameter for hydrodemetalization (HDM) of heavy oil exists around 20 nm (Smith et al., 1994). AAP catalyst having an optimum pore size obtained by manipulating A/P ratio and other preparation conditions can be effective in this type of reaction.

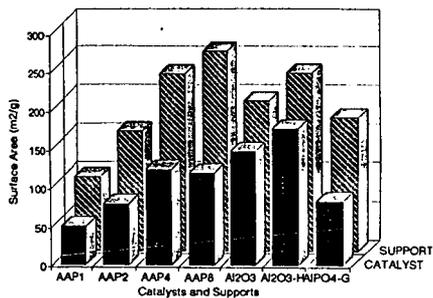
## REFERENCES

1. *Appl. Catal. A: General*, Volume 113, No.1-9, June 1994.
2. Tanabe, K., *Appl. Catal. A: General* 113, p147-152 (1994).
3. Tischer, R.E., *Ind. Eng. Chem. Res.* 1987, 26, 422-426.
4. Marcelin, G., *J. Catal.* 83, 42-49 (1983)
5. Moffat, J.B., *Catal. Rev.-Sci. Eng.*, 18(2), 199-258 (1978).
6. Rebenstorff, B., *J. Catal.* 128, 293-302 (1991).
7. Kearby, K., Proc. of the Second International Congress on Catalysis (1961), p2567, Paris.
8. Chen et al., *Ind. Eng. Chem. Res.* 29, 1830 (1990).
9. Cheung et al., *J. Catal.* 102, 10-20 (1986).
10. Mitchell, S.F., *J. Catal.* 105, 521-524 (1987).
11. Vogel, R.F., *J. Catal.* 80, 492-493 (1983).
12. Campelo et al., *J. Catal.* 101, 484-495 (1986).
13. H.S. Joo, X. Zhan, J.A. Guin, No.41d., AICHE Spring Meeting Houston, 1995.
14. K.J. Smith and L. Lewkowicz, *Canadian J. of Chem. Eng.*, 72, August, 637-643, 1994.

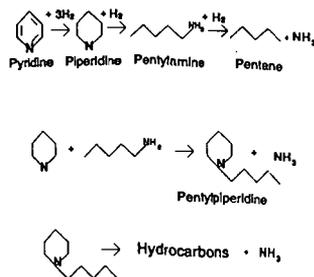


**Fig 1. Effect of variables on support properties**

(a) Surface area (m<sup>2</sup>/g) Vs Al/P ratio (b) Surface area (m<sup>2</sup>/g) Vs pH  
(c) Pore volume (cc/g) Vs P/Al ratio (d) Pore diameter (nm) Vs P/Al ratio



**Fig 2. Surface Area of Catalysts**



**Fig 3. Reaction Pathways for Pyridine HDN**

Support	Al		Mo		Ni		P		Al/P mole ratio- calc	Al/P mole ratio XPS	Mo/Ni mole ratio XPS
	ICP	calc	ICP	calc	ICP	calc	ICP	calc			
AAP1	19.0	18.2	na	13.3	3.06	3.23	19.1	19.1	1.09	1.2	21
AAP2	20.7	22.8	12.7	13.5	2.79	3.25	14.9	12.0	2.18	1.55	high
AAP4	na	41.8	12.8	13.3	2.84	3.21	na	11.1	4.3	4.25	2.07
AAP8	24.1	36.2	12.6	13.2	2.87	3.1	5.67	4.8	8.6	6.5	2.23
Al <sub>2</sub> O <sub>3</sub>	na	43.9	15.5	13.3	na	3.22	0.006	0			na
Al <sub>2</sub> O <sub>3</sub> -H	na	41.5	12.7	13.3	na	3.22	0.002	0			1.77
AlPO <sub>4</sub> -G	14.9	17.1	11.8	13.3	na	3.21	22.1	20.2	0.97	0.93	9.33

na: not available

Table 1. Calculated and Measured Catalyst Composition (wt%)

Support	Support Pore Volume (cc/g)	Surface Area(m <sup>2</sup> /g)	
		Support	Catalyst
AAP1	1.37	96	50
AAP2	1.69	154	79
AAP4	1.29	229	123
AAP8	0.85	259	118
Al <sub>2</sub> O <sub>3</sub>	0.42	194	146
Al <sub>2</sub> O <sub>3</sub> -H	0.71	230	176
AlPO <sub>4</sub> -G	1.02	172	82

Table 2. Physical Characteristics of Supports (Method C) and Catalysts

Support	Support Weight (g)	
	Expt	Calc
AAP1	29.18	28.99
AAP2	46.78	41.82
AAP4	25.2	33.71
AAP5	62.0	79.9
AAP8	57.0	59.19
Al <sub>2</sub> O <sub>3</sub>	12.03	12.73

Table 3. Comparison of Support Weights (g)

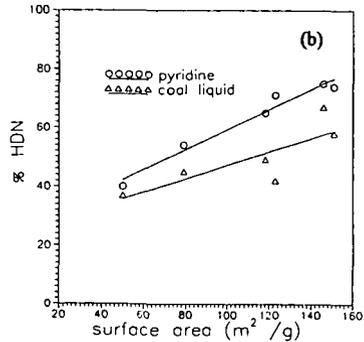
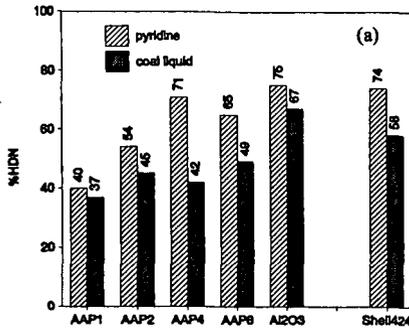


Fig 4. HDN with AAP Catalysts  
(a) HDN Activity  
(b) %HDN vs. Surface Area