

CHARACTERISATION AND MODEL COMPOUND STUDIES ON Pd AND Ni/Mo HYDROUS TITANIUM OXIDES

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ABSTRACT

Pd and Ni/Mo exchanged hydrous titanium oxides (HTOs) have high activities for hydrogenation and hydroprocessing reactions, respectively which arise principally from the effective dispersion of the active phases and the acidity of the substrate. This paper covers (i) the use of deuterated substrates to investigate the mechanism of pyrene hydrogenation with Pd-HTOs, (ii) the use of XPS and EXAFS to investigate the dispersion of the Pd and Ni/Mo and (iii) the impact of ion-exchange procedures on the activity of Ni/Mo-HTOs for hydrodesulphurisation (HDS) and hydrodenitrogenation (HDN). The deuteration experiments indicated that acidic hydrogen on the HTO does not participate in hydrogenation despite the broad correlation of activity with the substrate acidity. XPS and EXAFS indicated that the Pd and sulphided Mo phases on HTOs are smaller than on other substrates, such as γ -alumina where impregnation procedures are used. Indeed, EXAFS has provided evidence for the existence of a mixed "Ni-Mo-S" phase. Hydrogenation and hydrogenolysis activities and selectivities in HDS of dibenzothiophene and quinoline vary considerably as a function of substrate surface area, preparation procedure and calcination temperature.

INTRODUCTION

Hydrous metal oxide ion-exchange compounds of Ti, Zr, Nb and Ta were developed originally for the preparation of ceramic materials [1] and the decontamination of aqueous nuclear wastes [2]. However, the high surface areas and ion-exchange capacities, variable acidities and relatively good thermal stability make these amorphous materials ideal substrates for transition metal, metal oxide and metal sulphide catalysts. Indeed, research to date has shown that Pd-hydrous titanium oxides (HTOs, the cheapest hydrous metal oxide to prepare) have considerably higher activities than Pd- γ -alumina catalysts for the hydrogenation of polynuclear aromatic compounds, such as pyrene [3]. Active carbon is the only widely-used support for Pd that has been found to give comparable activities to the HTOs [4]. Moreover, activities of Ni/Mo-HTOs have been found to be broadly comparable to their γ -alumina counterparts for hydroprocessing coal tars [5] and heavy coal liquids [6] and they do not undergo rapid deactivation. However, there are a large number of variables involved in the preparation of HTOs and their compositions, particularly in relation to catalytic activity, remain important topics for research.

In this paper, the following aspects of structure and reactivity of HTOs are addressed.

- (i) The use of X-ray photoelectron spectroscopy (XPS) and extended X-ray adsorption fine structure (EXAFS) to investigate the dispersions of Pd and sulphided Ni/Mo, respectively.
- (ii) The use of deuterated substrates to investigate whether acidic hydrogen participates in the mechanism for pyrene hydrogenation with Pd-HTOs.
- (iii) The impact of ion-exchange and calcination procedures on activity and selectivity in hydrodesulphurisation (HDS) and hydrodenitrogenation (HDN).

EXPERIMENTAL

Catalyst preparation

Sodium hydrous titanium oxide substrates (Na-HTOs) were prepared as described [3-6] previously by hydrolysing the soluble intermediate formed from titanium tetraisopropoxyl and a methanolic solution of sodium hydroxide. The atomic ratio of Na to Ti was 0.5 for all the substrates used in this investigation. To increase the surface areas of the HTOs, about 15% w/w of silica was incorporated into the substrates using the appropriate amount of silicon tetraethyl in the preparation [7]. Pd was ion-

exchanged onto the Na-HTOs to give nominal loadings in the range 1-20% w/w using two procedures. In the first, Pd was dissolved in a mixture of concentrated nitric and hydrochloric acids and diluted to a pH of 1. Following ion-exchange with the appropriate volume of solution, the Pd-HTO was filtered, washed with acetone/water and dried under vacuum. In the second method, The Na-HTO was contacted with an aqueous solution of $\text{Pd}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}$ and, after filtration and washing, the catalyst was acidified with phosphoric acid to a pH of 3-4. All the Pd-HTOs were calcined at 350°C for 10 minutes. For deuteration experiments, Pd-HTOs were prepared by these two methods but using the corresponding deuterated mineral acids.

A series of Ni/Mo-HTOs were prepared with a nominal loading of 10% Mo and the Ni concentration was varied between 1 and 7% w/w. Table 1 summarises the variables in the preparation procedure which included the substrate surface area, the order of ion-exchanging Ni and Mo in conjunction with substrate acidity, calcination temperature and whether or not the HTO was calcined in between ion-exchanging Ni and Mo. The nickel was loaded from nickel nitrate solution at a pH of 4 and Mo from ammonium heptamolybdate solution at the same pH. Sulphuric acid was used to acidify the HTOs in all the preparation stages.

Characterisation

Nitrogen BET surface areas of most of the HTOs were determined and typical values are summarised in Table 2. Incorporating silica into the substrate and exchanging Pd for Na greatly increased the surface area from the typical baseline value of $80 \text{ m}^2 \text{ g}^{-1}$ for the Na-HTO. Mo concentrations were determined directly from XRF and indirectly by AA using the ammonium heptamolybdate solutions after ion-exchange.

The Pd and Ni/Mo HTOs have been analysed using XPS at each stage in their preparation procedures. The spectrometer comprised a Vacuum Science Workshop 100 mm hemispherical analyser with an Al anode as the X-ray source giving AlK_α radiation at 1486.6 eV. The powdered samples were adhered to conventional SEM stubs with double-sided cello tape and evacuated to 10^{-6} torr before transfer from the entry to the main chamber for analysis. Ni EXAFS was carried out at the Daresbury laboratory using station 7.1. with monochromatic X-rays having a wavelength of 1.488 Å.

Activity measurements

Pyrene was hydrogenated at 100°C and 10 bar pressure using stainless steel tubing bomb microreactors (TBMR) immersed in a fluidised sandbath and agitated via a flask shaker and ball bearings in the reactors [3]. 0.1g of pyrene was used with n-hexadecane as an inert diluent and 20mg of catalyst. After the desired reaction period, the TBMRs were quenched in water and the reaction mixture was recovered for gas chromatographic (GC) analysis.

HDS and HDN activities of the Ni/Mo catalysts were assessed using dibenzothiophene and quinoline respectively. For purposes of comparison, tests were also carried out with a commercially available Ni/Mo- γ -alumina catalyst (Akzo 153). The catalysts were pre-sulphided at 400°C prior to the tests using a large stoichiometric excess of hydrogen sulphide in hydrogen. Both the HDS and HDN tests were conducted at 350°C and 70 bar pressure (cold) in TBMRs. These were loaded with 20 mg of catalyst and 1 cm^3 of 0.06 molar solutions of dibenzothiophene and quinoline in n-decane or n-hexadecane containing a different n-alkane as internal standard [8]. After the desired reaction period, the solutions were recovered and the product distributions were determined by GC.

RESULTS AND DISCUSSION

Hydrogenation activity and XPS characterisation of Pd-HTOs

The hydrogenation of pyrene to di- and tetrahydropyrenes can be conveniently modelled as a pseudo first order reaction [3]. The rate constants on a weight of catalyst basis are presented in Figure 1 for the two methods used to ion-exchange Pd onto the HTOs. As the Pd concentration is increased from 1 to 20% (maximum ion-exchange capacity of Pd is about 23% w/w of dry catalyst), the rate constants increase linearly, i.e. they remain virtually constant with respect to the weight of Pd. However, the activities of the HTOs prepared from Pd dissolved in aqua regia are vastly higher than those prepared from the tetra-amine salt. Apart from a possible inhibiting effect from the amine ligands, the key difference in the two methods is that with the tetra-amine salt, the catalyst is acidified after rather than during ion-exchange. As reported previously [3], activity does broadly correlate with substrate acidity

as demonstrated by the fact that the neutral Pd-HTO gave an extremely low conversion, but other more subtle effects such as the Pd precursor used can also be important. For a given preparation method, the hydrogenation activity has been found to broadly correlate with the substrate BET surface area [4].

Figure 2 presents the surface atomic Pd/Ti ratios for the two methods used to prepare the Pd-HTOs. For the method employing the tetraamine salt as the Pd precursor, the Pd/Ti increases linearly with Pd concentration up to the highest loading used of 20% w/w in accord with the increase in the rate constant for pyrene hydrogenation (Figure 1) and suggesting that the dispersion of the Pd does not vary markedly. In contrast, for the method using Pd dissolved in aqueous regia, the Pd/Ti ratios plateau at approximately 5% Pd despite the hydrogenation rate constant increasing linearly with Pd concentration. Up to a loading of 5% Pd, both methods give the same Pd/Ti ratio. It is proposed that this apparent difference arises from a kinetic effect with much faster ion-exchange of Pd occurring on the HTO surface when the Pd is dissolved in acid.

The results above and previous work [3] suggest that the acidic protons on the HTOs may participate in the hydrogenation reaction in much the same way as with super acids. To test this ascertainment, the Pd-HTOs deuterated acids were used instead of the corresponding mineral acids in the preparations of the Pd-HTOs. Moreover, the reactions with deuterium-labelled Pd-HTOs were carried out under conditions where the concentrations of acidic deuterium on the catalyst were vastly in excess of the amount of hydrogen required. GC-MS analyses of the hydrogenated pyrenes indicated that the acidic deuterium had not been incorporated in measurable quantities and, therefore, it is suggested that the primary role of the acidic substrate in hydrogenation and indeed, also in HDS and HDN, is to facilitate the adsorption of aromatic species.

Characterisation of Ni/Mo HTOs

Figure 3 presents the XPS-determined surface Mo concentrations for two Mo- and a Ni/Mo-HTO, together with that for the commercial γ -alumina catalyst. The surface Mo concentrations increase linearly with the bulk concentration up to a loading of 20% w/w. For nominal bulk loadings of about 10% Mo, the surface concentration is higher on the HTOs (Figure 3). EXAFS provides evidence that the dispersion of Ni is also superior on the HTOs than on γ -alumina. In the EXAFS transforms for supports containing only sulphided Ni, the characteristic Ni-Ni peak at about 3.0 Å was virtually absent for the HTOs whereas it was a prominent feature for γ -alumina. For the Ni/Mo catalysts, the peak due to the mixed Ni-Mo-sulphide phase at about 2.8 Å was less pronounced for the HTO than for the commercial γ -alumina catalyst (Figure 4). However, this difference is attributed to the fact that the HTO was calcined in between ion-exchanging Ni and Mo and that the Ni concentration was higher (5 of 2.5%) meaning that a smaller proportion of the Ni is likely to be in the mixed phase.

Hydrodesulphurisation and hydrodenitrogenation

Figures 5 and 6 summarise the product distributions obtained from the HDS and HDN tests on dibenzothiophene and quinoline, respectively with the Ni/Mo HTOs (M1A-M7A, Table 1) and the commercial γ -alumina catalyst. The highest activities for the HTOs were observed for those samples not calcined between ion-exchanging the Ni and Mo (M2A and M7A) possibly due to maximising the concentration of the catalytically active mixed Ni-Mo-sulphide phase. Indeed, the activities of these HTOs were comparable to that of the γ -alumina catalyst for HDS (Figure 5) and superior for HDN where higher concentrations of propylcyclohexane and propylbenzene were obtained (Figure 6). However, it should be pointed out that the activities of commercial γ -alumina catalysts can vary considerably and the HDN activity of Akzo 153 may be less than that of other corresponding samples.

All the HTOs discussed above were calcined at 500°C because results for thiophene indicated that HDS activity increased markedly as the calcination temperature is increased above 400°C. Figures 7 and 8 present the variations in HDS and HDN activity for dibenzothiophene and quinoline, respectively as the calcination temperature is increased from 350 to 550°C. For HDS, the activity increases considerably and the extent of hydrogenation as indicated by the concentrations of bicyclohexyl decreases. Similarly for HDN, an increase in hydrogenolysis activity for removal of the heteroatom is observed. Interestingly, these significant changes in activity with increasing temperature must be accompanied by increasing amounts of the amorphous HTOs being converted into crystalline titania (primarily anatase as indicated by XRD).

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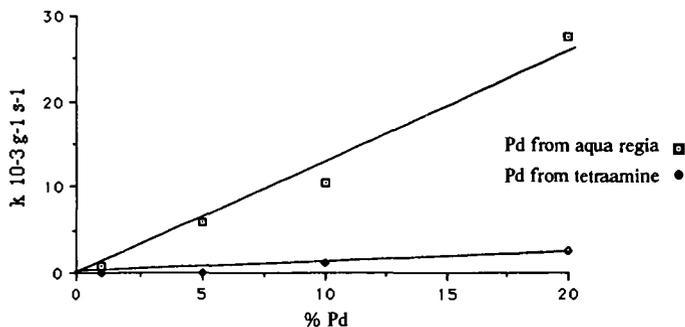


FIGURE 1 RATE CONSTANTS FOR PYRENE HYDROGENATION

Table 1 Typical BET surface areas of the HTOs

Type of HTO	Surface area m ² g ⁻¹
Na-HTO (atomic Na/Ti ratio = 0.5)	98
Na-HTO/silica (about 15% w/w silica)	204
10% Pd-HTO	170
10% Pd-HTO/silica	310
Ni/Mo-HTO (about 3% Ni, 10% Mo)	73
Ni/Mo-HTO/silica	270

Table 2 Summary of high surface area Ni/Mo HTO/silica catalysts prepared

Designation	Ion-exchange sequence		No. of calcinations ^a	Removal of Na ^b
M1A	1. Mo	2. Ni	2	No
M2A	1. Mo	2. Ni	1	No
M3A	1. Ni	2. Mo	2	No
M4A	1. Mo	2. Ni	2	No
M5A	1. Mo	2. Ni	2	Yes (pH 2.5)
M6A	1. Mo	2. Ni	2	Yes (pH 4)
M7A	1. Ni	2. Mo	1	No

^a = two corresponds to calcining between the ion-exchange steps.

^b = sodium removed via acidification prior to ion-exchange of Mo.

The pH of the molybdate solution was adjusted to 4 except for M1A where it was 2.5.

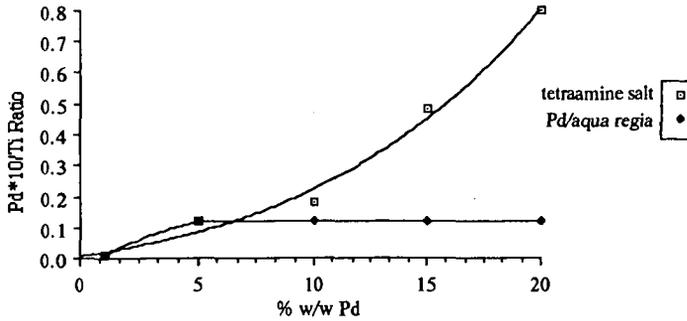


FIGURE 2 Pd/Ti RATIOS VS. BULK Pd CONCENTRATIONS

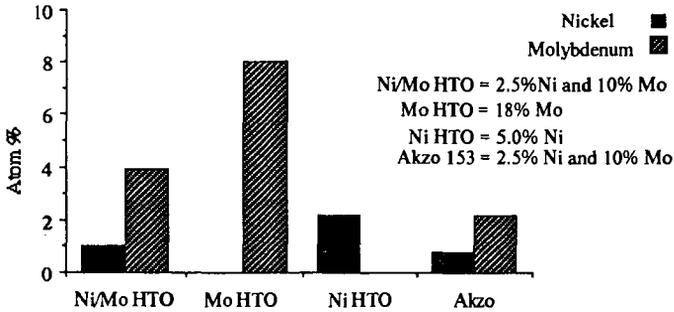
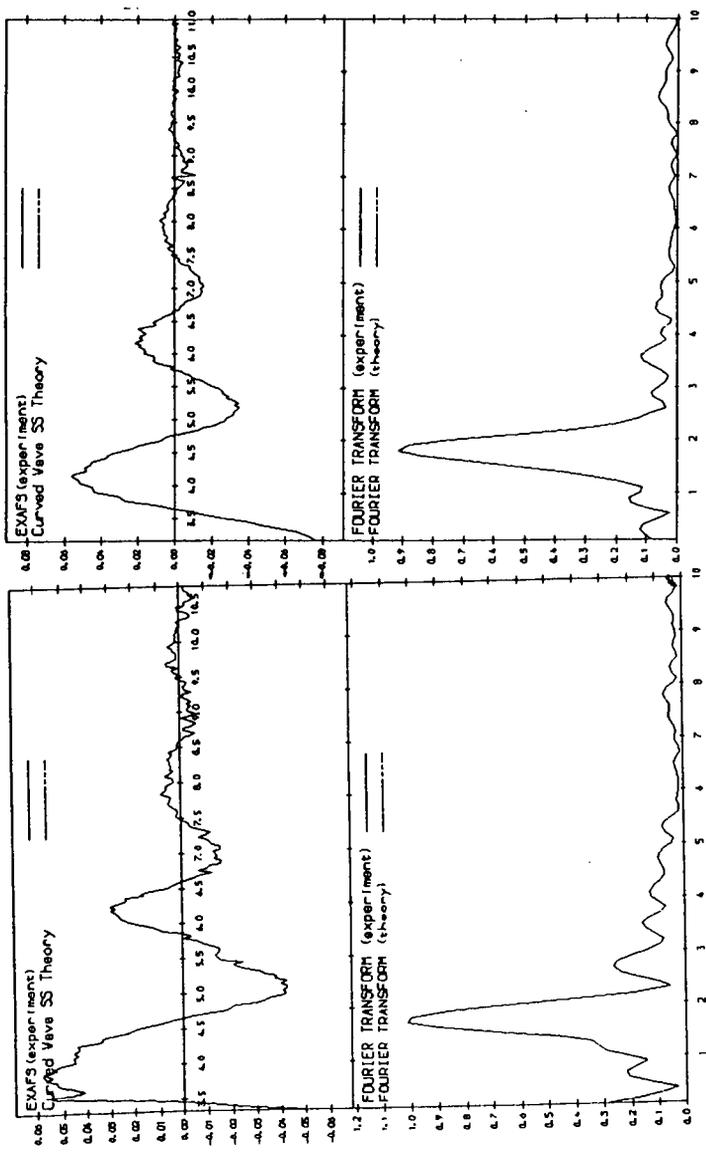


FIGURE 3 XPS-DETERMINED SURFACE CONCENTRATIONS



(a) (b)

FIGURE 4 RAW AND TRANSFORMED NI EXAFS DATA FOR NI/MO (a) γ -ALUMINA AND (b) HTO CATALYSTS

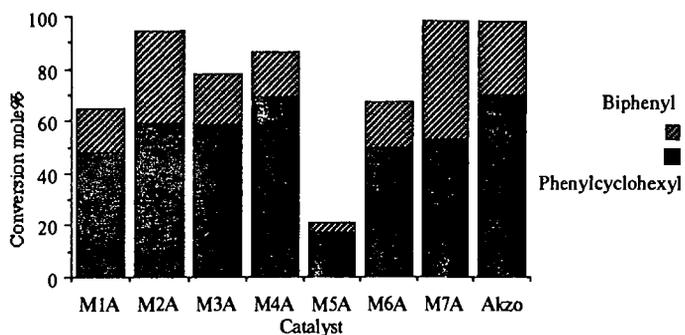


FIGURE 5 HDS OF DIBENZOTHIOPHENE

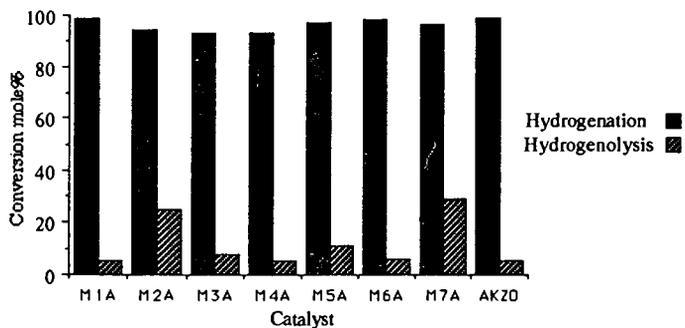


FIGURE 6 HDN OF QUINOLINE

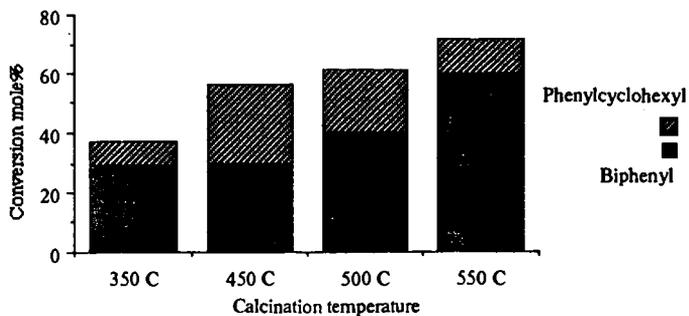


FIGURE 7 EFFECT OF CALCINATION TEMP. ON HDS ACTIVITIES

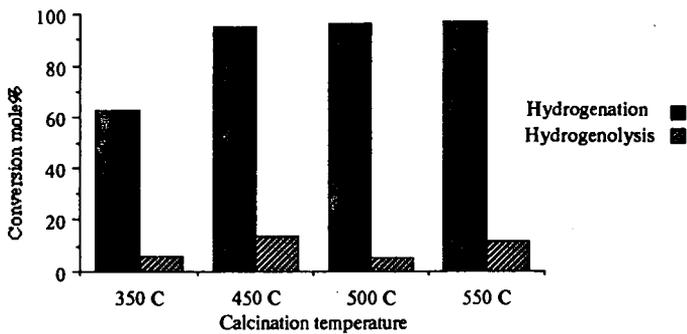


FIGURE 8 EFFECT OF CALCINATION TEMP. ON HDN ACTIVITIES