Catalysis Letters 33 (1995) 175–192

Tungsten–alumina based catalysts. I. Genesis by impregnation with different tungsten solutions

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Received 21 November 1994; accepted 19 March 1995

The preparation of hydrotreating catalysts by means of alumina impregnation with ammonia metatungstate, sodium tungstate and ammonium tungstate solutions, was studied. The use of several precursors, concentration levels, impregnation times and pH determined the presence of different polymeric or monomeric species in the impregnating solutions. Such species led to different tungsten distributions in the support. The impregnation with ammonium metatungstate solutions led to egg shell profiles, owing to pore blockage of the support, which results from the size exclusion of metatungstate ions. In the impregnations performed with solutions of sodium or ammonium tungstate, the resultant profiles were flat as a result of the presence of WO_4^{2-} ions in solution, which, owing to its small size, penetrated deep into the spheres. The experimental tungsten concentration profiles were compared to those obtained with a theoretical model previously developed for this particular purpose. Coincidence between both was observed in profiles obtained from sodium tungstate solutions, which did not occur in results obtained from ammonium metatungstate solutions because of the obstruction mentioned above. The effect of concentration and contact time on the resultant profile shape was also studied. The profile shape obtained by impregnation with ammonium metatungstate or sodium tungstate solutions did not vary when solution concentrations were increased. When longer impregnation times were used, an increase of the total tungsten concentration was detected, but without changes in the profile type obtained. In impregnations with metatungstate solutions, little penetration of tungsten towards the sphere centre was observed, owing to blockage of alumina pores. Characterization studies on impregnated and calcined solids showed the predominant presence of the WO_4^{2-} monomeric species, regardless of the precursor used in the impregnating solution.

Keywords: tungsten catalysts; impregnation; concentration profiles; alumina

1. Introduction

Hydrotreatment of petroleum fractions is a process that may include reactions such as hydrocracking (HC), hydrogenation (HY), hydrodenitrogenation (HDN),

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hydrodesulphurization (HDS) and hydrodeoxygenation (HDO). In this process, the catalysts commonly employed are composed of molybdenum or tungsten supported on alumina which, in turn, are promoted by cobalt or nickel [1]. Catalysts based on Mo–Co are generally preferred for HY and HDS reactions, while W–Ni based catalysts tend to be preferred when reactions of HC, HDN or HDO are also desired [2].

Research studies have been less concerned with tungsten-based catalysts than with those containing molybdenum. One of the subjects about which there is scarce information is the influence of preparation conditions on the distribution of the active component precursor along the support pellet radius. In this regard, it must be emphasized that such distribution influences the activity of the finished catalyst. Thus, for a given reaction, the ideal distribution will depend on whether there are diffusional limitations or not, and also on the presence of deactivating species [3,4]. It is important, therefore, to perform studies leading to an improved knowledge about preparation conditions so as to obtain the desired distribution of the active component.

Maitra et al. [5] have studied the preparation of tungsten catalysts supported on alumina obtained by pellet impregnation with ammonium paratungstate solutions. They found that the metal distribution profile within the pellet is a function of pH, precursor concentration and impregnation time. Besides, they concluded that pore blockage, which is produced under certain impregnation conditions, limits the precursor penetration. Such blockage is caused by adsorption of polymeric species containing twelve tungsten atoms, which is the predominant form at low pH.

Mauchausse et al. [6] have prepared a series of tungsten–nickel and tungsten–cobalt based catalysts on alumina, to test them in the hydrotreatment of liquid hydrocarbons obtained from coal. The distribution of tungsten within the catalyst was varied by adjusting the pH of the solution and the impregnation time, which allowed one to obtain catalysts of uniform metal distribution and also those having "egg shell" profile.

The use of coal-derived liquids confirmed and extended results previously obtained by these authors with model compounds. Coal derived liquids are more difficult to process but, as was the case with model compounds, material contained in the outermost third of the catalyst pellet was responsible for most of the catalytic activity. Then, the authors conclude that it is advantageous to use catalysts in which metals are concentrated more towards the exterior of a pellet of support.

Catalysts based on tungsten by means of the impregnation of dry alumina support can be prepared by the pore filling method (incipient wetness impregnation) or in a solution excess (wet impregnation). In the first method, the solution transport into the porous support is only performed by capillary action, while, in the second technique, the solute transport is the result of convective movement till the pores are filled up and, then, by diffusive mechanism if there exists a solute–support interaction.

The advantages of the pore filling method with respect to wet impregnation are mainly a lower impregnation time and a smaller volume of impregnating solutions, whereas the necessity of using more concentrated impregnating solutions, which implies preparative difficulties and not exceeding the solubility limit, is one of the principal drawbacks when the pore filling technique is employed. Another disadvantage is the less homogeneous distribution of the active component in the pellet.

Incipient wetness impregnation can also be performed by using an excess of solution, if support and solution are contacted during the time needed for the pores to fill up. Here, the possibility of obtaining an inhomogeneous distribution is minimized, because the pore entrances have more accessibility to the solute at the same time.

The activity and selectivity of the catalysts can be affected by the use of different precursors, concentrations, impregnation times and pH, since these variables determine the presence of either monomeric species or several polymeric species in the impregnating solution [7]. These species, in turn, can lead to different tungsten distributions in the support, depending on the characteristics of the solute–support interaction or on the precursor diffusivity.

In the present work, the precursor distribution along the pellet radius of catalysts obtained by pore filling impregnation of alumina spheres with tungsten solutions prepared from ammonium metatungstate or from ammonium or sodium tungstate is studied. An excess of solution and a contact time equal to the required pore filling time was used. The relation between tungsten concentration profile and tungsten species both in solution and in the solid is also studied. Furthermore, the effect of solute concentration and impregnation times longer than required for the pores to fill up was also shown.

2. Experimental

2.1. MATERIALS

Spheres of γ-alumina (Spheralite) with 4 mm diameter, 280 m^2/g surface area, 0.53 ml/g pore volume and 4.2 nm mean pore diameter, were used.

The impregnating solutions were prepared from ammonium metatungstate (Fluka AG pa) or sodium tungstate (Baker Analyzed) in distilled water. Ammonium tungstate solution was, in turn, prepared with ammonium hydroxide (Mallinckrodt, AR) and ammonium metatungstate.

2.2. IMPREGNATION

In this stage, 20 g of alumina spheres, previously dried at 353 K for 24 h to eliminate the retained moisture, were used. The dried spheres were placed in a plastic basket and then immersed in 50 ml of the impregnating solution, the latter being kept under stirring so as to ensure homogeneity during the impregnation stage. Once the impregnation time was over, the basket was removed and the excess solution surrounding the solid was eliminated. The solid was then dried at 343 K for 24 h and calcined at 723 K for 24 h.

2.3. IMPREGNATION WITH AMMONIUM METATUNGSTATE SOLUTIONS (AMT)

Alumina spheres were impregnated with AMT solutions of initial concentrations (C_{so}) of 4960, 14850, 30900, 42400 and 67750 ppm W at pH given by the dissolution of salt in water: 7.5, 6.2, 6.1, 5.9 and 5.8, respectively. An impregnation time of 71 s, estimated previously [8] as the period required for the pore filling up procedure, was used.

Alumina spheres were also impregnated with AMT solutions of 67550 ppm W but, in this case, several impregnation times were used: 30, 60, 120, 180 and 1440 min.

2.4. IMPREGNATION WITH SODIUM TUNGSTATE SOLUTIONS (ST)

The alumina spheres were impregnated until pore filling using ST solutions with C_{so} values of 68580 and 163775 ppm W, at pH given by the dissolution of the salt in water: 9.2 and 9.5 respectively.

Alumina spheres were also impregnated with ST solutions of 68580 ppm W but, in this case, various impregnation times were used: 30, 60, 120, 180 and 1440 min.

2.5. IMPREGNATION WITH AMMONIUM TUNGSTATE SOLUTIONS (AT)

The AT solution was prepared from an AMT solution having a tungsten content of 67750 ppm, the pH of which was adjusted by $NH_4(OH)$ addition up to 8.1. The solution thus obtained was allowed to stabilize for 48 h and then used to impregnate the alumina spheres by the pore filling technique.

2.6. EXPERIMENTAL TUNGSTEN CONCENTRATION PROFILES

The tungsten concentration along the pellet radius was determined by quantitative electron microprobe analysis. A Philips 505 model scanning electron microscope with electron probe was used. The sample had to be placed on a high purity carbon support, which would act as a sample holder inside the electron microscope chamber. Several holes were made in the support, so as to be able to place different samples and standards simultaneously, thus ensuring similar instrumental conditions.

A thick polishing was carried out with silicon carbide abrasives of different grain sizes (420–260) and was followed by fine polishing with 1 μm diamond paste.

Electrolytic gold was used in the metallizing process.

Measurement of the intensities was carried out, at a voltage of 25 kV, on small areas of approximately 100 μm^2 along the diameter of each sphere, the counting time for each area being 100 s. Once the counting time in each area had elapsed, an X-ray spectrum from 0 to 25 kV was obtained, exhibiting two principal peaks: Al $K\alpha$ and W $L\alpha$.

Background subtraction was carried out using the EDAX system software, using identical conditions for both sample and standard. Once the background had been subtracted, peak intensities had to be corrected. Conventional correction methods exhibit difficulties when the characteristic absorption is strong. The program MULTI [9,10] was used, which permits the selection of the most suitable correction models and coefficients.

The average concentration of tungsten measured on each small area was used to obtain the concentration profile along the sphere diameter.

Further details about sample preparation procedure, measuring conditions and characteristics of standards used as references, are given in previous works [9,10].

2.7. UV–VISIBLE AND DIFFUSE REFLECTANCE SPECTROSCOPY

UV–visible spectra of solutions used for support impregnation were obtained in a Varian Super Scan 3 double-beam spectrophotometer. Quartz cells of 0.5 mm optical path were employed.

For wet, dried and calcined samples obtained by pore filling impregnation of the alumina spheres with AMT and ST solutions, the diffuse reflectance spectra were recorded in the above-mentioned spectrophotometer but now fitted with a diffuse reflectance camera having a 73 mm diameter integrating sphere with internal surface of barium sulphate. γ-alumina was used as a reference.

2.8. X-RAY DIFFRACTION

The X-ray diffraction patterns of dried and calcined samples of alumina spheres impregnated as described above, were obtained with a Philips PW1714 equipment using Cu $K\alpha$ radiation, Ni filter, 40 kV and 20 mA.

3. Results and discussion

Tungsten solutions used for the preparation of W/Al_2O_3 catalysts can contain different polymeric and monomeric tungsten species, which can not only be responsible for the particular type of species present in the catalyst but also for the distribution of the active component precursor along the radius of the support. The transformations likely to be found in such solutions are too complex to describe thoroughly, but the most important ones are:

$$\begin{tikzcd} & \underset{\text{tungstate}}{WO_4^{2-}} \arrow[d, shift left] & \\ \underset{\text{metatungstate}}{[H_2W_{12}O_{40}]^{6-}} \arrow[r, shift left, "\text{weeks}"] & \underset{\text{paratungstate A}}{[W_7O_{24}]^{6-}} \arrow[l, shift left] \arrow[u, shift left] \arrow[r, shift left, "\text{days}"] & \underset{\text{paratungstate B}}{[H_2W_{12}O_{42}]^{10-}} \arrow[l, shift left] \end{tikzcd}$$

The transformations represented by vertical arrows rapidly approach the equilibrium state (in minutes or even seconds) while the remaining reactions take hours or even weeks to reach equilibrium.

UV–visible spectra of solutions prepared from AMT at the dissolution pH of salt in water indicated that, at the time of use, the major species present was the metatungstate ion $[H_2W_{12}O_{40}]^{6-}$, as was found in a previous work [7]. The presence of this ion was indicated by the existence of the characteristic band at $\lambda = 257$ nm [11].

When the alumina support is impregnated with AMT solution during a time equal to that necessary to fill up pores (71 s), the transformation of metatungstate species in the solutions into monomeric tungstate is negligible. This effect is due to the fact that the concentration of adsorbed tungsten is small compared to the total concentration in the solid [8] and hence, tungsten is mainly in the solution occluded in the pores. The occluded solute has no interaction with the alumina support and as it was concluded in a previous paper [7] that interaction is one of the reasons of metatungstate depolymerization in solution.

In turn, the pH increase of the impregnating solution, from 7.5–5.8 up to 7.6–7.0 according to the solution concentration, does not change fundamentally the species in solution for short impregnation times [7], and does not affect in a significant way the total tungsten concentration in the sphere.

However, for the impregnation at times up to 1440 min, both the pH increase and the tungsten–alumina interaction lead to a partial depolymerization from metatungstate into tungstate ions.

In solutions prepared from ST at pH given by the dissolution of salt in water, the predominant species at the time of use was WO_4^{2-}, as concluded from its UV–visible spectrum [7].

Monomeric WO_4^{2-} is the only species of which the concentration is appreciable in AT solutions. This solution was prepared from an AMT solution, which was made alkaline with NH_4OH so as to transform the $[H_2W_{12}O_{40}]^{6-}$ ion into WO_4^{2-}. The transformation was verified by spectrophotometry until appearance of the characteristic spectrum of the monomeric species [12].

For the impregnation with AT or ST solution, the pH of the impregnating solution is initially 8.0 and 9.0 respectively, and remains in a strongly alkaline value (8.0–9.0) during the impregnation. Therefore, the tungsten species present in the solution after impregnation is WO_4^{2-}.

3.1. IMPREGNATION WITH AMT SOLUTIONS

The experimental tungsten concentration profiles obtained by pore filling impregnation of the alumina spheres with AMT solutions of 4960, 14850, 30900, 42400 and 67750 ppm W, are shown in fig. 1. Results were expressed as total concentration (C_t) as a function of the dimensionless radius (r/R).

These profiles can be classified as the egg shell type [13]. The tungsten concentration rapidly decreases from average surface values of 2.58, 3.47, 6.41, 6.10 and 11.60% W (w/w) to a zero value at dimensionless radii of about 0.8–0.9.

On the other hand, the experimental tungsten profiles in alumina spheres impregnated with a 67750 ppm W solution for impregnation times of 30, 60, 120, 180 and 1440 min are shown in fig. 2.

It was found that the profile obtained in spheres impregnated for 30 min does not differ substantially from that obtained after 71 s of impregnation.

In spheres impregnated for 60, 120, 180 and 1440 min, the decrease of tungsten concentration along the dimensionless radius is less steep, reaching zero values at

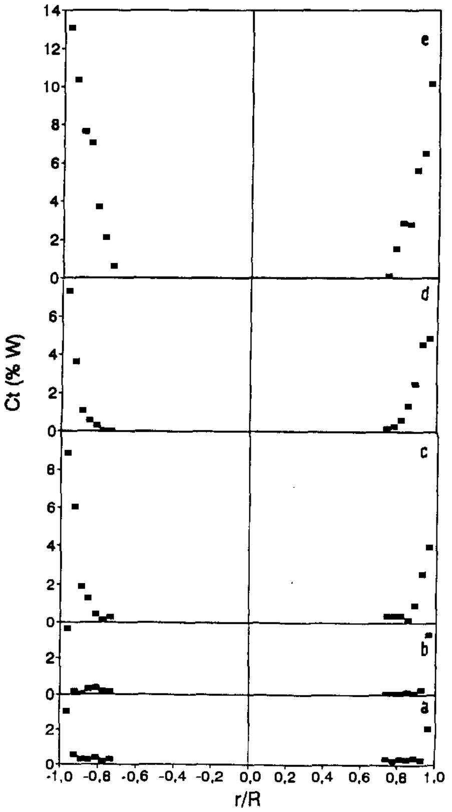

Fig. 1. Tungsten concentration profiles in alumina spheres impregnated with AMT solutions of C_{so} (ppm W): (a) 4960, (b) 14850, (c) 30900, (d) 42400 and (e) 67750. Impregnation time: 71 s.

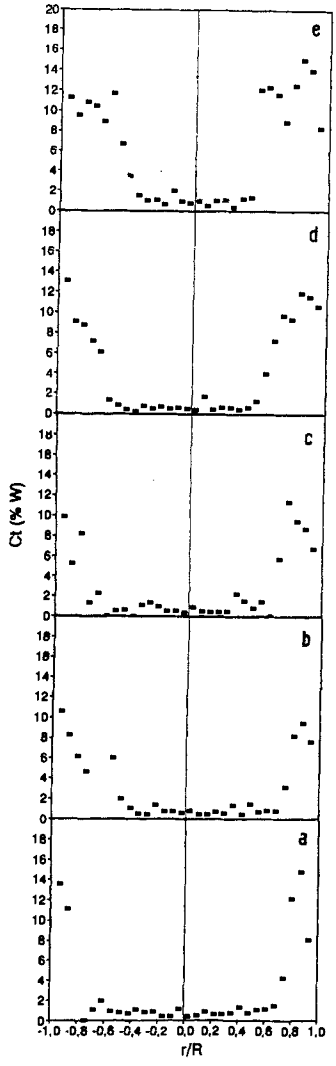

Fig. 2. Tungsten concentration profiles in alumina spheres impregnated with AMT solutions of C_{so} 67750 ppm W using different impregnation times (min): (a) 30, (b) 60, (c) 120, (d) 180 and (e) 1440.

r/R close to 0.7 for the first two impregnation times and at 0.5 and 0.4 for the last two, respectively. Therefore, during the impregnation a very slow tungsten penetration towards the sphere center is observed, even for impregnation times of one day. This was corroborated with the total tungsten concentration values of the impregnated spheres, which were 5.39, 4.91, 4.72, 6.87 and 8.79% W (p/p) for the above-mentioned times, respectively. Then it was observed that there is a solute contribution by diffusion for impregnation times of 3 and 24 h. Moreover, in previous studies [8], the adsorption kinetics of tungsten on alumina ground to a size smaller than 150 μm from metatungstate solutions was investigated and an adsorption equilibrium time of 1440 min was determined.

In fig. 3, the experimental concentration profile, obtained by pore filling impregnation of alumina spheres using a 67750 ppm W ATM solution, is compared with the theoretical profile. The latter was predicted by a previously developed theoretical model which interprets the pore filling impregnation process [14]. Here, previously determined equilibrium adsorption parameters and kinetic constants of tungsten adsorption from AMT solutions were used [15].

The theoretical profile shown in fig. 3 is almost flat, whereas the experimental one exhibits a marked decrease of the tungsten concentration towards the inner part of the sphere. A similar behaviour was observed for the other concentrations tested. It can be assigned to tungsten deposition in the outer part of the spheres as a result of size exclusion of AMT species, since the diameter of metatungstate ions is 2 nm [16] while the average pore diameter of the alumina used is 4.2 nm. This situation can lead to obstruction, either total or partial, of support pores.

The existence of pore blockage was verified by the impregnation tests performed for contact times longer than those required for pore filling up. In such experiments, the profiles were less steep than those found in the samples obtained using the incipient wetness impregnation method. Still, however, no case was found with appreciable tungsten concentration in the central region of the sphere, as should be observed if an unrestricted diffusive process were present after the pore filling up. Thus, pore obstruction would prevent free access of tungsten species to the sphere center.

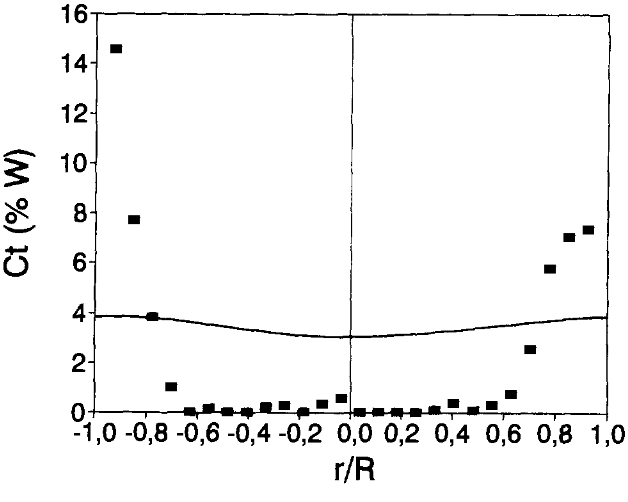

Fig. 3. Tungsten concentration profiles in alumina spheres impregnated during 71 s with AMT solutions of C_{so}: 67750 ppm W. Experimental data (■). Theoretical model (——).

3.2. IMPREGNATION WITH ST SOLUTIONS

Fig. 4 shows experimental tungsten concentration profiles in alumina spheres impregnated with ST solutions of 68580 and 163775 ppm W during the time required for pore filling up.

In the sample obtained with an impregnating solution of 68850 ppm W, a slight decrease of the tungsten concentration from the sphere surface to the center can be observed. Although less prominent, the decrease is also observed in spheres impregnated with a tungsten solution of 163750 ppm W. These profiles result from low solute adsorption owing to slow interaction between the solute and the support, which, in turn, is a consequence of low adsorption kinetic constants.

Fig. 5 shows experimental tungsten concentration profiles in alumina spheres impregnated with a ST solution of 68580 ppm W during 30, 60, 120, 180 and 1440 min. For impregnation times of 30 and 60 min, profiles are similar to those obtained by pore filling impregnation, except for a slightly higher concentration in the sphere center.

Profile shapes obtained after impregnation times of 120, 180 and 1440 min did not differ one from the other nor from those obtained after 30 and 60 min, though an increase of the total tungsten concentration within the spheres was detected. This is because, as long as the time increases, there is an increase of tungsten concentration within the sphere as a consequence of the driving force established for tungsten diffusion towards the sphere center, which is generated by concentration difference between the external solution and the solution in the interior of the pores.

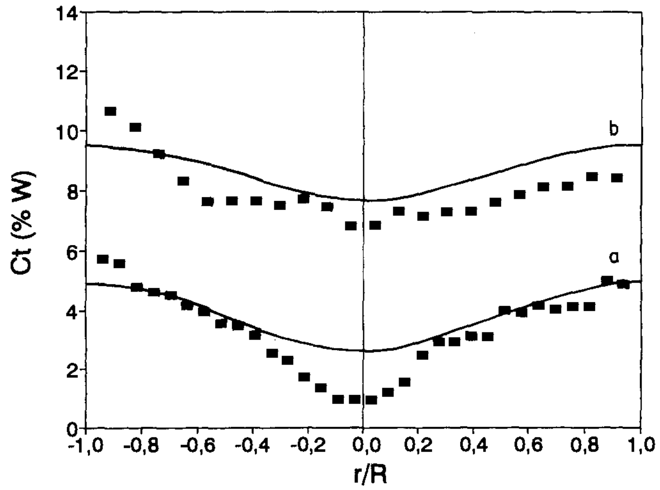

Fig. 4. Tungsten concentration profiles in alumina spheres impregnated with ST solutions of C_{so} (ppm W): (a) 68580 and (b) 163775. Impregnation time: 71 s. Experimental data (■). Theoretical model (——).

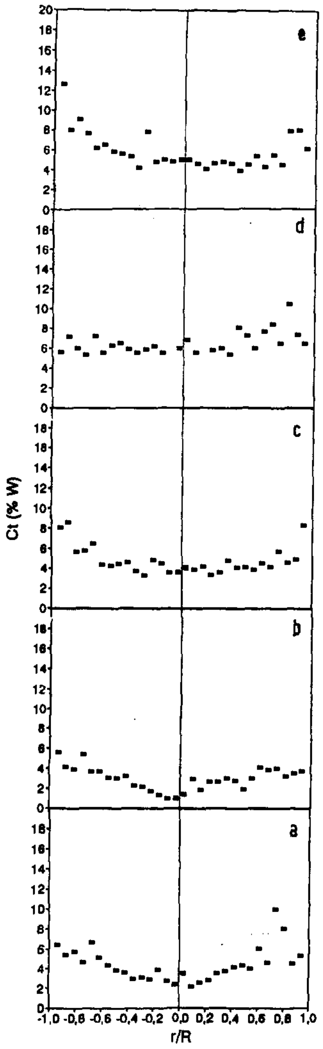

Fig. 5. Tungsten concentration profiles in alumina spheres impregnated with ST solutions of C_{so} 68580 ppm W using different impregnation times (min): (a) 30, (b) 60, (c) 120, (d) 180 and (e) 1440.

In fig. 4, the experimental concentration profiles in spheres impregnated with ST solutions of 68580 and 163775 ppm W are compared with the theoretical profiles, as predicted by the above-mentioned model [14], taking into account the corresponding equilibrium adsorption parameters and kinetic constants for tungsten adsorption from ST solutions previously determined [17]. It can be seen that, in spheres impregnated with ST solutions of 68680 ppm W, there is very good agreement between theoretical model and experimental values, except for r/R values between 0 and 0.2, though the volume of this zone is negligible (0.8%) in relation to the total volume. The cause of this discrepancy may lie in the existence of a harder and more compact zone in the center than in the rest of the sphere. This nucleus presents a pore volume of 0.31 ml/g Al_2O_3, significantly smaller than the average value of the whole sphere, which is 0.53 ml/g Al_2O_3 [8]. Evidently, the characteristics of the nucleus influence the penetration of the solution into the pores. Besides, a smaller pore volume implies a smaller amount of occluded solute.

On the other hand, fig. 4 shows coincidence between experimental and theoretical profiles in spheres impregnated with ST solution of 163775 ppm W. In this case, however, the influence of the nucleus is possibly less important because the profile is the average of those of several spheres, the majority of which showed a less evident influence of the nucleus.

Pore obstruction, likely to be found when impregnation is performed with AMT solutions, is not observed in spheres impregnated with ST solutions, because of the smaller diameter of the WO_4^{2-} ion (1 nm [16]). This behaviour was confirmed in sphere impregnation tests involving long contact times (fig. 5) where, after pore filling up, penetration by diffusion was important to such an extent that, at 1440 min, the tungsten concentration profile obtained with ST solution became flat, and this concentration value was greater than the total amount determined in pore filling impregnation.

3.3. IMPREGNATION WITH AT SOLUTIONS

Fig. 6 shows the experimental tungsten concentration profile in alumina spheres impregnated with AT solutions of 67750 ppm W during time required for pore filling up. Such a profile is essentially flat, and its characteristics are similar to that obtained from ST solutions at equal impregnation time, because the size of WO_4^{2-}

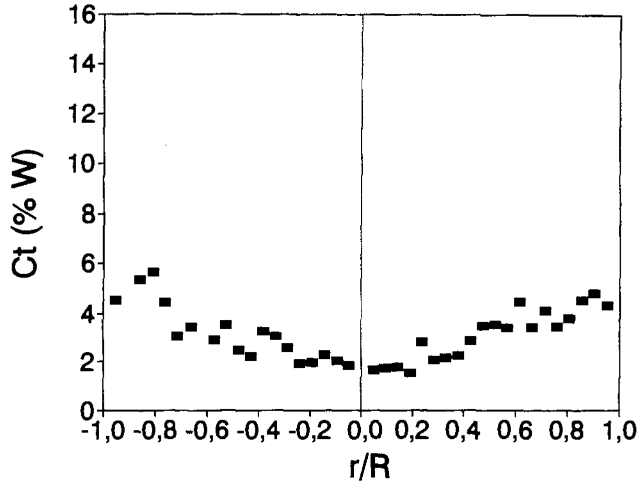

Fig. 6. Tungsten concentration profiles in alumina spheres impregnated with AT solutions of C_{so}: 67750 ppm W. Impregnation time: 71 s.

ions, which are present in both the AT solution and the ST one, allows penetration into the porous structure of the alumina, without the hindrance observed in AMT impregnation.

3.4. DIFFUSE REFLECTANCE SPECTROSCOPY

The spectra of wet, dried and calcined tungsten–alumina samples obtained by pore filling impregnation with AMT solutions, are shown in fig. 7. It can be observed that the impregnated wet solids show a first band with a maximum at 215 nm and a second one, as intense as the first, with a maximum at 265 nm.

The spectra of dried samples show a first band at 210–215 nm and a second less intense band, at 240–250 nm. From the spectra of calcined samples the presence of a wide band in the 220–250 nm range is seen. On the other hand, for spheres impregnated with solutions of 4960 and 14850 ppm W, the bands are very weak owing to low tungsten concentration in the solid.

The ratio of the absolute remission function of Schuster–Kubelka–Munk between the first and second maxima ($F_{R\infty}215/F_{R\infty}250$) was calculated for wet, dried and calcined samples obtained after impregnation with the solutions of high concentration. Values thus obtained are shown in table 1.

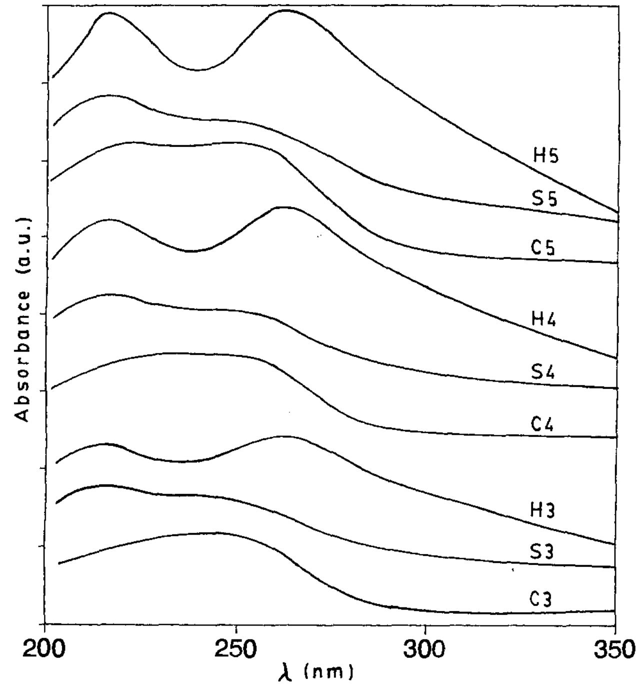

Fig. 7. UV–visible spectra of wet (H), dried (S) and calcined (C) alumina spheres impregnated with AMT solutions of C_{s0} (ppm W): 30900 (3), 42400 (4) and 67750 (5). Impregnation time: 71 s.

Table 1
Values of $F_{R\infty}215/F_{R\infty}250$ in spheres impregnated with AMT solutions

C_{so} (ppm W)	C_T (% W)	$F_{R\infty}215/F_{R\infty}250$		
		wet sample	dried sample	calcined sample
30900	1.34	0.7345	0.8736	0.5654
42400	1.37	0.7537	1.0198	0.6915
67750	4.16	0.7551	0.9777	0.6794

The remission function ratio varies slightly with the total tungsten concentration (C_T) in wet, dried and calcined samples. This is because the adsorbed amount of tungsten is negligible with respect to C_T. Therefore, the increase of C_T is mainly caused by the tungsten occluded with the pores and this would imply that, within the concentration range under study, the ratio of species does not change appreciably with an increase in the total concentration in the solid.

The remission function ratio of wet samples yields lower values than those of dried samples. This allows one to deduce that, in wet samples, the major species is metatungstate while, during drying at 343 K, the weak interaction with the alumina leads to depolymerization of $[H_2W_{12}O_{40}]^{6-}$ and to adsorbed WO_4^{2-} species [7]. It should be remarked that, in dried samples, the 240–250 nm band results mainly from distortions in the tetrahedral symmetry of the WO_4^{2-} ions, owing to its interaction with the alumina [18].

On the other hand, in calcined samples, the remission function ratio is less than that of the dried ones, owing to increased WO_4^{2-}–alumina interaction during calcination, which leads to greater distortions.

Diffuse reflectance spectra of wet, dried and calcined samples from spheres previously impregnated with ST solutions, show an intense band in the 210–215 nm region, and a shoulder at 255–260 nm (fig. 8). As the monomeric species is the only one present during this impregnation, the thermal treatment applied to the samples does not alter the shape of the spectra in a significant form, unlike in samples impregnated with AMT solutions.

The remission function ratio of both maxima decreases in dried samples and, particularly, in calcined ones (table 2). This is because there is a relative increase of the intensity of the second band, assigned to the distorted monomeric species, since the drying and calcination favours tungsten–support interaction.

3.5. X-RAY DIFFRACTION

X-ray diffraction patterns of samples of alumina spheres impregnated with AMT solutions and subsequently dried and calcined, allow one to observe that the sample impregnated with a 67750 ppm W solution is the only one leading to a low intensity peak group.

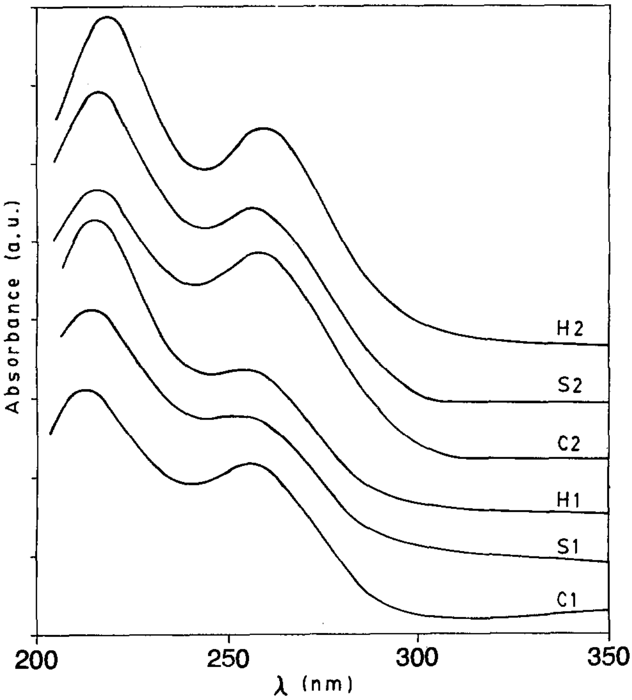

Fig. 8. UV-visible spectra of wet (H), dried (S) and calcined (C) alumina spheres impregnated with ST solutions of C_{so} (ppm W): 68580 (1) and 163775 (2). Impregnation time: 71 s.

In samples subjected only to drying at 343 K, not only the above-mentioned peaks are seen but also some other peaks that were absent in calcined samples. The peak intensity decreases at lower concentrations of the impregnating solution, as can be observed in fig. 9. In samples prepared with solutions whose concentrations were below 30000 ppm W, only the alumina pattern is observed.

None of the patterns show peaks at low 2θ values which are typical of tungsten polyanions, as can be seen in the diffraction patterns of ammonium metatungstate (fig. 9).

Comparisons between the diffraction patterns obtained and those of different tungsten compounds found in the literature [19] did not allow identification of the

Table 2
Values of $F_{R\infty}215/F_{R\infty}250$ in spheres impregnated with ST solutions

C_{so} (ppm W)	C_T (% W)	$F_{R\infty}215/F_{R\infty}250$		
		wet sample	dried sample	calcined sample
68580	3.80	2.9354	2.1433	1.5652
163775	9.71	1.8074	2.0240	1.2945

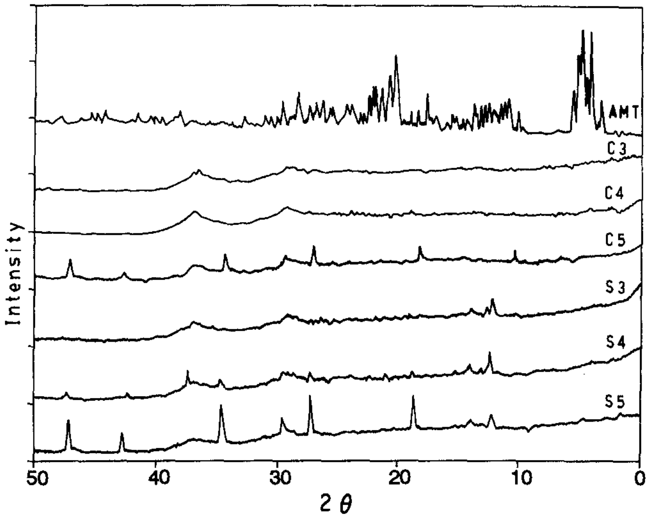

Fig. 9. X-ray diffraction patterns of ammonium metatungstate (AMT) and alumina spheres impregnated with AMT solutions of C_{so} (ppm W): 30900 (3), 42400 (4) and 67750 (5); dried (S) and calcined (C).

crystalline phase present in the samples under analysis. Moreover, only in calcined samples having higher tungsten content do the patterns obtained possess some similarity with that of the crystalline phase $WO_3 \cdot H_2O$ [20].

For samples of alumina spheres impregnated with ST solutions and then dried, the diffraction patterns did not allow one to detect the presence of crystalline phases. The existence of a crystalline phase in spheres impregnated with AMT, which is not detected in spheres impregnated with ST solutions of equal or greater concentration, can be related to the deposition of the polymeric species in the outer region of the sphere, owing to solute exclusion and alumina pore obstruction. During drying, the metatungstate depolymerizes to species containing NH_3 and H_2O, which is detected by the X-rays.

4. Conclusions

The studies on pore filling impregnation of alumina spheres have shown that the concentration profiles depend on the nature of the tungsten species present in the solution. The species are, in turn, directly related not only to the tungsten compound used in the preparation of the impregnating solution, but also to the concentration level, the pH and the elapsed time from the solution preparation to the start of impregnation.

Impregnation with AMT solutions lead to egg shell profiles because of obstruction in support pores, which is the result of size exclusion of the metatungstate ion. When impregnation is performed with ST or AT solutions, profiles obtained are almost flat as a consequence of the presence of WO_4^{2-} ions in solution, which can penetrate into the sphere without steric hindrance.

The shape of profiles obtained by impregnation with AMT solutions does not vary when the impregnating solution concentration increases, though there is an increase of the tungsten concentration in the sphere periphery. Impregnations performed for times longer than that required for pore filling up, lead to a very slow penetration of tungsten towards the sphere center, as a consequence of obstruction in alumina pores.

When impregnations are made with ST solutions of increasing concentrations, the shapes of profiles thus obtained do not change, though total concentration does increase. In profiles obtained from long time impregnations, an increase of the total tungsten concentration is verified, although the type of profile obtained remains unchanged.

From the diffuse reflectance spectra of impregnated spheres, it can be deduced that the species present in the calcined samples is mainly the monomeric one, which is distorted due to interactions with the alumina. The characterization of the solid allowed us to conclude that the thermal treatments applied to the samples lead primarily to WO_4^{2-} monomeric species, regardless of the precursor used in the impregnating solution. Therefore, the same species is present in different macroscopic distributions.

Likewise, the use of different precursors allows the preparation of W/Al_2O_3 catalysts with predetermined concentration profiles, i.e. either flat or "egg shell". The profile shape leading to the best yields depends on the reaction control mechanism, and on the possible presence of deactivating species. The mass transfer can influence the kinetics of hydrotreating reactions and the catalyst fouling during the operation may increase mass transfer limitations. Even though the conditions were adjusted to minimize fouling, since the molecules to be hydrotreated can be of different size, mass transfer in a fixed pore structure will vary. The small size and high mobility of molecules as thiophene can be expected to lead to a great penetration into the pellets. As a result, tungsten deposited near the center of the pellet may catalyse the hydrodesulphurization of thiophene but not the hydrotreating of molecules as phenanthrene because their concentration, limited by mass transfer, will be low in the center. Otherwise, the optimal catalyst distribution for stability with respect to poisoning depends on the way of poison deposition.

Measurements of the hydrotreating activity of the catalysts prepared, promoted by Ni, are being carried out to correlate it with the precursor type used and the concentration profile to be obtained. The relative merits of different distribution patterns will be examinated using a feedstock with molecules of different size in which hydrotreating can occur.

References

[1] E. Furimsky, Catal. Rev. Sci. Eng. 22 (1980) 371.

[2] T. Sahin, L. Berg and F.F. Mc Candless, Ind. Eng. Chem. Proc. Des. Dev. 23 (1984) 195.
[3] N. Komiyama, Catal. Rev. Sci. Eng. 27 (1985) 341.
[4] L.L. Hegedus and J.G. Summers, J. Catal. 48 (1977) 345.
[5] A.M. Maitra, N.W. Cant and D.L. Trimm, Appl. Catal. 27 (1986) 9.
[6] C. Mauchausse, E. Kural, D.L. Trimm and N.W. Cant, Fuel 71 (1992) 203.
[7] L.R. Pizzio, C.V. Cáceres and M.N. Blanco, Adsorp. Sci. Technol. 9 (1992) 36.
[8] L.R. Pizzio, Thesis, Universidad Nacional de La Plata, Argentina (1994).
[9] P.G. Vázquez, Thesis, Universidad Nacional de San Luis, Argentina (1993).
[10] H. Vituro, D. Bonetto, L.R. Pizzio, P.G. Vázquez, M. Sánchez and A.G. Alvarez, X-ray Spectrom. 24 (1995).
[11] P. Souchay, F. Chauveau and B. Le Meur, Compt. Rend. Acad. Sci. C 270 (1970) 1401.
[12] A. Iannibello, S. Marengo and P. Tittarelli, J. Chem. Soc. Faraday Trans. I 80 (1984) 2209.
[13] A.V. Neimark, L.I. Kheifets and V.B. Fenelonov, Ind. Eng. Chem. Prod. Res. Dev. 20 (1981) 439.
[14] L.R. Pizzio, C.V. Cáceres and M.N. Blanco, *Actas del XIV Simposio Iberoamericano de Cátalisis*, Concepción, Vol. 3 (1994) p. 1375.
[15] L.R. Pizzio, C.V. Cáceres and M.N. Blanco, Adsorp. Sci. Technol. 8 (1991) 142.
[16] D.L. Kepert, Progr. Inorg. Chem. 4 (1962) 199.
[17] L.R. Pizzio, C.V. Cáceres and M.N. Blanco, Adsorp. Sci. Technol. 11 (1995).
[18] A. Iannibello, P.L. Villa and S. Marengo, Gazz. Chim. Ital. 109 (1979) 521.
[19] Powder diffraction file, ed. Joint Committee on Powder Diffraction Standards.
[20] Powder diffraction file, 18-1418, ed. Joint Committee on Powder Diffraction Standards (1974).