TUNGSTEN AND RHENIUM AS HYDROGENATION AGENTS IN THE HYDRODENITROGENATION OF PYRIDINE USING STACKED BED CATALYST SYSTEMS

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ABSTRACT

This study analyses the hydrodenitrogenation (HDN) of pyridine using a stacked bed catalyst system, composed of a first hydrogenating bed of Re/ γ -Al₂O₃ or W/ γ -Al₂O₃, over a second bed of Ni-Re/ γ -Al₂O₃ (HDN bed). Using potentiometric methods, it can be seen that the Re/ γ -Al₂O₃ shows higher acidic strength than the W/ γ -Al₂O₃. The results show that higher activity levels are obtained working with stacked bed systems compared to the separate catalysts. These results suggest that the incorporation of the catalyst Re/ γ -Al₂O₃ or W/ γ -Al₂O₃ beds would favour the formation of hydrogenated intermediary products, facilitating the removal of N-containing molecules via HDN on the Ni-Re/ γ -Al₂O₃ catalyst.

Keywords: Hydrodenitrogenation (HDN); Hydrogenation; Stacked beds; Pyridine.

1. INTRODUCTION

In recent years, several different reports have shown that petroleum will continue to be one of the main energy sources until the year 2030 and that the global energy system will continue to be dominated by fossil fuels¹. However, as the high demand for petroleum is unavoidable, deeper search and exploitation of oil fields, obtaining heavier crude oil as a result, will lead to more difficult purification processes, particularly hydrotreatment (HT) processes. These processes contribute to decreasing atmospheric pollution caused by the combustion of petroleum and its derivatives. In addition, environmental regulations have forced the oil industry to reduce nitrogen and sulphur levels in fuels. In order to comply with these demands, is fundamental to find more active catalysts for HT processes than the classic Co-Mo/ γ -Al₂O₃¹ one. Specifically, one HT process, namely hydrodenitrogenation (HDN), has been the focus of study in recent years²⁻⁶, as many N-containing compounds that are resistant to HDN are present in petroleum, and mainly because these molecules inhibit hydrodesulphurisation (HDS) and other HT reactions⁷⁻⁹ due to preferential adsorption of such N-containing molecules on catalytic sites. Laredo et al.¹⁰ evaluated the inhibiting effect of nitrogenised compounds on the HDS of dibenzothiophene (DBT), reporting that the inhibiting effect of non-base nitrogen on indole and carbazole compounds in the HDS of DBT is comparable to that of base nitrogen compounds, such as quinoline. The inhibiting effect of these compounds is very strong, even at low concentrations close to 5 ppm of nitrogen. As a result, it is necessary to implement new catalyst systems that offer improved activity and selectivity for HDN. Therefore, in order to study HDN, different model molecules have been used¹¹⁻¹⁴, one of which is pyridine¹⁵⁻¹⁷. Valdebenito et al.¹⁷ worked with stacked bed systems in the HDN of pyridine, proving that it is possible to achieve this process through the formation of hydrogen spillover (Hso), generating an effect similar to that observed for the HDS reaction¹⁸⁻²³. This proposal is based on prior work by Ojeda et al.²⁴, who give direct proof of the hydrogen spillover effect, under conditions similar to those used in industry, and using gas oil as the feed source. This study reported the existence of synergism in the stacked bed systems of Co/SiO₂/SiO₂/Mo/SiO₂ (donor/separator/acceptor), where the donor and the acceptor were separated using the amount of SiO₂ needed to create a distance of 5 mm between the two beds. Under these conditions the synergism is determined only by the remote control model, via Hso, as there is no possibility of the formation of the Co-Mo-S phase.

Several studies have been carried out into the mechanism of the HDN of pyridine. McIlvried et al.²⁵ reported that the reaction is composed of three successive stages: hydrogenation of the pyridine ring, hydrogenolysis of the C-N bond forming pentylamine and denitrogenation to give the end products pentane and ammonia, where the hydrogenation is an essential step for achieving nitrogen removal. Anabtawi et al.²⁶ used an integral flow reactor to study the hydrogenation of pyridine in gaseous phase, using Ni-W/ γ -Al₂O₃ as catalyst, finding that pyridine hydrogenation follows three stages. The first is

saturation of the double bond of the pyridine to form piperidine, the second is disproportionation of the pyridine to produce ammonia and n-pentylpiperidine, and the third is the formation of n-pentane from the pentylpiperidine.

Considering that hydrogenation is one of the most important steps in the conversion of N-containing molecules, and that the hydrogenating properties of tungsten and rhenium have been proven in hydrotreatment reactions²⁷, the objective of the present study was to analyse the HDN reaction of pyridine in a stacked bed system composed of a first hydrogenating bed over a second HDN bed.

2. MATERIALS AND METHODS

2.1 Preparation of catalysts

All the catalysts were prepared as reported previously¹⁸⁻²³, using excess solvent impregnation for monometallic catalysts (Re/ γ -Al₂O₃ or W/ γ -Al₂O₃) and successive impregnation for bimetallic catalysts (Ni-Re/ γ -Al₂O₃ or Ni-Mo/ γ -Al₂O₃). As precursor salts, NH₄ReO₄ (Aldrich), (NH₄)₆MoO₂₄·xH₂O (Merck pa.) and (NH₄)₁₀W₁₂O₄₁·xH₂O (BDH Chemicals Ltda.) were used respectively. Ni was used as promoter, and was prepared from Ni(NO₃)₂·6H₂O (Merck pa.). The support for all catalysts was γ -Al₂O₃, BASF D10-10 (N₂ BET 212 m²g⁻¹) with a particle size of 0.84 and 1.19 mm. The nominal metal content of the precursors was 0.5, 1.5 and 3.0 atoms nm⁻² for the monometallic catalysts while for bimetallic catalysts, 1.6 atoms nm⁻² Ni, 2.9 atoms nm⁻² Mo and 0.5 atoms nm⁻² Re were used. After metal impregnation, the samples were dried at 373 K for 12 h. Subsequently, the impregnated samples with W or Mo were calcined at 823 K for 4.5 hours, while the Re catalyst was calcined at 573 K for 0.5 h.

2.2 Reaction conditions

Prior to carrying out the HDN of pyridine, each system (single and stacked bed) was *in situ* sulphided using a gas mixture of 10% H₂S/N₂ at atmospheric pressure and 623 K for 4 h.

Catalytic activity was measured as reported previously¹⁸⁻²³ using a stainless steel continuous-flow micro-reactor under conditions similar to those used in industry. Total H₂ pressure was 3 MPa and the reaction temperatures were 573, 598 and 623 K. The feed solution was a synthetic mixture of 5000 ppmv pyridine in decalin at a flow rate of 30 mL min⁻¹. The reactor was loaded as shown in Figure 1. For single beds, it was loaded with 1 g of catalysts (Ni-Re/ γ -Al₂O₃, Ni-Mo/ γ -Al₂O₃, Re/ γ -Al₂O₃ or W/ γ -Al₂O₃) and for stacked beds, 0.5 g of catalyst was loaded onto each of the beds, such that the hydrogenating bed (Re/ γ -Al₂O₃ or W/ γ -Al₂O₃) was above the HDN bed (Ni-Re/ γ -Al₂O₃), the stacked bed are represented as HYD bed/HDN bed. As in previous studies¹⁸⁻²³ beds were diluted with SiO₂ (BASF D11-10) at a v/v ratio of 1:1, and the remainder of the reactor was filled with SiC.

Under these conditions, four samples were taken every 30 min. The first and second were discarded and the third and fourth were analysed using GC-FID. After obtaining the fourth sample, the system temperature was lowered and the same sampling process was carried out for each reaction temperature.

Figure 1. Scheme of reactor loading in single bed (left) and stacked bed (right).

2.3 Activity measurements

The reaction products were identified by measuring the samples in a gas chromatograph provided with a flame ionization detector. The equipment used was a SHIMADZU GC-2010 model, with a SPB-5 column measuring 30 m in length, with a thickness of 0.25 mm and a film of 0.25 μm , 0.5 μL sample injections with an autosampler. The heating procedure was initiated, maintaining the column temperature at 333 K for 5 min. It was then increased to 373 K at a rate of 288 K min^{-1} and maintained at this temperature for 8 min. Finally, the temperature was increased to 473 K at a rate of 323 K min^{-1} , and maintained at this temperature for 2 min. The molecules present in the samples were identified by doping the feed with standard molecules of possible products that are expected from this catalytic reaction.

3. RESULTS AND DISCUSSION

3.1 Characterisation of monometallic catalysts

Optical emission spectroscopy with inductively coupled plasma (ICP) was used to determine the real metal content of the catalysts after preparation from the respective precursor salts. As can be seen in Table 1, there is close association between the nominal metal content and the real metal content by ICP.

Table 1. Metal content (determined by ICP) of the catalysts.

Catalyst	Theoretical loading (atoms nm^{-2})	Measured loading (atoms nm^{-2})
W(0.5)/ $\gamma\text{-Al}_2\text{O}_3$	0.50	0.47
W(1.5)/ $\gamma\text{-Al}_2\text{O}_3$	1.50	1.41
W(3.0)/ $\gamma\text{-Al}_2\text{O}_3$	3.00	2.67
Re(0.5)/ $\gamma\text{-Al}_2\text{O}_3$	0.50	0.44
Re(1.5)/ $\gamma\text{-Al}_2\text{O}_3$	1.50	1.43
Re(3.0)/ $\gamma\text{-Al}_2\text{O}_3$	3.00	2.69

The acidity of the surface of the oxidised catalysts was determined by potentiometric evaluation with *n*-butylamine in acetonitrile using an Ag/AgCl electrode, in accordance with a procedure described previously²⁸. Figure 2 shows the acid strength results, in which it can be seen that in the studied range of metallic content the Re/ $\gamma\text{-Al}_2\text{O}_3$ catalyst shows higher acid strength than the W/ $\gamma\text{-Al}_2\text{O}_3$ one. This is because the Re/ $\gamma\text{-Al}_2\text{O}_3$ has a greater capacity for converting a base into its acid conjugate than the W/ $\gamma\text{-Al}_2\text{O}_3$ one.

Therefore, it can be concluded that these catalysts have metal loadings in agreement with the nominal values and that both the tungsten and the rhenium catalysts supported on $\gamma\text{-Al}_2\text{O}_3$ are acidic. Indeed, acidity can play a crucial role in the adsorption of nitrogenised molecules²⁹, thus facilitating pyridine conversion.

3.2 Sample analysis and activity results

Figure 3 shows a section of the chromatogram obtained after the HDN of pyridine using Ni-Re/ $\gamma\text{-Al}_2\text{O}_3$ as catalyst. With the use of a standard, the identified molecules were pentylamine and pentane as the hydrogenation and HDN products at retention times 1.15 and 1.60 min, respectively. The

unreacted pyridine was observed at retention time 1.90 min. These products are in agreement with the reaction mechanism proposed by McIlvried et al.²⁵ (Figure 4), who stated that to obtain the above reaction products, piperidine must be first formed. However, piperidine was not detected in the present study, as this molecule is very unstable. Once it is formed, and converted rapidly to pentylamine or pyridine.

Figure 2. Acid strength of the catalysts W(x)/ $\gamma\text{-Al}_2\text{O}_3$ and Re(x)/ $\gamma\text{-Al}_2\text{O}_3$.

Figure 3. Chromatogram obtained after HDN of pyridine using Ni-Re/ $\gamma\text{-Al}_2\text{O}_3$ as catalyst.

Figure 4. Reaction mechanism for the HDN of pyridine²⁵.

In order to determine the effect of intercalation of a hydrogenating bed over the HDN catalyst it was necessary to evaluate the conversion and selectivity of each catalyst in a single bed system and then evaluate the same parameters in a stacked bed system.

The extent of pyridine HDN reaction was evaluated for each catalytic system by measuring pyridine concentration at the inlet and exit of the reactor. These results are reported in Table 2 as pyridine conversion (Py) and formation

of reaction products, were calculated as follows: % Py conversion: $((Py_o - Py_m) / Py_o) \times 100$ and % product formation: $(Pe(Pa/P)) \times 100$, where Py_o is the area of the pyridine chromatogram peak seen in the feed, Py_m is the area of the pyridine after the catalytic reaction, Pe is the area of pentane, Pa is the area of the pentylamine and P is the sum of the area of the reaction products.

Table 2 shows the pyridine conversion percentages and the relative product formation percentages for the monometallic catalysts, $Re/\gamma-Al_2O_3$ and $W/\gamma-Al_2O_3$, and for the bimetallic $Ni-Re/\gamma-Al_2O_3$ and $Ni-Mo/\gamma-Al_2O_3$ catalysts. Initially, the performance of the monometallic catalysts was evaluated. Table 2 shows the effect of the metal content of the $Re(x)/\gamma-Al_2O_3$ and $W(x)/\gamma-Al_2O_3$ in the intercalated catalysts beds on pyridine conversion. Table 2 shows that as the metal content increases, higher pyridine conversion rates are obtained. This behaviour is displayed for both catalysts. It can also be seen that for all metal loadings, the rhenium has higher pyridine conversion rates than tungsten. This result is in line with the acid strength data shown in Figure 1 which indicate that $Re(x)/\gamma-Al_2O_3$ catalysts presented a higher number of acidic sites. The reaction products formed using these catalysts at different metal content levels are shown in Table 2. In these cases, the HDN reaction proceeds were pentane and pentylamine. Comparing the two catalysts, it can be stated that the $Re(x)/\gamma-Al_2O_3$ catalyst favours hydrogenation as confirmed by the greater formation of pentylamine, because the $Re/\gamma-Al_2O_3$ catalyst has high hydrogenating properties²⁷. Based on these findings, it was interesting to see what happens when using $Re/\gamma-Al_2O_3$ as the upper bed in the stacked bed system.

It is also important to evaluate the results obtained for the bimetallic catalysts. In Table 2 it can be seen that for the $Ni-Re/\gamma-Al_2O_3$ catalyst the pyridine conversions at all temperatures are higher than those obtained with the $Ni-Mo/\gamma-Al_2O_3$ one. This is interesting, because the $Ni-Mo/\gamma-Al_2O_3$ catalyst is the most commonly used system in petroleum hydrotreatment. It is also necessary to evaluate what happens with the reaction products for each catalyst system. The data collected in Table 2 show that the $Ni-Mo/\gamma-Al_2O_3$ catalysts favours pentane formation, while for the $Ni-Re/\gamma-Al_2O_3$ system, both pentane and pentylamine are formed. The formation of pentylamine is in line with the products observed for the $Re/\gamma-Al_2O_3$ catalyst, because rhenium favours pyridine hydrogenation to a greater extent. Considering that $Ni-Re/\gamma-Al_2O_3$ is more active than the conventional $Ni-Mo$ one, it was then of interest to use $Ni-Re/\gamma-Al_2O_3$ as the lower bed in the stacked bed catalyst systems.

Table 2: Conversion of pyridine and formation of reaction products at 623 K.

Bed	Pyridine Conversion (%)	Relative Products Conversion (%)	
		Pentylamine	Pentane
Ni(1.6)-Mo(2.9)/$\gamma-Al_2O_3$	37.7	0.0	100
Ni(1.6)-Re(0.5)/$\gamma-Al_2O_3$	63.7	15.8	84.2
W(0.5)/$\gamma-Al_2O_3$	55.7	36.9	63.1
W(1.5)/$\gamma-Al_2O_3$	57.2	24.3	75.7
W(3.0)/$\gamma-Al_2O_3$	67.0	23.5	76.5
Re(0.5)/$\gamma-Al_2O_3$	60.8	50.7	49.3
Re(1.5)/$\gamma-Al_2O_3$	70.5	55.7	44.3
Re(3.0)/$\gamma-Al_2O_3$	81.1	73.3	26.7

Based on the results described in Table 2, $Re/\gamma-Al_2O_3$ catalyst was selected as the hydrogenating bed over the catalyst $Ni-Re/\gamma-Al_2O_3$, forming a stacked bed catalyst system. The $Re/\gamma-Al_2O_3$ catalyst selected for this system showed a rhenium content of 0.44 atoms nm^{-2} , because the growth in catalytic activity above Re loadings of 0.44 atoms nm^{-2} is no longer linear, and it is therefore not economically viable to use higher rhenium content levels.

Another observation that can be made from the data collected in Table 2 is that the pentane formation of $Ni-Re/\gamma-Al_2O_3$ catalyst is higher than for the $Re(0.44)/\gamma-Al_2O_3$ one, which is expected because in the bimetallic $Ni-Re(0.44)/\gamma-Al_2O_3$ catalyst the Ni promotes the catalytic activity of Re ²³.

Figure 5 represents the pyridine conversions at three temperatures, with the following contents within the reactor:

- Only the catalyst $Re/\gamma-Al_2O_3$, the mass of $Ni-Re/\gamma-Al_2O_3$ is 0.0 g,
- Only the catalyst $Ni-Re/\gamma-Al_2O_3$, the mass of $Ni-Re/\gamma-Al_2O_3$ is 1.0 g, and
- Stacked beds of $Re/\gamma-Al_2O_3//Ni-Re/\gamma-Al_2O_3$, the mass of $Ni-Re/\gamma-Al_2O_3$ is 0.5 g.

It is important to note that the total mass of the catalyst(s) within the reactor was maintained constant at 1.0 g, and therefore if there was no synergism between the two beds ($Re/\gamma-Al_2O_3$ and $Ni-Re/\gamma-Al_2O_3$) they would have the same level of activity as the sum of their separate characteristics, which is shown by the dotted line.

Figure 5. Conversion percentage of pyridine in $Re(0.44)/\gamma-Al_2O_3$, $Ni-Re/\gamma-Al_2O_3$ singles beds and $Re(0.44)/\gamma-Al_2O_3//Ni-Re/\gamma-Al_2O_3$ stacked bed system.

Figure 5 shows that the activity of the stacked beds is greater than the simple beds, as they give a higher value than the corresponding sum shown by the dotted line. Therefore, it is possible to state that the intercalation of a hydrogenating rhenium bed favours pyridine conversion of the catalyst $Ni-Re/\gamma-Al_2O_3$.

It is also interesting to know which reaction products are formed, in order to establish whether it is possible to favour the conversion of the products of the HDN of pyridine, i.e. pentane. Figure 6 shows the pentane formation results for the stacked bed system $Re(0.44)/\gamma-Al_2O_3//Ni-Re/\gamma-Al_2O_3$. It can be seen that the use of a hydrogenating catalyst over $Ni-Re/\gamma-Al_2O_3$ favours the formation of pentane, as the pentane formation percentages for the stacked beds are higher than those obtained for the single beds at all working temperatures. This is probably due to the fact that the $Re(0.44)/\gamma-Al_2O_3$ favours the formation of intermediate pentylamine which facilitates the removal of nitrogen in the catalyst $Ni-Re/\gamma-Al_2O_3$, thus obtaining higher pentane formation levels.

Figure 6. Conversion percentage to pentane in $Re(0.44)/\gamma-Al_2O_3$, $Ni-Re/\gamma-Al_2O_3$ singles beds and $Re(0.44)/\gamma-Al_2O_3//Ni-Re/\gamma-Al_2O_3$ stacked bed system.

4. CONCLUSIONS

The study of Ni-Re/ γ -Al₂O₃ and Ni-Mo/ γ -Al₂O₃ catalysts shows that the Ni-Re/ γ -Al₂O₃ one gives higher levels of pyridine conversion, yielding pentane and pentyamine as end products. This result emphasizes the hydrogenating properties of rhenium, which is a fundamental step in the HDN of pyridine. The catalyst Ni-Mo/ γ -Al₂O₃ shows lower pyridine conversion levels, however it does achieve pyridine conversion exclusively to pentane.

The study shows that both Re/ γ -Al₂O₃ and W/ γ -Al₂O₃ catalysts favour pyridine hydrogenation, the Re/ γ -Al₂O₃ shows more activity and a higher hydrogenating capacity than W/ γ -Al₂O₃. Finally, the study conducted using stacked bed catalyst systems clearly shows that the Re/ γ -Al₂O₃ bed favours the hydrogenation of pyridine, facilitating catalyst Ni-Re/ γ -Al₂O₃ the elimination of nitrogen.

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