Hydrodenitrogenation of Quinoline on Ni-Mo and Co-Mo Catalysts

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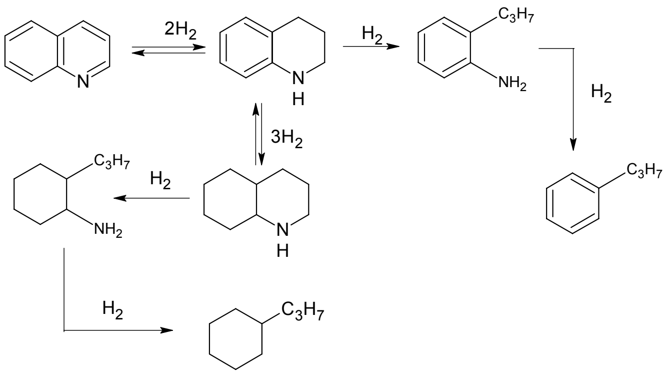
Introduction

In this work we studied the activity of Ni-Mo and Co-Mo catalysts in the Hydrodenitrogenation reaction of quinoline (HDN). Pilot plant studies were carried out and we measured the effect of space velocity (LHSV), hydrogen/hydrocarbon ratio (H_2/Hc) and temperature reaction in quinoline conversion. Quinoline was diluted in industrial straight run naphta.

The Hydrodenitrogenation reaction involves the selective removal of nitrogen contained in insaturated polycyclic compounds. The reported results of this reaction indicate that it is carried out on the catalytic surface [1].

The reaction mechanism of HDN reaction is sequential, involving similar hydrodesulfurization (HDS) reaction mechanisms [2]. The HDN proceeds through two alternative steps (Figure 1): 1. Starting with reversible hydrogenation followed by a terminal hydrogenolisis. The adsorption of nitrogen occurs on catalytic surface after the ring has been opened up for hydrogenation. 2. An alternative step continues trought the hydrogenation of aromatic ring and then, the breakage of C-N bond [3, 4].

Figure 1 Hydrodenitrogenation reaction mechanism for quinoline



Experimental

Operating conditions for pilot plant tests are included in Table 1. They were settled down considering information from industrial units at Salamanca Refinery.

They are in the operation range of most of the units HDS of this type of cut.

Table 1 Operating conditions for pilot plat testing

Variable	**Value**
Temperature, °C	270 to 320
Pressure, kg/cm^2	22
H_2/Hc ratio, m^3/B	10 to 20
LHSV, h^{-1}	5 to 7

Ni-Mo and Co-Mo IMP´s commercial catalysts were used. Feedstock used was industrial straight naphtha contaminated with quinoline in order to get 5 ppm weight of nitrogen.

Results and discussion

Effect of Temperature: The results show that quinoline conversion is increased when the temperature is increased. This effect is more pronounced in the Co-Mo catalyst. Ni is more active for hydrogenation, therefore the reaction rate constant is less sensitive to reactor temperature.

Effect of Space Velocity: Increasing feedstock time of contact increases quinoline conversion. The results show that Ni-Mo catalyst is more active than Co-Mo catalyst. However, the conversion Co-Mo catalyst is more sensitive to increments in LHSV.

Effect of H_2/Hc ratio: The presence of higher amounts of hydrogen in the reactor favors quinoline removal. For Co-Mo catalyst the slope of the curve is more pronounced. A small increment in H_2/Hc ratio increases nitrogen removal substantially. On the other hand, for Ni-Mo catalyst, because of its higher activity for hydrogenation, the slope is less pronounced, it holds always high quinoline conversion.

The obtained results show that Ni-Mo catalyst is more active than Co-Mo catalyst in the HDN reaction of quinoline. Due to its lower activity, Co-Mo catalyst is more sensitive to variations in temperature, space velocity and H_2/Hc ratio. The combined effects of increasing time of contact and higher hydrogen partial pressure confirm the two alternative reaction paths for conversion of nitrogen compounds in the hydrotreatment process: The insaturated ring hydrogenation that contains the nitrogen atom followed by the adjacent aromatic ring hydrogenation.

The increment of conversion with temperature indicates that the reaction is not limited by thermodynamic effect in the hydrogenation step.

References

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