Use of Ni Based Catalyst for Toluene Hydrocracking

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Introduction

Due to the increasing use of heavy crude oils and its derivates there is a surplus of low quality and unfriendly to the environment streams on different stages of crude oil refining. A typical example is pyrolysis gasoline, a byproduct from ethylene plants, which is rich in aromatics. This environmental hazard could be transformed in an opportunity to produce higher value hydrocarbons such as light paraffins to be used as feedstock for petrochemical processes [1]. For this purpose hydrocracking of aromatics have been tackled using bi-functional catalysts, which have a hydrogenating function mostly performed on the metal and a cracking function that is carried out by an acidic support [2].

Typical metals used on these catalysts are noble metals, namely Pd and Pt. These metals are not only expensive but also easily deactivate in the presence of sulphur or nitrogen molecules [3]. There is a great debate about the effect of catalyst preparation on reactivity. In a previous work, the incorporation of high metal load via incipient wet impregnation (WI) and solid state ion exchange (SS) was studied in the hydroconversion of n-nonane [4]. Zeolites have been proven as a desirable support for this process because of its tailored acidity, its ability to restrict isomerization, alkylation, and the formation of coke avoiding the deactivation of the catalyst, the possibility of industrial production, and its high surface area that assure a high dispersion of the metallic phase on the potential catalyst. In the present work we have studied the effect of WI and SS in the incorporation of Ni in a MFI-type zeolite for hydrocracking of toluene

Materials and Methods

Ni based catalysts have been prepared via two methods, Incipient Wet Impregnation and Solid State Ion Exchange. Ni nitrate was the precursor salt employed to obtain a load of 1 wt% of Ni. A ZSM-5 with a Si/Al ratio of 15 supplied by Lopez C. M. [5] was used as support. The materials were characterized by X-Ray Difraction (XRD) to verify the ZSM-5 structure, Scanning Electron Microscopy (SEM) to study the morphology of the support and the catalysts, EDS to get the real Si/Al ratio and the Ni content of the final catalysts, ^{27}Al NMR to get some insight in the nature of the coordination of Al in the catalyst. The toluene hydrocracking activity of the catalysts prepared was tested by using 500 mg of sample in a fixed bed reactor at 400 ºC, a WHSV (h^{-1}) of 0.7, a total pressure of 6 MPa. After reaction gases and liquids (if produced) are directed to be analyzed by Gas Chromatography.

Results and Discussion

XRD results showed a ZSM-5 zeolite structure in our support, this structure is stable after calcination and metal loading. Moreover, the diffractograms do not show the formation of any Ni phase in the catalysts, this could be due to the low load used and/or that the Ni particles formed are sufficiently small to not produce a XRD pattern. There is not a big change in surface area between the calcined zeolite, 290 m^2/g, and the final catalyst with a load of 1% of Ni, has a surface area of 310 m^2/g. This is an indication that the metal load is not blocking the surface of the support, which will allow enough acid sites to perform the cracking of the previously hydrogenated hydrocarbons on the metal sites.

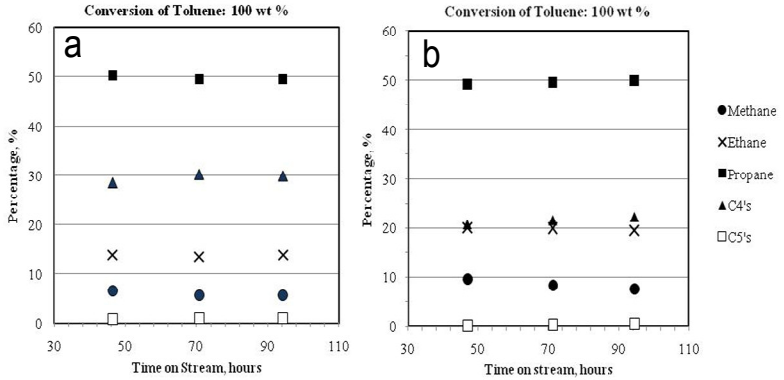

Figure 1. Hydrocracking of toluene on 1% Ni load catalysts.

Both catalysts, under the conditions we used to perform the test, totally hydroconverted toluene while producing only light paraffins (C_1 to C_4's). The selectivity towards propane in both cases is similar, and close to 50%. Since ethane and methane are produced via secondary cracking it seems that the catalyst prepared by WI (Fig 1b) has a higher cracking activity, and maybe stronger acidity, than the one prepared by SS (Fig 1a). The total productivity of light paraffins (C_2-C_4's) ranged from 90 to 95 wt%.

Significance

The present work is promising in the use of non-noble metals in such important process as the hydrocracking of aromatics rich streams.

References

1. De Plessis, D., Laureshen, C. 1st World Heavy Oil Conference, Beijing China, November 2006.
2. Scherzer, J., Gruia, A. J. in "Chemical Hydrocracking Science and Technology", p. 305. Marcel Dekker, New York, 1996.
3. Weitkamp, J., Ernst, S., Bock, T., Kromminga, T., Kiss, A., Kleinschmit, P. 1996, *US Patent # 5,529,964*.
4. Kinger, G., Lugstein, A., Swagera, R., Ebel, M., Jentys, A., and Vinek, H. *Microporous and Mesoporous Materials* 39, 307 (2000).
5. Lopez C. M., Scott J. *Department of Chemistry Universidad Central de Venezuela.*