Hydrodesulfurization Kinetics under Diffusion Limitation-Free Conditions on Planar Model HDS Catalysts.

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Introduction

Hydrodesulfurization (HDS) is one of the largest processes in petroleum refining to produce clean transportation fuels. In recent years, HDS has gained importance due to more stringent legislations for vehicular emissions and fuel quality and an increasing need to process low-quality oils, which contain larger amounts of sulfur compounds.
Most studies on HDS kinetics were performed using model sulfur compounds such as thiophene, benzothiophene and dibenzothiophene. Although thiophene hydrodesulfurization has been widely studied and is one of the simplest HDS reactions, the kinetics and the reaction mechanism are still debated. Most kinetic studies were performed in a restricted temperature range and usually at low temperature, i.e. lower than 350 °C, in order to avoid diffusion limitations. The kinetic parameters reported in the literature strongly depend on the reaction conditions and the nature of the catalysts. This fact clearly indicates that no reliable kinetic data are available for this reaction and, therefore, kinetic studies over a broad temperature range and without diffusion limitations are required.
The use of planar model catalysts has several advantages in kinetic studies. One of the main benefits is that catalytic measurements can be performed under diffusion limitation-free conditions. Thus, the intrinsic kinetic parameters can be obtained, giving insight into the reaction kinetics and mechanism. The aim of this work is to use planar model catalysts for a full kinetic study under diffusion limitation-free conditions for the gas-phase HDS of thiophene.

Results and Discussion

Planar model catalysts consisting of a silicon disc covered by a thin layer of SiO_2 as support were prepared by spin-coating as previously described (1). This approach successfully mimics the pore volume impregnation technique normally applied for industrial hydrotreating catalysts.
Thiophene HDS measurements were carried out on Ni-Mo/SiO_2 model catalysts. Catalytic experiments were performed in batch mode at a total pressure of 1.5 bar. About 5 cm^2 of a NiMo/SiO_2 model catalyst was placed in a glass reactor and sulfided at 400 °C. Then, a thiophene/H_2 mixture was passed through the reactor at the desired reaction temperature. After 5 min, the reactor was closed and operated as a batch reactor. After 1 hour, a sample was taken from the reactor with a chromatographic syringe and then analyzed by GC.
We have studied the thiophene hydrodesulfurization over a broad temperature range (300-400 °C). Catalytic measurements at different H_2, thiophene and H_2S partial

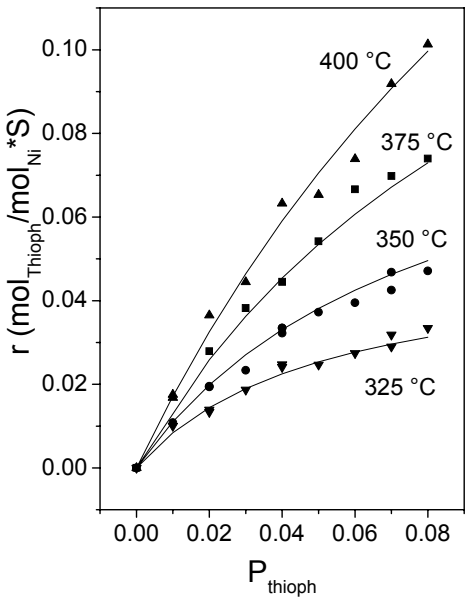

Figure 1 Catalytic activity for thiophene HDS vs. thiophene partial pressure at different temperatures. Experimental data (points) and L-H fitting (solid lines)

pressure were performed. The kinetic data were analyzed considering both power-law and Langmuir-Hinshelwood (L-H) kinetics. At 400 °C, positive orders in thiophene and hydrogen, 0.8 and 0.93 respectively, and a moderately negative order in H_2S, -0.4, were obtained. These results are in line with a relatively strong adsorption of thiophene and competitive with H_2S.

A more detailed analysis consisted of assuming a two sites reaction mechanism, in which thiophene exclusively adsorbs on sulfur vacancies and H_2 adsorbs dissociatively on all the sites. The experimental data were satisfactorily fitted with this L-H kinetic and the values of the adsorption constants at 400 ° C are: 3.5 bar^{-1} for thiophene, 23.9 bar^{-1} for H_2S and close to zero for H_2. These values clearly indicate a relatively strong adsorption of thiophene and in particular H_2S, while hydrogen is very weakly adsorbed.

Figure 1 displays the experimental data (points) as a function of the thiophene partial pressure, obtained at different temperatures. Fitting with a L-H kinetic model leads to the equilibrium constant K_T for the adsorption of thiophene and the intrinsic kinetic constant k, which allow for the calculation of both the heat of adsorption of thiophene and the activation energy. Figure 1 also shows the quality of the fitting (solid lines), obtained using non-linear multivariable regression. From this fitting, the estimated value of the activation energy is 83.3 ± 7.3 kJ/mol over the analyzed temperature range. The estimated value for the heat of adsorption of thiophene is –57.8 ± 10.9 kJ/mol. These values offer a significant improvement over data reported in the literature because they were obtained in a broad temperature range and under diffusion-free limitations.

It should be emphasized that, as far as we know, these are the first kinetic experiments performed on a square centimeter model of an industrial catalyst. This work demonstrates how measuring intrinsic kinetics on planar surface science models can become an important tool to unravel the mechanisms of catalytic reactions. Therefore, planar model catalysts offer an excellent opportunity to study reaction mechanism and kinetics without diffusion limitations.

References

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