Chemistry and Kinetics of Gasoline Sulfur Reduction

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Regulations to reduce the sulfur level in gasoline to less than 50 wppm are in place or planned in many countries. The primary source of sulfur in gasoline is FCC cat naphtha, which contributes approximately 50 wt% of gasoline pool volume but nearly 95% of gasoline sulfur. Critical to the economics of any gasoline desulfurization process is the ability to effectively remove sulfur from the mercaptans, thiophenes, and benzothiophenes in FCC naphtha without saturating the important high octane olefins present. Several processes have been developed to meet these goals and have seen broad commercial application. For example, ExxonMobil's SCANfining I and II processes have over 1 MBD of committed or installed world-wide capacity. Three critical steps are typical parts of most commercial FCC naphtha HDS processes. The first of these is a step designed to react or remove the mercaptan sulfur found in the lightest fraction of FCC naphtha (LCN, C₅-75 C) without saturating the large amount of important C_5/C_6 olefins in this boiling range. The second critical step is a selective HDS process to maximize the desulfurization of thiophenic sulfur, while minimizing the saturation of important C_7/C_8 olefins in intermediate or combined intermediate/heavy cat naphtha. Selective HDS of ICN and ICN/HCN requires combination of optimized process conditions and selective catalyst (for example RT-225) technology to maximize thiophene HDS while minimizing olefin saturation. The third critical process step involves minimizing formation or converting mercaptans formed through reaction of product H₂S with feed olefins (mercaptan reversion). Examples of all three critical process steps in selective HDS will be discussed, including kinetic and mechanistic aspects of selective cat naphtha HDS.