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Preface

Effect of support in hydrotreating catalysis for ultra clean fuels

Industrial development brought with its prosperity environmental pollution [1]. While major advances have been achieved in reducing automotive vehicle emissions, transportation vehicles with hydrocarbon fuels still contribute significantly to air pollution through the emission of SO_x and NO_x, which are well known health hazards. Sulfur and nitrogen species present in fuels lead to SO_x and NO_x emissions after combustion in IC engines. Sulfur content is also related to the particulate emissions from IC engines. It has been realized that the best way to control SO_x and NO_x emissions is to produce ultra clean fuels in the refinery. Consequence of such thinking is stringent environmental regulations on fuels, especially transportation fuels, by various governments around the world. The sulfur content in the motor fuels is continuously reduced by regulations to lower and lower levels. New sulfur limits of 30–50 ppm in gasoline and diesel marketed in Europe and USA will be introduced starting from January 2005. The sulfur in diesel fuel will be reduced to as low as 15 ppm by regulation in the USA in 2006. Germany will limit the sulfur in diesel and gasoline down to 10 ppm. In addition, fuels for fuel cell applications such as proton exchange membrane fuel cells demand the sulfur levels close to zero. Zero sulfur emissions and near zero sulfur fuels are desired in the future [2,3].

Ultra clean transportation fuels is a topic of enormous interest in petroleum and automotive industries and research community worldwide. Stricter fuel specifications demand redrawing of refinery flow sheets with inclusion of desulfurization units at many stages of petroleum refining. The challenges in producing ultra low sulfur fuel in an economically affordable fashion are among the main reasons for refineries to upgrade existing technologies and develop new technologies including catalysts, processes, and reactors. The development and application of more active and stable catalysts are among the most desired options because they can enhance the productivity and improve product quality without negative impacts on capital investment. On the other hand, it is difficult to meet the ultra-low-sulfur challenge through incremental improvement in HDS catalyst activity. Calculations revealed that to meet such stringent sulfur specifications from 500 to 0.1 ppm sulfur, require about seven times more active catalysts [2]. In addition to sulfur, to meet density, polyaromatics and T_{95} specifications simultaneously may demand even more active catalysts.

There are many approaches to prepare better catalysts to meet these challenges, like changing the active component, varying the preparation method and changing the support or such permutations and combinations. In recent years, there has been heightened interest in new supports for the HDS catalysts, due to the need to develop better catalysts, and the availability of large number of new materials of high surface area that may be suitable for support application, as well as the initial success in increasing the activity by using novel supports. For a support to see commercial applications, it is not enough to have suitable chemical characteristics; it should also have proper physical and mechanical properties in order to withstand the rigors of high-pressure operation and regeneration in commercial reactors.

Effect of support on catalytic actions is an intriguing topic [5]. The alteration of catalytic activities due to support may arise as a result of important factors like variation in dispersion and morphology of active component and possible metal support interactions.

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Ideally, one would like to have every atom of the active component to be present on the surface. The dispersion of active components is also a function of metal support interaction and there is always an optimum interaction for a support-active component pair. Increase in dispersion and decrease in particle size alter the proportion of edge and corner atoms and the anion vacancies that are associated with it on the sulfided phase. Support can also influence the reactivity by favoring exposure of some crystallographic planes in preference to other by edge bonding or basal plane bonding of the sulfided phase. This can manifest as mild perturbation of electronic levels to subtle alteration of electron acceptor and donor abilities of the active sites. Morphological changes and metal support interactions that the support induces may change the activity and/or selectivity of the catalysts. In reality various morphological changes, metal support interactions present themselves in innumerable ways in HDS catalysis. More often both electronic and geometric effects contribute to the observed activity which are difficult to distinguish and assess separately.

Understanding support effects in HDS is intimately connected with other areas of HDS related research, such as structure of the catalyst and origin of catalytic functionalities. This in turn depends on knowledge about accurate description of active site. Once one is sure of what constitutes active site it becomes easier to establish role of the support. Support has an indirect role in determining the promotional effect by altering the number of promoted atoms that can be accommodated at the edges and the energetics of the site with which promoter is associated. Another aspect that can shed light on support effect is knowledge about the forces that bind the active component to the support, especially in sulfided state. Detailed knowledge about support effects, active sites, nature of promotion and dependence of catalytic functionalities on the above said parameters will help to prepare more effective catalysts for ultra deep desulfurization of gasoline and diesel.

γ-Al_2O_3 is the only support that is being used in most commercial HDS catalysts [4]. Before the 1980s, the alternative supports other than γ-Al_2O_3 that were used in most of the investigations were SiO_2 and SiO_2–Al_2O_3. The use of carbon-supported catalysts which showed outstanding activities for HDS reaction at laboratory level, stimulated some research interest in such systems. Availability of methods to prepare oxides such as ZrO_2, TiO_2, MgO with high surface area generated more interest on these materials as supports. These materials when used as supports could impart four to five times higher activities in Mo and W catalysts. To take advantage of their high intrinsic activities mixed oxides such as TiO_2–Al_2O_3, ZrO_2–TiO_2 supports figured in many investigations. In the recent years mesoporous materials such as MCM-41, zeolite supported catalysts and hydrotalcite derived catalysts received considerable attention due to their potential for possible application in ultra deep desulfurization. Carbon-supported systems [5,6] and oxides and mixed oxides as supports were reviewed a decade ago [7,8]. Since then a wealth of information on support effects accumulated from research efforts from active groups all over the world.

This special issue is brought out with an aim to review the state-of-the-art knowledge on support effects with special reference to clean fuels and identify new directions of research relating to scientific and technological aspects on desulfurization area. The articles published here will contribute immensely to the body of knowledge of HDS catalysts. We trust the special issue will stimulate further research and generate new ideas in addition to summarizing the state-of-the-art knowledge in this important area. It is hoped that the readers will enjoy reading these communications.

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