

Transition Metal Sulphide Catalysts for Petroleum Upgrading

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Editorial

Environmental catalysis researchers across the globe have been concentrating their efforts on the development of catalytic systems capable of reducing the sulphur content of petroleum feedstocks to levels globally established by recently enacted environmental protection laws. In this regard, the maximum sulphur content present in diesel fuel to produce Ultra Low Sulphur Diesel (ULSD) has been set at 10 ppm in the European Union since the beginning of 2009, when the Euro V fuel standard directive went into effect. Because transition metal sulphides (TMS) are known to be efficient systems for catalysing hydro treating reactions, they have traditionally been used as active phases in hydro treating catalysts. Concretely, cobalt or nickel-promoted molybdenum–tungsten sulphides are well established as the active species for commercial hydrodesulfuration (HDS) catalysts, with porous-alumina as the primary support. Although the nature of the active phase has hardly changed over many decades, amelioration has been achieved by modifying the properties of these sulphide systems. One area of current research is the use of new types of supports.

According to research on nickel sulphide catalysts, supports such as Al_2O_3 strongly interact with Ni^{2+} ions, preventing sulfidation. Ni^{2+} -alumina interactions can be weakened by using carriers like alumina-pillared compounds, in which aluminium oxide is diluted within a layered inorganic matrix, resulting in permanent porosity. These materials were used as catalyst supports in hydro treating reactions, yielding intriguing results. Mesoporous silica sieves, on the other hand, have emerged as a viable alternative to alumina due to their hexagonal array of uniform mesopores and very high surface area, presenting potential catalytic application for reactions involving bulky molecules, such as hydro desulfurization of petroleum fractions.

Similarly, HMS type materials have been extensively researched in this type of reaction. Intercalation of heteroatoms such as Al, Ti, Ga, or Zr into the silica framework not only improves material stability but also generates new acid, basic, or redox functions, allowing them to be used in new fields of catalysis. Thus, zirconium doped mesoporous silica with high surface area, mild acidity, and high stability has shown promising properties

as a support for catalytic fuel processing in reactions such as tetralin hydrogenation, hydrogenolysis, and hydrocracking. The use of SBA-15 as a support for hydro treating catalysts has several advantages over HMS and MCM-41 mesoporous solids, because SBA-15 material has thicker pore walls and better hydrothermal stability, both of which are critical properties in hydro treating processes due to the harsh reaction conditions used. Pecoraro and Chianelli's pioneering work revealed the high catalytic activity of bulk transition metal sulphides (TMS). Such metals were plotted on a curve known as a "volcano plot," which plotted HDS activity per mole of metal versus M-S bond strength, with the RuS_2 phase being the most active.

On the one hand, its activity was reduced to metallic ruthenium under the reducing conditions used in the catalytic test, and if it is supported on alumina, sulfiding temperatures greater than 773 K are required to form the RuS_2 phase with pyrite-like structure, which is the true active phase for hydrotreating reactions. Nevertheless, it has been disclosed that a $\text{Ru}/\text{Al}_2\text{O}_3$ catalyst sulfided in 100% H_2S at 673 K had approximately 7-fold higher thiophene conversion rates than a $\text{CoMo}/\text{Al}_2\text{O}_3$ catalyst when the active area's surface is considered. This describes perfectly how many factors must be considered during the synthesis of ruthenium sulphide catalysts in order to control their physicochemical properties and, as a result, achieve good performance with these types of catalysts. No calcination is recommended after the incorporation of ruthenium chloride, and the sulfiding mixture should be $\text{H}_2\text{S}/\text{N}_2$ to achieve a high degree of sulfurization and avoid the reduction of the RuS_2 phase formed.

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