Chapter 7

Ni/ZnO Nano Sorbent for Reactive Adsorption Desulfurization of Refinery Oil Streams

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ABSTRACT

The aim of this chapter is to present the Ni/ZnO nano-sorbent for reactive adsorption desulfurization (RADS) of refinery oil streams. The preparation and modification of nano-sorbent are reviewed. Various characterizations involving in the relation of properties with components, structures and dynamic phase change during RADS, are extensively provided. The mechanisms of desulfurization, sulfur transfer and sulfur adsorption are proposed. The contradictionarys in literature about active structures and reaction mechanism are discussed and the solutions are suggested. This chapter unfolds the impressive application of RADS of Ni/ZnO nano-sorbent to produce a cleaner gasoline. It also delves into the inadequately engineer areas which require further attention so as to make the RADS process more economic and more efficient. The perspective applications other than gasoline desulfurization are also presented.

INTRODUCTION

Desulfurization is one of the most important processes in the petroleum refining industry. The conventional measure is by hydrodesulfurization (HDS) where molybdenum or tungsten supported on an alumina carrier with addition of cobalt or nickel is used as catalyst (Babich and Moulijn 2003). For eliminating
the detrimental impact of acid rain, many governments have made more stringent regulations controlling
the sulfur content in fuels. For example, in the new Europe V standard, the sulfur content in gasoline and
diesel is limited below 10 ppm. But the HDS process faces challenge to achieve this objective. Thus other
desulfurization technologies are heavily investigated. Among them, reactive adsorption desulfurization
(RADS) emerges as a perspective direction, which uses a sorbent to remove the sulfur impurity from
oil stream and keeps the sulfur in the sorbent. The great challenge for RADS technology is to develop
a sorbent with high desulfurization activity and high sulfur capacity. Nano Ni/ZnO sorbent is found an
ideal candidate for this objective, where metallic Ni catalyzes the HDS of sulfur-containing compounds,
meanwhile ZnO component as a sulfur acceptor regenerates Ni species from the sulfided to the metallic
(Tawara et al. 2000, 2001a).

Ryzhikov et al. (2008) observed that NiO/ZnO can be reduced in situ and shows better RADS of
thiophene than pre-reduced counterpart. It was suggested that the H₂ pretreatment results in the forma-
tion of Ni-Zn alloy and agglomeration of nano particles, leading the decrease of activity. However,
the pre-reduction for NiO/ZnO-SiO₂-Al₂O₃ sorbent improves the desulfurization capability (Fan et al.
2010), which is attributed to the additives of alumina and silica stabilizing the particles (Wen et al. 2012,
Meng et al. 2013). Decreasing the size of ZnO nano particles increases the efficient contact between
Ni and ZnO particles and enhances the desulfurization ability and sulfur adsorption capacity (Zhang et
al. 2012a). But ZnO particles are not stable under the calcination or reaction conditions, the sinter of
particles lead a noticeable drop of activity (Bezverkhy et al. 2008). Thus structure additives, such as
diatomite, perlite, attapulgite, silicasol, pseudoboehmite or their mixtures are often added to reinforce
the texture of nano sorbent (Shangguan et al. 2013, Zhou et al. 2013).

Babich and Moulijn (2003) proposed a RADS mechanism of Ni/ZnO sorbent. H₂S as a sulfur carrier
transfers the sulfur from Ni surface to ZnO bulk. It has been accepted by a lot of authors, but the recent
DFT calculation showed that the direct sulfur transfer from Ni site to Zn site has lower energy barrier.
This suggests a new mechanism that sulfur may be transferred through the interface between Ni and
ZnO phases (Zhang et al. 2012b). The sulfur accumulation in the sorbent leads a gradual deactivation.
Regeneration at above 500 °C can partly recover the RADS activity. However, the formation of new
species, such as Ni₃SO₄, ZnSO₄, NiAl or AlZn spinel, influences the performance of regenerated sorbent

The RADS of Ni/ZnO nano sorbent has been successfully applied in the desulfurization of gasoline.
The S-Zorb technology is the representative one. It was first developed by Conoco Philips Petroleum
Co. and then was bought out by China Petroleum & Chemical Corp. (Sinopec). This RADS process was
demonstrated to possess some valuable features like low hydrogen consumption and low loss in octane
number (Khare 1999, Gyanesh 2001). The first commercial S-Zorb unit was run at Borger refinery in
April of 2001. And over thirty units have been built and operated by the end of 2014 (Jia et al. 2014).

This chapter discusses the new emerged and fast developing RADS technology. It begins with the
preparation of nano Ni/ZnO sorbent as well as its modification. Various characterization methods are
used to reveal the structures and properties of the sorbent. Based on these data the relation of structure
with reaction activity and adsorption capacity is built. The RADS paths are simulated by DFT method.
And the reaction mechanism is postulated. The controversies regarding active structures and reactive
mechanism are raised hoping to be solved in future. The commercial application of Ni/ZnO nano sorbent
for RADS is presented. S-Zorb RADS technique is introduced historically and compared with HDS
technologies. The perspective of RADS is provided. And further engineering research is proposed.

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