

CHAPTER III

THEORY

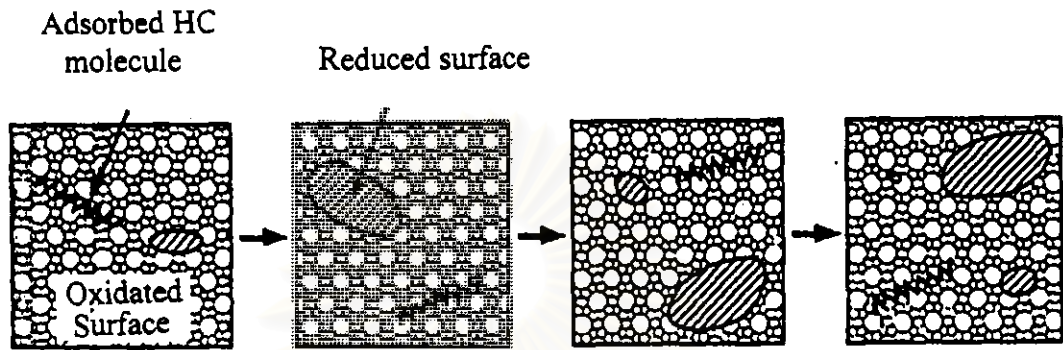
3.1 Reduction of NO_x by hydrocarbon: Microscopic Sequential Reaction Mechanism

Most recently, some studies on the NO elimination under the condition of an excess oxygen with a low concentration of hydrocarbon were reported using zeolitic catalysts such as H-type zeolites [35,36], metal-ion-exchange ZSM-5 [3,23,32,40,60], metal-incorporated zeolites [61] and some kinds of metallosilicates having MFI structure [18,19,20] which were prepared by rapid crystallization method [12]

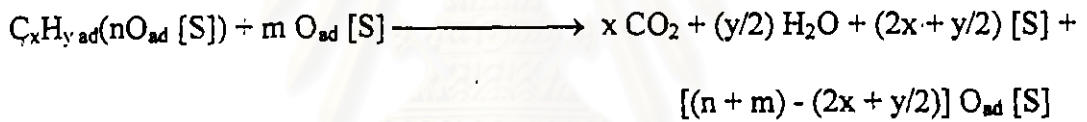
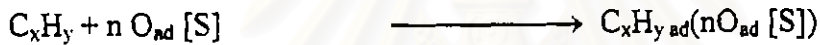
Many of them who have studied this kind of reaction have tried to understand the results of reaction as a selective reduction of NO by added hydrocarbons according to the conventional Langmuir-Hinshelwood type reaction mechanism [62]. They must suppose, but never verified, the existence of a partly oxidized highly active adsorbed hydrocarbon species as the intermediate to explained their reaction mechanisms. On the other hand, the new reaction mechanism " Microscopic Sequential Reaction Mechanism (MSR mechanism) " was proposed [61,63] which enables to understand, without any discrepancy, such a unusual and non-linear reaction phenomena occurred in extremely deviated conditions of reactants and existence of an excess oxygen which has a high potential to control predominantly the oxidation state of catalyst surface.

Zeolite matrix is considered as one of the indispensable requisites due to the intermediate oxidation state of catalyst metal during the reaction seems to be stably maintained, whereas the bulk state catalysts which are prepared by conventional impregnation method or precipitation method cannot maintain such an intermediate oxidation state. Furthermore, this difference indicates that the oxidation of catalyst metal on the surface of zeolitic crystallites could locally change during the reaction as illustrated in Figure 3.1 [64].

Namely, as the case of exhaust gases from diesel engine, components, such as O_2 , H_2O and CO_2 which retard the reaction, exist with an large excess: on the other hand both NO to be eliminated and hydrocarbon to be added are very low concentrations. It seems to be very unnatural that the NO can react with the hydrocarbons selectively by the bimolecular surface reaction. However, the following reaction mechanism rationally explained experimental facts. As known, catalytic combustion of hydrocarbon molecule easily cause the local reduction part on the surface of zeolitic catalyst, and on this reductive part NO decomposition can advance before oxidized by the excess oxygen at appropriate temperature range. Furthermore, the general experimental fact that at above that temperature, NO conversion decreases whereas hydrocarbon added can be combusted, can be explained reasonably as follows; at higher temperature range, the local reduction part which forms by combustion of hydrocarbon is immediately oxidized by excess oxygen and there is no chance any more to decompose NO. this kind of real heterogeneous reaction mechanism, expressed by the sequential reaction equation in Figure 3.1, has been pronounced as the Microscopic Sequential Reaction Mechanism (MSR mechanism) [61,63].



Oxidated surface



Reduced surface



Figure 3.1 Conceptual illustration of the Microscopic Sequential Reaction mechanism for deNO_x reaction under the oxygen excess condition [64]