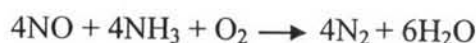


CHAPTER I

INTRODUCTION

In a combustion process, hazardous nitrogen compounds formed during the combustion are nitric oxide (NO), nitrogen dioxide (NO₂), and nitrous oxide (N₂O). These are commonly referred as NO_x. NO_x consists of mainly nitric oxide (NO), about 90% or more, and a small fraction of nitrogen dioxide (NO₂) and nitrous oxide (N₂O) remaining less than 10%. These pollutants, after emission into the atmosphere, are identified as greenhouse gases that participate in global warming and are the main components of acid rain, and they can form the toxic chemical such as HCN.

Selective catalytic reduction (SCR) is the most powerful method for the NO_x removal from flue gases. To enhance the reaction activity, ammonia (NH₃) is injected into the process as the reducing agent. It reacts with nitric oxide to produce nitrogen and water as the products. The main SCR reaction is:



The operating temperature depends on type of the catalyst, but the commonly operating temperatures are about 250-400°C.

The injected quantity of NH₃ must be controlled to prevent the excess ammonia from being released into the environment. This is called "NH₃-slip". In contrast, insufficient NH₃ will result in NO_x release into the environment.

The commercial catalyst used in SCR is V₂O₅-WO₃/TiO₂ that allows 67% NO conversion (Long and Yang, 1999). The disadvantage is that it catalyzes the oxidation of SO₂ to SO₃ which can give sulphuric acid corrosion problems downstream at the lower temperatures. In addition, in the SCR unit, ammonium sulphates can be formed. This can result in corrosive deposits in the SCR unit downstream as well as catalyst deactivation (Zevenhoven and Kilpinen, 2002). And, there were some reports about the toxicity of vanadium, itself.

Several supported materials have been shown to be active supports for SCR reaction. The most frequently studied supports are zeolites (i.e., ZSM-5), after

exchanged with metals (e.g., Fe, Cu, Co, and Ni), they can achieve nearly 100% NO conversion.

The most important application of zeolites is their use as catalysts. The active sites (acid and/or metal centers) are generated on the walls, and they will react only with those molecules that can penetrate into the channels. Then, the products formed in the interior of those micropores have to fast diffuse out to allow new reactant molecules to reach the catalytic active sites. Due to the NO_x reduction mechanism, both metal sites and Bronsted acid sites are needed with the large cavities to allow the fast diffuse of the products. To improve the efficiency of NO_x reduction, zeolitic materials that contain the size of cavities at least as that of ZSM-5 and contain more Bronsted acid sites are required. This could be achieved by the synthesis of a new large pore zeolite structure such as ITQ-21 series. A new zeolite named ITQ-21, containing Si, Ge, and optionally Al as framework cations, has been successfully synthesized (Corma *et al.*, 2002). This material presents a unique pore topology formed by nearly spherical large cavities of 1.18 nm diameter joined to six other neighboring cavities by circular 12-ring pore windows with an opening of 0.74 nm, which results in a three-directional channel system of fully interconnected large cavities. In this structure, molecules formed inside that cavity can readily diffuse out through the six windows that are opened to the exterior.

The synthesis of this material has been achieved through a combination of the structure directing effect of large and rigid organic structure-directing organic cation, N(16)-methylsparteinium, to fill the pores and, on the other hand, the directing effect of Ge toward the formation of structures containing double 4-rings as secondary building units. The combination of these two approaches results in the formation of the ITQ-21 zeolite structure.

The structure, which remains stable even in the presence of steam at 700°C with relatively large pore size and contains the highly Bronsted acid sites (when compared to ZSM-5) (Arribas *et al.*, 2004), allows ITQ-21 to be an active deNO_x catalyst, and especially in FCC unit in the refinery.

In this work, to enhance its activity on NO_x reduction, a set of metals composed of iron, copper, cobalt, and nickel was loaded on H-mordenite with or without ITQ-21 addition. The activities on NO_x reduction were examined on the

catalysts. Also, the effects of the type of metal, the type of support, germanium addition, and the reaction temperature were studied.