Boonruen Sunpetch 2009: Experimental and Theoretical Studies of Transition Metals in Petrochemical Zeolite Catalysts. Doctor of Philosophy (Chemistry), Major Field: Physical Chemistry, Department of Chemistry. Thesis Advisor: Professor Jumras Limtrakul, Dr.rer.nat. 130 pages.

Catalytic activity of metal supported zeolite catalysts were studied for N_2O decomposition and C_2H_6 oxidative dehydrogenation by N_2O. The activity for N_2O decomposition over different zeolites decreases in the following order, FER > BEA > ZSM5 >> MOR > FAU. With the presence of CH_4, the activities for N_2O decomposition over FER, BEA, ZSM5 and MOR were significantly enhanced. In addition, the C_2-C_3 gases were observed in small amount about 8 and 10% selectivity over FER and MOR zeolites, respectively. On ZSM5 zeolite, aromatic products were observed with selectivity of 20% at a conversion of 25%. However, the catalysts suffered with rapid deactivation due to coke formation. The steam treatment was found to improve the catalytic stability. In addition, ZSM5 is also active for C_2H_6 oxidative dehydrogenation. The C_2H_4 yield of 21% was obtained at a reaction temperature of 500°C. The catalytic reactivity for N_2O decomposition of the highly dispersed Fe species in different zeolite frameworks were also studied by computational simulations with the ONIOM method. The framework species played the role in the activity of Fe-zeolites in N_2O decomposition. In the transition state, the smallest pore FER zeolite exerts the strongest van der Waals interactions on the reacting species and, thus, results in the lowest activation energy. Therefore, the predicted intrinsic activity trend is Fe-FER>Fe-ZSM5~Fe-BEA~Fe-FAU. The very low activity of Fe-FAU that was observed experimentally could be due to the mass transfer limitation. Moreover, the catalytic N_2O decomposition on Fe-ZSM5, Co-ZSM5 and Ni-ZSM5 were compared. The predicted rate determining step for all catalytic samples is N-O bond breaking. The apparent activation energy predicted for Fe-ZSM5, Co-ZSM5 and Ni-ZSM5 are 46.0, 55.2, and 75.8 kcal/mol, respectively.

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