The zeolite framework and substituent effects on the reaction pathway of the Beckmann rearrangement has been investigated by both the quantum cluster and embedded cluster approaches at the B3LYP level of theory using the 6-31G(d,p) basis set. Single point calculations were carried out at MP2/6-311G(d,p) for improving the energetic properties. In the zeolite system, the most favored path is as follows: protonation of the oxime molecule → N-protonated species → O-protonated species → enol-formed amide complex → amide complex. From the bare cluster model of H-ZSM-5 and H-FAU zeolites, the rate determining step of the selected oximes is the rearrangement step which has the energy barrier between 50-70 kcal/mol. Taking into account the zeolite framework effects, the rate determining step of formaldehyde oxime on H-ZSM-5 zeolite is either the rearrangement or the tautomerization step which has an energy barrier about 30 kcal/mol, while on the H-FAU zeolite, it is the rearrangement step (50.4 kcal/mol). Including the methyl substitution at the carbon-end of formaldehyde oxime, the rate determining step of the methylated derivatives on the H-FAU zeolite becomes the 1,2 H shift step for Z-acetaldehyde oxime (30.5 kcal/mol) and acetone oxime (31.2 kcal/mol), while, in the E-acetaldehyde oxime, the rate determining step is either the 1,2 H-shift (26.2 kcal/mol) or the rearrangement step (26.6 kcal/mol). These results reveal that when the size of a guest molecule approaches the size of the pores and cavities of the zeolite, the electronic confinement from the zeolite framework has a significant influence on the catalytic activity of zeolite.

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