Hydrazine decomposition reactions on the small platinum cluster Pt_4

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INTRODUCTION

Hydrazine (N_2H_4) and its derivatives constitute an important group of energetic molecules widely utilized in aerospace applications. Another capability of hydrazine is its use in fuel cells due to its high-density storage of hydrogen. Fuel cells based on hydrazine catalyzed by platinum were tested experimentally with success.[1] An experimental study of the decomposition of hydrazine on Pt(111)[2] shows that the decomposition of N_2H_4 occurs through the successive breaking of N-H bonds in hydrazine leading to the formation of N_2, and it also detects the desorption of H_2 and NH_3, however it was not evident how the NH_3 molecule is formed. The hydrogenation of N_2H_4 is one of pathways suggested to the NH_3 formation and it can be formed through the N_2H_5 reaction intermediate.

In this work we studied reaction paths for N_2H_4 decomposition presented in scheme below.

$$(1A)\ N_2H_4 \xrightarrow{TS1A} HNNH_3;$$
$$(1B)\ HNNH_3 \rightarrow HN + NH_3$$
$$(2A)\ N_2H_4 + H \xrightarrow{TS2A} N_2H_5$$
$$(2B)\ N_2H_5 \xrightarrow{TS2B} NH_2 + NH_3$$
$$(3)\ N_2H_4 + H \xrightarrow{TS3} N_2H_3 + H$$

For each reaction, energies and barrier heights were studied in both the absence and the presence of the tetrahedral Pt_4 cluster.

METHODS

All geometry optimizations were carried out by using the DFT method, M06. The effective core potential LANL2DZ basis set was employed for the Pt atom and the 6-311++G(d,p) basis set was used for the N and H atoms. Geometry optimizations were carried out with partial constraints, the Pt-Pt distances were kept constant and equal to the experimental bulk distance, 2.775 Å. The IRC procedure identified the connectivity of the stationary points. The calculations were carried out using the Gaussian 09 code.

RESULTS AND DISCUSSION

The **Fig.1** summarizes the results showing the energetic profile for reactions of the scheme in the presence of the Pt_4 cluster.

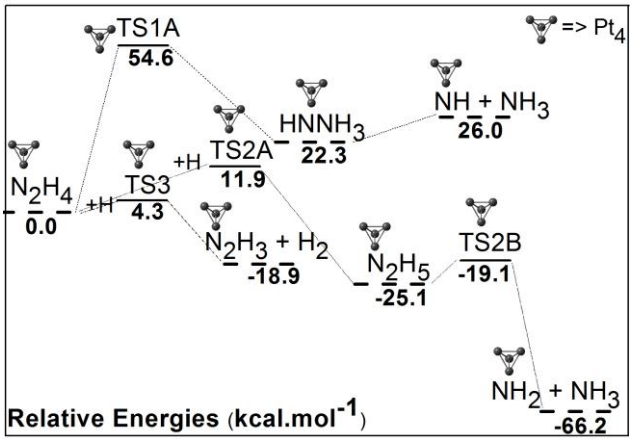

Fig.1 Reaction profile for adsorbed molecules. Relative energies are given in kcal.mol^{-1}.

CONCLUSIONS

The Pt_4 cluster assistance does not affect the energetic parameters in a systematic way. This is the first time that the N_2H_5 species has been characterized in the literature, and the reaction energies suggest the N_2H_5 as a reaction intermediate in pathway to produce ammonia, especially in the Pt_4 presence.

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