

Electronic Supplementary Information

Exploring Trimetallic Clusters Containing Alkali and Alkaline Earth Atoms with High Activity for Nitrogen Activation

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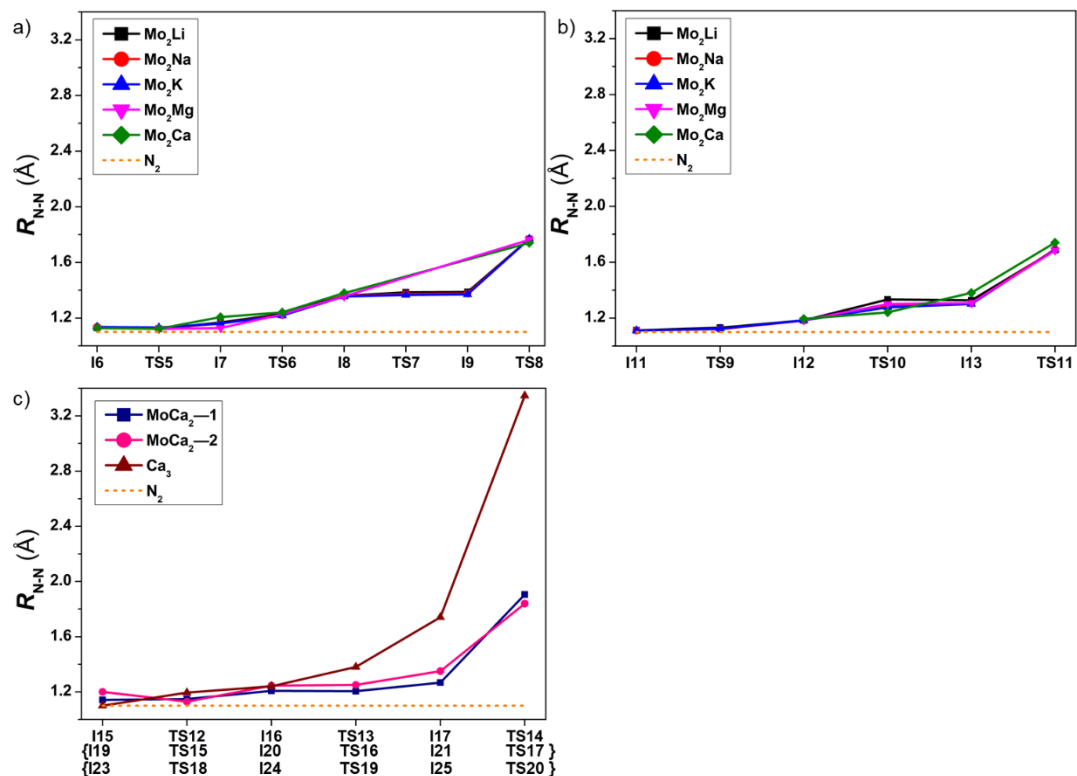


Fig. S1 N–N bond lengths (R_{N-N}) of the transition states and intermediates that indicate the activation of N–N bonds in the reactions of Mo_2 , Mo_2M ($M=Li, Na, K, Mg$, and Ca), and $Mo_{3-x}Ca_x$ ($x=2-3$) with N_2 . a) Mo_2M when N_2 is initially adsorbed on Mo, b) Mo_2M when N_2 is initially adsorbed on M, and c) reaction paths of $MoCa_2$ and Ca_3 with N_2 . $MoCa_2-1$ and $MoCa_2-2$ represent the initial adsorption of N_2 on Mo and Ca atoms, respectively. As a reference, the horizontal line in each figure indicates the R_{N-N} of the triple N–N bond in free N_2 .

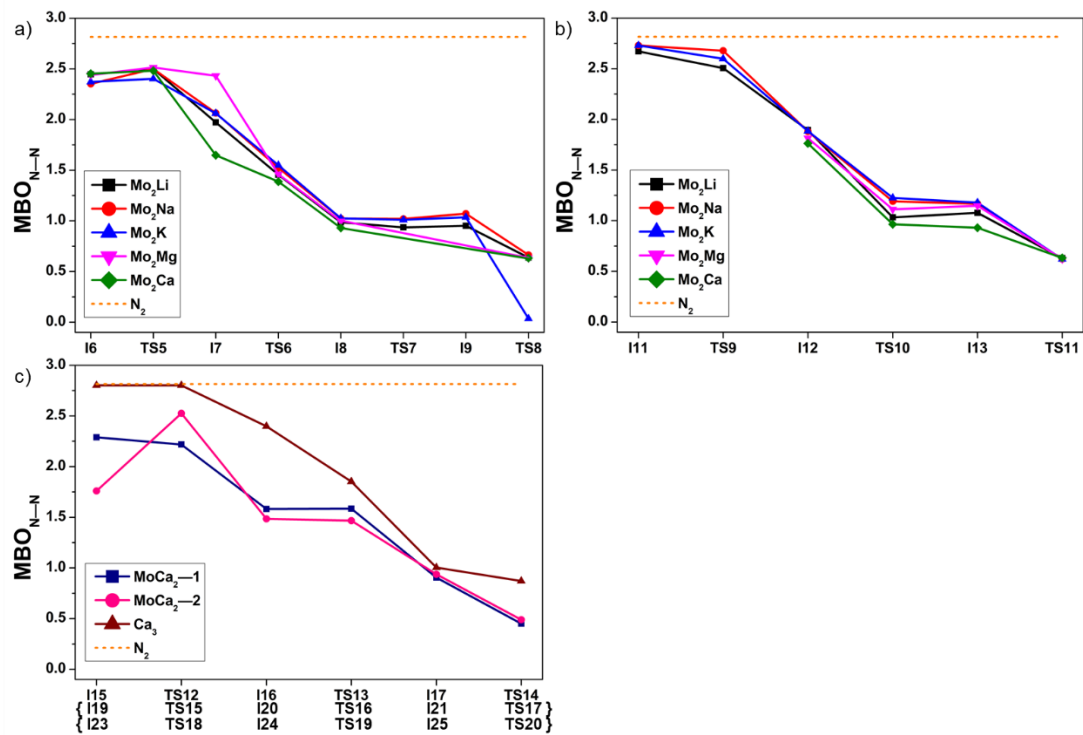


Fig. S2 Mayer bond order (MBO_{N-N}) of the transition states and intermediates that indicate the activation of N–N bonds in the reactions of Mo_2 , Mo_2M ($M=Li, Na, K, Mg$, and Ca), and $Mo_{3-x}Ca_x$ ($x = 2-3$) with N_2 . a) Mo_2M when N_2 is initially adsorbed on Mo, b) Mo_2M when N_2 is initially adsorbed on M, and c) reaction paths of $MoCa_2$ and Ca_3 with N_2 . $MoCa_2-1$ and $MoCa_2-2$ represent the initial adsorption of N_2 on Mo and Ca atoms, respectively. As a reference, the horizontal line in each figure indicates the MBO_{N-N} of the triple N–N bond in free N_2 .

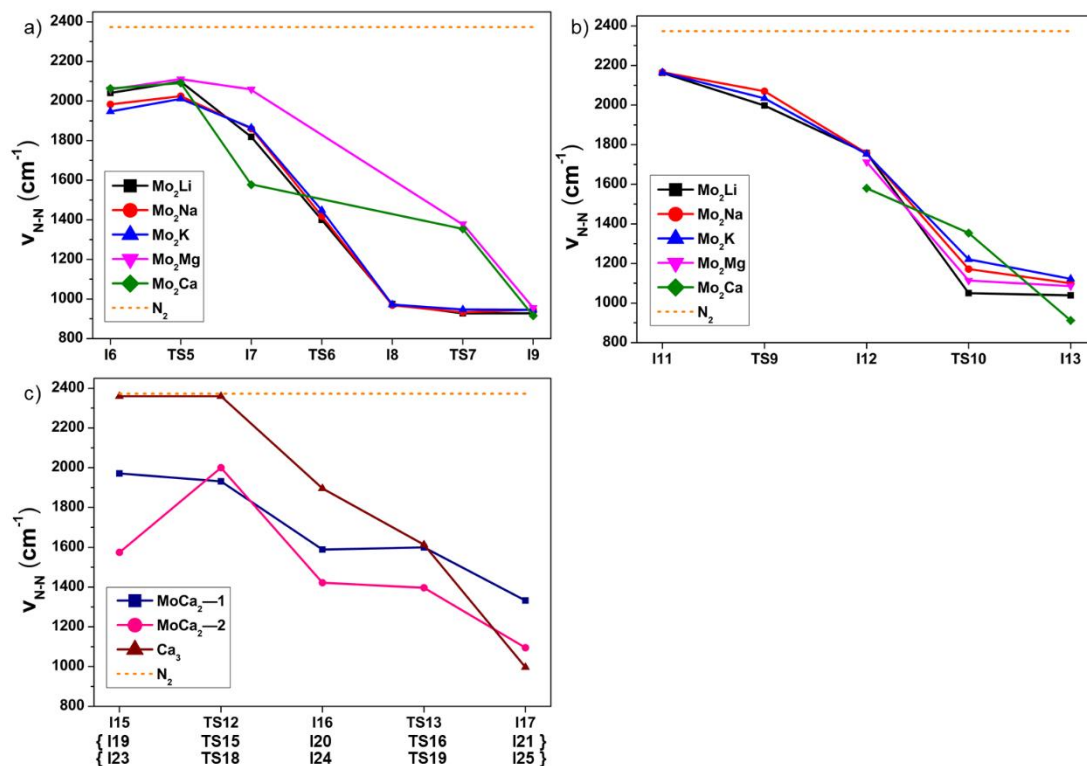


Fig. S3 N–N bond vibration frequency (ν_{N-N}) of the transition states and intermediates that indicate the activation of N–N bonds in the reactions of Mo_2 , Mo_2M (M=Li, Na, K, Mg, and Ca), and $\text{Mo}_{3-x}\text{Ca}_x$ ($x = 2-3$) with N_2 . a) Mo_2M when N_2 is initially adsorbed on Mo, b) Mo_2M when N_2 is initially adsorbed on M, and c) reaction paths of MoCa_2 and Ca_3 with N_2 . MoCa_2-1 and MoCa_2-2 represent the initial adsorption of N_2 on Mo and Ca atoms, respectively. As a reference, the horizontal line in each figure indicates the ν_{N-N} of the triple N–N bond in free N_2 .

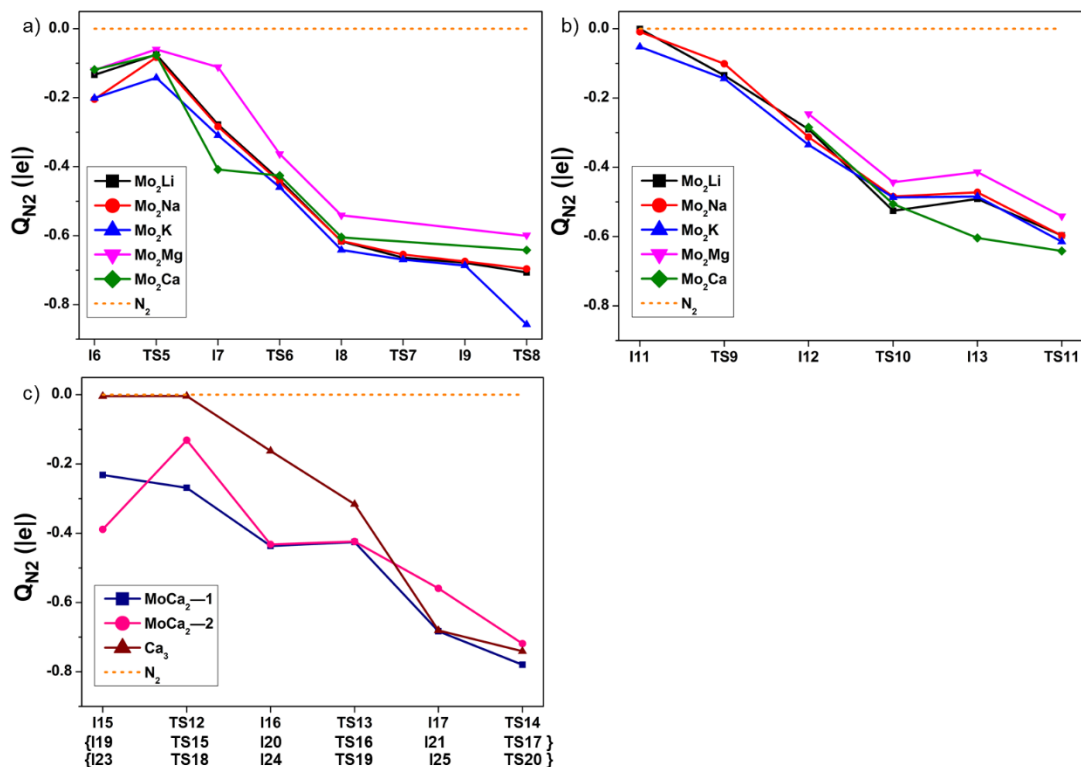


Fig. S4 Hirshfeld charge (Q_{N_2}) of the transition states and intermediates that indicate the activation of N–N bonds in the reactions of Mo_2 , Mo_2M (M=Li, Na, K, Mg, and Ca), and $Mo_{3-x}Ca_x$ ($x=2-3$) with N_2 . a) Mo_2M when N_2 is initially adsorbed on Mo, b) Mo_2M when N_2 is initially adsorbed on M, and c) reaction paths of $MoCa_2$ and Ca_3 with N_2 . $MoCa_2-1$ and $MoCa_2-2$ represent the initial adsorption of N_2 on Mo and Ca atoms, respectively. As a reference, the horizontal line in each figure indicates the Q_{N_2} of the triple N–N bond in free N_2 .