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Article

Theoretical investigation into the Co^+ catalytic activity in the cycle reaction of N_2O with C_2H_6 in the gas phase

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ABSTRACT

The spin-forbidden mechanism of the reaction between N_2O and C_2H_6 catalyzed by Co^+ has been investigated using UB3LYP density functional theory. The Harvey method has been applied to optimize five minimum energy crossing points (MECP) on both triplet and quintet potential energy surfaces. Possible spin inversion processes are discussed by means of spin-orbit coupling calculations. According to the calculation of probability of electron hopping using the Landau-Zener formula, effective intersystem crossing may occur at each MECP. The energetic span model proposed by Kozuch has been applied to the catalytic cycles, and shows the turnover frequency reaches $3.35 \times 10^{-21} \text{ s}^{-1}$ when Co^+ catalyzes the reaction to produce CH_3CHO at 298K.

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1. Introduction

The catalytic oxidation of alkanes is a hot research topic in both theoretical and experimental studies for chemical reactions. Small alkanes, such as CH_4 and C_2H_6 , are high-quality fuel gases and important raw materials. C_2H_6 is more reactive than CH_4 . Transition metals have been used as catalysts for the oxidation of these compounds. They effectively activate both C–H and C–C bonds and lower the energy barrier to facilitate the oxidation reactions. Previously, first-row transition-metal oxide ions, such as MnO^+ , FeO^+ , CoO^+ , and NiO^+ , have been shown to exhibit high catalytic activity for the oxidation of small alkanes [1–6]. MnO^+ and FeO^+ exhibit high catalytic efficiency but low selectivity for the oxidation of commercially useful alcohols and aldehydes, whereas NiO^+ exhibits a higher selectivity but a lower catalytic efficiency, and only in the presence of CoO^+ as a

co-catalyst. In 1994, Ryan et al. [7] reported the catalytic performance of CoO^+ and found a high reaction rate could be achieved for the activation of C_2H_6 . The proposed reaction mechanisms are shown in Eqs. (1)–(4). In 2012, Zhao et al. [8] further investigated the reaction mechanism in detail.

In transition-metal-mediated reactions, high spin-state transition-metal complexes usually contain multiple unpaired electrons, which can easily undergo spin inversion (SI) to change the spin states by spin-orbit coupling, and intersystem crossing (ISC) can occur between the potential energy surfaces of different spin states [9–13]. Schröder et al. [14] denoted this as “two-state reactivity” (TSR) for the reactions involving a SI

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that enable the system to find and follow low-energy reaction pathways that would be otherwise inaccessible. To better understand the SI processes of Co^+ and further explore the catalytic activity of Co^+ in the reactions, density functional theory (DFT) was applied to analyse the electronic hopping possibilities between the conjugates of potential energy surfaces. This will help find the minimum energy reaction pathways in the oxidation of N_2O and C_2H_6 catalyzed by the triplet and quintuplet states of Co^+ . Moreover, the energetic span model proposed by Kozuch [15–19] was used to calculate the turnover frequency (TOF) of Co^+ to evaluate its catalytic activity for N_2O oxidation of C_2H_6 . This study aims to provide a theoretical guideline for future studies.

2. Calculation and theoretical method

2.1. Geometrical optimization

Computations were carried out using the Gaussian03 program package [20]. Geometry optimizations and frequency calculations were carried out for all the relevant species using DFT [21], UB3LYP [22] method together with the DZVP(opt+3f) [23,24] for Co^+ and 6-311++G(2d,2p) basis set for all other nonmetal atoms. The DZVP(opt+3f) set built up by Choido has proved reliable for the first-row transition metals. Intrinsic reaction coordinate (IRC) calculations were performed to identify the pathways between transition states and their connection minima. All energy are reported with a zero-point energy (ZPE) correction.

To locate the crossing points (CPs) between states of different spin multiplicities, the single-point vertical excitation method of Yoshizawa et al. [25] has been selected. The energy-gradient optimization method based on the CP, reported by Harvey, was used to obtain the minimum energy crossing points (MECPs). The natural population, bonding analysis, and charge distributions were calculated using the NBO5.0 program [26] to better understand the electronic properties of the reaction species.

2.2. Probability of ISC calculations

At the MECPs, the two different degenerate spin states were mixed, and the energy separation ($\Delta\epsilon = 2H_{\text{SOC}}$) was attributed to the spin-orbit coupling (SOC) effects. The probabilities of ISC between the different potential energy surfaces were calculated using the Landau-Zener formula [27–29] as follows:

$$P^{\text{LZ}} = \exp\left(-\frac{4\pi^2 H_{\text{SOC}}^2}{h|\Delta F|} \sqrt{\frac{\mu}{2(E - E_{\text{MECP}})}}\right) \quad (5)$$

The electronic hopping probability between the potential energy surfaces for the two-spin states was estimated by the transition probability (P^{LZ}) from the Landau-Zener formula, and the relationship between the first and second surface-hopping probabilities was calculated using the following equations:

$$P_1^{\text{ISC}} = 1 - P^{\text{LZ}} \quad (6)$$

$$P_2^{\text{ISC}} = (1 - P^{\text{LZ}})(1 + P^{\text{LZ}}) \quad (7)$$

The spin-orbit coupling effects at the MECP (H_{SOC}) were evaluated using the GAMESS Program [30].

2.3. Energetic span model theory

To evaluate the effect of the catalyst, an energy representation (E -representation) TOF was calculated. On the basis of Eyring's transition state (TS) theory [31], an important formula (Eq. (8)) was deduced by Kozuch for catalytic reactions with n steps [15–17,32,33]. This provided a theoretical calculation for the TOF.

$$\text{TOF} = \frac{\Delta}{M} = \frac{k_{\text{B}}T}{h} \cdot \frac{\exp(-\Delta G_{\text{r}}/RT) - 1}{\sum_i \sum_j \exp[(T_i - I_j - \Delta G_{ij})/RT]} \quad (8)$$

$$\Delta G_{ij} = \begin{cases} \Delta G_{\text{r}} & i > j \\ 0 & i \leq j \end{cases}$$

where Δ is the difference between the positive and negative reaction rate constants, M is the matrix constructed by the specific positive and negative reaction rate constants, ΔG_{r} is the Gibbs free energy difference between the initial reactants and final products for the overall reaction, and T_i and I_j are the Gibbs free energies of the i^{th} transition state and the j^{th} intermediate, respectively. When $T_i - I_j$ is the highest, the matrix element has the biggest effect on the entire matrix and thus this step plays the major role in a multistep reaction. Therefore, Kozuch defined the degree of control (X_{TOF}) for the corresponding state (TS or intermediate) as the following equation:

$$X_{\text{TOF},T_i} = \frac{\sum_j \exp(T_i - I_j - \Delta G_{ij})/RT}{\sum_i \sum_j \exp(T_i - I_j - \Delta G_{ij})/RT}$$

$$X_{\text{TOF},I_j} = \frac{\sum_i \exp(T_i - I_j - \Delta G_{ij})/RT}{\sum_j \sum_i \exp(T_i - I_j - \Delta G_{ij})/RT} \quad (9)$$

$$\Delta G_{ij} = \begin{cases} \Delta G_{\text{r}} & i > j \\ 0 & i \leq j \end{cases}$$

In the overall reaction, the transition state T_i affects the TOF and is the TOF-determining transition state (TDTS), whereas the intermediate I_j affects the TOF as a TOF-determining intermediate (TDI). The TDTS and TDI are not necessarily adjacent.

Once the TOF-determining states have been calculated, the TOF approximation can thus be calculated when $\Delta G_{\text{r}} < 0$, and $\exp(-\Delta G_{\text{r}}/RT) \gg 1$:

$$\text{TOF} \approx \frac{k_{\text{B}}T}{h} \cdot \exp(-\delta E/RT) \quad (10)$$

$$\delta E = \begin{cases} T_{\text{TDTS}} - I_{\text{TDI}} & \text{if TDTS appears after TDI} \\ T_{\text{TDTS}} - I_{\text{TDI}} + \Delta G_{\text{r}} & \text{if TDTS appears before TDI} \end{cases}$$

where δE is the apparent activation energy, or the energetic span, in the cycle reaction.

3. Results and discussion

3.1. Crossing between the two PESs

The Co electronic configuration is $3d^7 4s^2$, and Co^+ has singlet, triplet, and quintuplet states. After the calculations, the energy of all the stationary points in the singlet state was higher than in the triplet and quintuplet states; therefore, the singlet state was not considered in this study. The triplet electronic configuration of Co^+ is 3F [34], with an energy 6.0 kcal/mol less than the excited quintuplet (5F) [34]; therefore, Co^+ enters the reaction pathway in the low-spin triplet state. The reaction pathway of the catalysis of N_2O and C_2H_6 by Co^+ is shown in Fig. 1.

Figure 1 shows that three potential energy surface crossings and an important intermediate, CoC_2H_4^+ , are present in the catalysis of N_2O and C_2H_6 to $\text{C}_2\text{H}_5\text{OH}$ by Co^+ . The conjugate CP1 occurs after the transition state $^5\text{T}1$; the transition state $^3\text{T}1$ transforms into the intermediate $^5\text{I}1$ with a lower potential energy surface in the bonding process between Co^+ and N atoms. When CoO^+ reacts with C_2H_6 , CoO^+ can take two different paths: (a) from directly above and (b) from below. In path (b), independent of the spin state, the energy of both the interme-

diate $\text{I}2\text{b}$ and transition state $\text{T}3\text{b}$ was higher than that in path (a). Therefore, the reaction proceeds through the low-energy pathway (a), and a study of the conjugate before the transition state $\text{T}3\text{b}$ is not significant. In the transition state $\text{T}3\text{a}$, electron-donating and electron-withdrawing effects were observed between the C–H bond and Co atom. The interaction intensity was estimated from the second-order perturbation energy equation ($\Delta E(2) = -2 \langle \sigma | \hat{F} | \sigma^* \rangle / \epsilon \sigma^* - \epsilon \sigma$) [35]. In $^5\text{T}3\text{a}$, $E(2)_{\text{BD}(\text{C-H}) \rightarrow \text{LP}^*(\text{Co})}$ was 22 kcal/mol. In $^3\text{T}3\text{a}$, $E(2)_{\text{BD}(\text{C-H}) \rightarrow \text{LP}^*(\text{Co})}$ and $E(2)_{\text{BD}(\text{C-H}) \rightarrow \text{BD}^*(\text{Co-O})}$ were 15.64 and 30.67 kcal/mol, respectively. The higher second-order perturbation energy of the triplet states indicates more electron transfer, not to the C–H bonding orbital, but into the corresponding antibonding orbital. Thus, the stability of the C–H bond is decreased. After the $\text{T}3\text{a}$ transition state, the potential energy surface crossing (CP2) occurs, and $^3\text{I}3$ is more stable than $^5\text{I}3$. The reactions operate in parallel with the production ratio $\text{Y}1:\text{Y}2$ ($\text{C}_2\text{H}_5\text{OH}$ to CoC_2H_4^+) of 0.21:0.79 [7].

Figure 2 shows that the potential energy surface crossing

Fig. 1. Partial path diagram of Co^+ catalyzing the N_2O and C_2H_6 reaction up to the intermediate, CoC_2H_4^+ .

Fig. 2. Reaction path diagram for the loss of ethanol in the CoC_2H_4^+ oxidation by N_2O .

(CP3) occurs after the transition state T8 in the reaction between CoC_2H_4^+ and N_2O . The second-order perturbation energy between the Co and N–O in the transition state T8 was as follows: $E(2)_{\text{LP}(\text{Co}) \rightarrow \text{BD}^*(\text{N}-\text{O})} = 3.90$ kcal/mol in $^3\text{T8}$ and $E(2)_{\text{BD}^*(\text{Co}-\text{N}) \rightarrow \text{BD}^*(\text{N}-\text{O})} = 11.31$ kcal/mol in $^5\text{T8}$. The second-order perturbation energy of the quintuplet state was higher, whereas the N–O bond is more prone to cleavage than in the triplet state. The intermediate $^5\text{I8}$ had a lower potential energy than $^3\text{I8}$. When $^5\text{CoOC}_2\text{H}_4^+$ transfers H atoms, the crossing point (CP4) appears before the potential barrier T9, and the reaction inverts the potential energy of the states, giving a lowest energy triplet state. $^3\text{I10}$ is the lowest point in the entire reaction potential energy surface. The dissociation of the compound from here requires a large amount of energy, which hinders product formation.

Figure 3 shows the parallel reactions of CoC_2H_4^+ with N_2O to afford CH_3CHO and $\text{CH}_2\text{CH}_2\text{O}$. The energies of $^3\text{T11}$ and $^5\text{T11}$ are similar to each other, and the crossing point (CP5) appears before the transition state T11. If effective intersystem crossing occurs at the CP, the system would hop to the triplet surface with a lower potential energy. The barrier potential in $^3\text{T11}$ was low, which could effectively decrease the energy barrier and facilitate the reaction.

In conclusion, the catalysis of N_2O and C_2H_6 by Co^+ occurs on two potential energy surfaces, and five potential energy surface crossing points were observed, which represents a typical two-state reaction.

3.2. The MECPs and the minimum energy reaction paths

3.2.1. The MECPs

Fig. 3. Energy profile for the loss of ethylene oxide and acetaldehyde in the CoC_2H_4^+ oxidation by N_2O .

According to the rules of spin-orbit coupling effects, the variation in the total spin for the five CPs in the catalytic cycle reaction must fit the spin-orbit coupling selection law ($\Delta S = \pm 1$) with the possibility of spin inversion. To locate each MECP, the single-point vertical excitation method of IRC by Yoshizawa was used to calculate the single point of vertical excitation of IRC in the triplet state, and five vertical projections on the potential energy surface in the quintuplet states. The Crossing2004 Program Package developed by Harvey et al. [36] was used to estimate the approximate CP location for the interaction of two potential energy surfaces and optimization to afford the MECP. The geometries of the five MECPs are shown in Fig. 4.

The structure of the triplet and quintuplet states is similar near the MECP, which was attributed to the mixing of the triplet

Fig. 4. Potential energy curve-crossing diagrams for the different spin-state potential energy surfaces along with the quintet and geometry of the MECP. (a) MECP1; (b) MECP2; (c) MECP3; (d) MECP4; (e) MECP5.

Table 2

The X_{TOF} of transition states and intermediates in the catalysis of N_2O and C_2H_6 by Co^+ to produce $\text{C}_2\text{H}_5\text{OH}$ at 298 K.

Species	$^3\text{I}0$	$^5\text{I}1$	$^5\text{I}2$	$^3\text{I}3$	$^3\text{I}4$
X_{TOF}	0.000	0.000	0.000	0.000	1.000
Species	$^3\text{Co}^+$	$^3\text{T}1$	$^5\text{CoO}^+$	$^5\text{T}3$	$^3\text{T}4$
X_{TOF}	0.010	0.989	0.000	0.000	0.000

As shown in Fig. 5(a), $\text{C}_2\text{H}_5\text{OH}$ is generated at the end of the reaction. After undergoing intersystem crossing at the two transition states, part of the reaction path occurs on the high-spin quintuplet potential energy surface. The transition state with the highest Gibbs free energy in the reaction was $^3\text{T}1$, whereas the intermediate with the lowest Gibbs free energy was $^3\text{I}4$. The Gibbs free energy change was -51.01 kcal/mol. According to the definition of the TOF degree of control (X_{TOF}), the degrees of control for each transition state and intermediate to the reaction TOF were calculated at 298 K and are listed in Table 2.

Table 2 shows that the X_{TOF} of $^3\text{T}1 \approx 0.99$ and $^3\text{I}4 \approx 1$, indicating that the TDTS and TDI in the cycle reactions are $^3\text{T}1$ and $^3\text{I}4$, respectively. $^3\text{T}1$ and $^3\text{I}4$ primarily determine the TOF in the catalysis of N_2O and C_2H_6 by Co^+ to afford $\text{C}_2\text{H}_5\text{OH}$. The TDTS, $^3\text{T}1$, appears before the TDI, $^3\text{I}4$, where $i < j$. The energetic span (δE) in the reaction can be represented as follows:

$$\delta E = {}^3\text{T}1 - {}^3\text{I}4 + \Delta G_r$$

The calculated δE was 50.08 kcal/mol. The approximated TOF of the reaction obtained from Eq. (10) was $\sim 1.16 \times 10^{-24} \text{ s}^{-1}$.

For the catalysis of N_2O and C_2H_6 by Co^+ to afford CH_3CHO , the transition state with the highest Gibbs free energy in the reaction was $^3\text{T}1$, and the intermediate with the lowest Gibbs free energy was $^3\text{I}13$. The Gibbs free energy variation, ΔG_r , was -117.22 kcal/mol. In this study, the TOF was calculated, and the corresponding X_{TOF} values for each state are listed in Table 3.

Table 3

The X_{TOF} of transition states and intermediates in the catalysis of N_2O and C_2H_6 by Co^+ to produce CH_3CHO at 298 K.

Species	$^3\text{I}0$	$^5\text{I}1$	$^5\text{I}2$	$^3\text{I}3$	$^3\text{I}5$	$^3\text{I}6$	$^3\text{I}7$	$^5\text{I}8$	$^3\text{I}11$	$^3\text{I}13$
X_{TOF}	0.000	0.000	0.000	0.000	0.000	0.117	0.000	0.000	0.000	0.883
Species	$^3\text{Co}^+$	$^3\text{T}1$	$^5\text{CoO}^+$	$^5\text{T}3$	$^3\text{T}5$	$^3\text{T}6$	$^3\text{CoC}_2\text{H}_4^+$	$^3\text{T}8$	$^3\text{T}11$	$^3\text{T}12$
X_{TOF}	0.010	0.873	0.000	0.000	0.000	0.000	0.000	0.117	0.000	0.000

Table 4

The X_{TOF} of transition state and intermediates in the catalysis of N_2O and C_2H_6 by Co^+ to produce $\text{CH}_2\text{CH}_2\text{O}$ at 298 K.

Species	$^3\text{I}0$	$^5\text{I}1$	$^5\text{I}2$	$^3\text{I}3$	$^3\text{I}5$	$^3\text{I}6$	$^3\text{I}7$	$^5\text{I}8$	$^3\text{I}11$	$^3\text{I}12$
X_{TOF}	0.000	0.000	0.000	0.000	0.000	0.399	0.000	0.045	0.000	0.556
Species	$^3\text{Co}^+$	$^3\text{T}1$	$^5\text{CoO}^+$	$^5\text{T}3$	$^3\text{T}5$	$^3\text{T}6$	$^3\text{CoC}_2\text{H}_4^+$	$^3\text{T}8$	$^3\text{T}11$	$^3\text{T}12$
X_{TOF}	0.007	0.590	0.000	0.000	0.000	0.000	0.000	0.400	0.000	0.000

Table 5

The X_{TOF} of transition state and intermediates in the catalysis of N_2O and C_2H_6 by Co^+ to produce CH_2CHOH at 298 K.

Species	$^3\text{I}0$	$^5\text{I}1$	$^5\text{I}2$	$^3\text{I}3$	$^3\text{I}5$	$^3\text{I}6$	$^3\text{I}7$	$^5\text{I}8$	$^3\text{I}9$	$^3\text{I}10$
X_{TOF}	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.990
Species	$^3\text{Co}^+$	$^3\text{T}1$	$^5\text{CoO}^+$	$^5\text{T}3$	$^3\text{T}5$	$^3\text{T}6$	$^3\text{CoC}_2\text{H}_4^+$	$^3\text{T}8$	$^3\text{T}9$	$^3\text{T}10$
X_{TOF}	0.010	0.990	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

The results showed that X_{TOF} of $^3\text{T}1$ and $^3\text{I}10$ are approximately 0.87 and 0.88, respectively. Relatively high degrees of control of 0.12 were observed for $^3\text{I}6$ and $^3\text{T}8$; however, they were still far less than that of $^3\text{I}13$. $^3\text{T}1$ and $^3\text{I}13$ significantly affect the TOF of the reaction and are the TDTS and TDI in the reaction, respectively. The TDTS appears before the TDI. The energetic span (δE) in this cycle reaction can be expressed as follows:

$$\delta E = {}^3\text{T}1 - {}^3\text{I}10 + \Delta G_r$$

The δE was 45.36 kcal/mol. The TOF of the reaction obtained from approximating Eq. (10) was $\sim 3.35 \times 10^{-21} \text{ s}^{-1}$.

The ΔG_r was <0 for both $\text{CH}_2\text{CH}_2\text{O}$ and CH_2CHOH , generated from the other reactions. In this study, the TOFs were calculated, and the corresponding X_{TOF} values for each state are listed in Tables 4 and 5.

The ΔG_r of the generation of $\text{CH}_2\text{CH}_2\text{O}$ was -89.86 kcal/mol. The X_{TOF} values for the different states are as follows: $X_{\text{TOF}}(^3\text{T}1) \approx 0.59$, $X_{\text{TOF}}(^3\text{T}8) \approx 0.40$, $X_{\text{TOF}}(^3\text{I}6) \approx 0.40$, and $X_{\text{TOF}}(^3\text{I}12) \approx 0.56$. The X_{TOF} of all the other states were approximately 0. Significant effects on the TOF values of $^3\text{T}1$, $^3\text{T}8$, $^3\text{I}6$, and $^3\text{I}12$ states in the reaction were observed. $T_i - I_j$ showed relatively higher values with $^3\text{T}1 - {}^3\text{I}12$, the highest at 136.04 kcal/mol. Therefore, $^3\text{T}1$ and $^3\text{I}12$ were judged to be the rate-determining states, which determined the value of the TOF. The calculated δE and TOF were 46.18 kcal/mol and $8.37 \times 10^{-22} \text{ s}^{-1}$, respectively.

In the reaction that leads to CH_2CHOH , ΔG_r was -108.47 kcal/mol. After the calculation, the TDTS and the TDI were $^3\text{T}1$ and $^3\text{I}10$, respectively. The energetic span δE and TOF of the catalyst were 54.12 kcal/mol and $1.26 \times 10^{-27} \text{ s}^{-1}$, respectively.

From these data, the catalyst TOF can be indirectly estimated based on the energetic span. When $\Delta G_r < 0$, the corresponding TOF increased with decreasing energetic span. Multiple parallel reactions exist in the reaction system of N_2O and C_2H_6 . All the ΔG_r values of the reactions were <0 ; the reaction that leads to CH_3CHO achieved the lowest energetic span and the highest TOF. The TOF was defined as the number of reaction cycles per unit catalyst concentration per unit time. Co^+ showed

the highest catalytic activity in the production of $\text{CH}_2\text{CH}_2\text{O}$. The catalytic activity that produced $\text{C}_2\text{H}_5\text{OH}$ was less than that produced $\text{CH}_2\text{CH}_2\text{O}$. For the reaction that produced CH_2CHOH , the reaction possessed the largest energetic span, the lowest TOF, and the lowest catalytic activity of Co^+ . Therefore, the major product of the catalysis of N_2O and C_2H_6 by Co^+ was CH_3CHO , which was consistent with the catalysis of C_2H_6 by CrO^+ , MnO^+ , or FeO^+ [37,38].

4. Conclusions

Based on the UB3LYP/6-311 method from the DFT, the surface-hopping possibility at the crossing points of potential energy surfaces in the catalytic reactions of N_2O and C_2H_6 by Co^+ (^3F and ^5F states) have been investigated. Moreover, the catalytic activity of Co^+ for the four steps of the reaction was also studied. The results show that the reaction of N_2O and C_2H_6 catalyzed by Co^+ in the gas phase is a typical two-state reaction. At the five MECPs between two different spin-state potential energy surfaces, significant spin-orbit coupling effects, and surface-hopping probabilities were observed. At these points, effective hopping reduced the reaction potential energy, and facilitated the reaction by opening up an additional minimum energy pathway. The calculation of the maximum TOF of Co^+ by the energetic span model showed that Co^+ possessed the highest catalytic activity for the reaction to produce CH_3CHO with the maximum TOF, but the lowest catalytic activity in the reaction to produce CH_2CHOH . The major product of the catalysis of N_2O and C_2H_6 by Co^+ should therefore be CH_3CHO .

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Graphical Abstract

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Theoretical investigation into the Co^+ catalytic activity in the cycle reaction of N_2O with C_2H_6 in the gas phase

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The reaction of N_2O and C_2H_6 catalyzed by Co^+ is a typical two-state reaction. An energy span model has been applied to evaluate the catalytic performance of Co^+ .

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气相中 Co^+ 催化 N_2O 与 C_2H_6 循环反应催化剂活性的理论研究

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摘要: 采用密度泛函理论UB3LYP方法对 Co^+ 在三重态及五重态势能面上催化 N_2O 与 C_2H_6 进行循环反应的两态反应机理进行了研究. 运用Harvery方法优化了两自旋态势能面5个最低能量交叉点(MECP), 计算了MECP处自旋-轨道耦合作用. 采用Landau-Zener公式计算了自旋翻转处的系间窜越几率, 各MECP处均可发生有效系间窜越. 通过应用Kozuch提出的能量跨度模型, Co^+ 催化 N_2O 与 C_2H_6 在298K下反应生成 CH_3CHO 时有最大的TOF值 $3.35 \times 10^{-21} \text{ s}^{-1}$.

关键词: 一氧化二氮; 乙烷; 循环反应; 密度泛函; 两态反应; 系间窜越; 能量跨度; 转化频率

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1. 前言

烷烃催化氧化反应在实验和理论上是化学反应研究中的一个热点. 其中, 小分子烷烃如甲烷、乙烷等, 不但是优质的气体燃料, 同时也是十分重要的化工原料. 相对于甲烷, 乙烷有着更高的反应活性. 运用过渡金属作为烷烃反应的催化剂, 在一定程度上可以有效活化C-H键及C-C键, 并降低势垒, 促进反应发生. 研究发现, 第一排过渡金属氧化物离子 MnO^+ , FeO^+ , CoO^+ , NiO^+ 对于小分子烷烃均有很好的活化性能^[1-6]. 其中 MnO^+ 和 FeO^+ 有较高的催化效率, 但对有用的醇类及醛类产物的选择性较低; 虽然 NiO^+ 的选择性很高, 但其催化效率很低, 而仅 CoO^+ 同时具有较好催化效率和选择性. 1994年, Ryan等^[7]对 CoO^+ 的催化性能进行了实验研究, 发现 CoO^+ 活化乙烷发生反应有较好的反应速率, 并提出了相应的反应机理, 如式(1)–(4). 赵联明等^[8]对其反应机理进行了详细研究.

在有过渡金属参与的反应中, 高自旋态过渡金属复合物常常具有多个未成对电子, 在自旋-轨道耦合作用下易发生自旋翻转而引起自旋态的变化, 反应体系会在不同自旋态势能面上发生系间窜越^[9-13]. 此类涉及到自旋翻转现象的反应, 也就是所谓的“两态反应”^[14]. 它可以有效降低反应能垒, 直接改变反应机理, 使得反应沿低能路径进行, 从而促进反应发生. 为了研究 Co^+ 在催化过程中的自旋翻转现象, 进而讨论 Co^+ 在催化循环中的催化活性, 本文运用密度泛函理论(DFT)计算方法, 以 Co^+ 在三重态及五重态势能面上催化 N_2O 与 C_2H_6 循环反应为研究体系, 通过计算势能面交叉处的系间窜越几率, 寻找最低能量反应路径. 并应用Kozuch提出的能量跨度模型^[15-19], 对反应体系中 Co^+ 的转化频率TOF进行了计算, 用以评价催化剂 Co^+ 在催化 N_2O 与 C_2H_6 反应生成不同产物时的催化活性, 希望对其他相应的研究工

作提供参考依据。

2. 计算方法及理论背景

2.1. 几何构型优化

所有分子结构和反应体系势能面的计算均采用 Gaussian03^[20]程序完成。采用已被广为认可和应用的 DFT^[21]和 B3LYP 方法^[22]。在基组的选择上,对 C, H, O, N 非金属元素采用 6-311++G(2d, 2p) 基组, Co⁺ 采用 DZVP(d)(opt+3f) 基组^[23,24]。DZVP(d)(opt+3f) 基组由 Chiodo 等^[23]对 DZVP 基组进行扩展及优化所建立,已证实对第一过渡金属元素具有良好的计算效果。对反应体系势能面上的所有反应物、中间体、过渡态及其产物均进行了全参数优化,并经频率计算分析。过渡态及相邻的稳定点进行了内禀反应坐标 IRC 计算,证实了过渡态分别到反应物和产物基元步骤的可靠性。所有能量均进行了零点能(ZPE)校正。

反应过程中两反应势能面交叉点(CP)的计算采用 Yoshizawa 等^[25]的内禀反应坐标单点垂直激发法,再以 CP 点构型为依据,使用 Harvey 的能量梯度优化法得到最低能量交叉点(MECP)。为更好的理解反应物种的电子特性,采用 NBO5.0 程序^[26]计算了自然键布居和电荷分布。

2.2. 跃迁几率的计算

在最低能量交叉点区域,准简并的两个不同自旋态发生混合,在自旋-轨道耦合作用下,能量发生分离(分离能为 $2H_{\text{SOC}}$),不同势能面间的跃迁几率可用跃迁公式 Landau-Zener 公式^[27–29]来计算:

$$P^{\text{LZ}} = \exp\left(-\frac{4\pi^2 H_{\text{SOC}}^2}{h|\Delta F|} \sqrt{\frac{\mu}{2(E - E_{\text{MECP}})}}\right) \quad (5)$$

两自旋态势能面间的系间窜越的几率大小可用以下 Landau-Zener 跃迁几率 P^{LZ} 与一次系间窜越几率 (P_1^{ISC}) 和二次系间窜越几率 (P_2^{ISC}) 的关系进行估算。

$$P_1^{\text{ISC}} = 1 - P^{\text{LZ}} \quad (6)$$

$$P_2^{\text{ISC}} = (1 - P^{\text{LZ}})(1 + P^{\text{LZ}}) \quad (7)$$

MECP 处的自旋-轨道耦合作用能 (H_{SOC}) 用 GAMESS 程序^[30]完成。

2.3. 能量跨度模型

TOF 计算用于评价催化剂催化效果,基于 Eyring 过渡态理论^[31], Kozuch 等建立了 n 步反应催化循环的 TOF 表达式^[15–17,32,33](式(8))。

$$\text{TOF} = \frac{\Delta}{M} \cdot \frac{k_{\text{B}}T}{h} \cdot \frac{\exp(-\Delta G_{\text{T}}/RT) - 1}{\sum_i^n \sum_j^n \exp[(T_i - I_j - \Delta G_{ij})/RT]}$$

$$\Delta G_{ij} = \begin{cases} \Delta G_{\text{T}} & i > j \\ 0 & i \leq j \end{cases} \quad (8)$$

其中, Δ 为各基元反应正、逆反应速率常数积之差; M 为各基元反应的正、逆反应速率常数积所构成的矩阵; ΔG_{T} 为总反应初始反应物和最终产物的 Gibbs 自由能差。 T_i 和 I_j 分别为第 i 个过渡态与第 j 个中间体的 Gibbs 自由能。当有一项 $T_i - I_j$ 值最大时,该矩阵元会对整个矩阵的值产生最大程度的影响,相应地对多步循环反应的反应速率起决定作用。据此, Kozuch 将各反应态 (T_i , I_j) 对 TOF 的影响程度定义为控制度 X_{TOF} 。不同过渡态及中间体的 X_{TOF} 为:

$$X_{\text{TOF}, T_i} = \frac{\sum_j \exp(T_i - I_j - \Delta G_{ij})/RT}{\sum_i \sum_j \exp(T_i - I_j - \Delta G_{ij})/RT}$$

$$X_{\text{TOF}, I_j} = \frac{\sum_i \exp(T_i - I_j - \Delta G_{ij})/RT}{\sum_i \sum_j \exp(T_i - I_j - \Delta G_{ij})/RT} \quad (9)$$

$$\Delta G_{ij} = \begin{cases} \Delta G_{\text{T}} & i > j \\ 0 & i \leq j \end{cases}$$

在整个反应中,对 TOF 影响最大的过渡态 T_i 为决速过渡态(TDTS),对 TOF 影响最大的中间体 I_j 为决速中间体(TDI), TDTS 与 TDI 不一定相邻。

根据计算所得到的反应决速态对 TOF 表达式做近似处理。当 $\Delta G_{\text{T}} < 0$, $\exp(-\Delta G_{\text{T}}/RT) \gg 1$, 则:

$$\text{TOF} \approx \frac{k_{\text{B}}T}{h} \cdot \exp(-\delta E/RT) \quad (10)$$

$$\delta E = \begin{cases} T_{\text{TDTS}} - I_{\text{TDI}} & \text{if TDTS appears after TDI} \\ T_{\text{TDTS}} - I_{\text{TDI}} + \Delta G_{\text{T}} & \text{if TDTS appears before TDI} \end{cases}$$

式中 δE 为催化循环反应过程的表现活化能,也就是能量跨度。

3. 结果与讨论

3.1. 势能面的交叉

Co 电子排布为 $3d^7 4s^2$, Co⁺ 有单、三、五重态。经计算,其中单重态所有驻点的能量均高于三重态和五重态,因此本文不做讨论。三重态 Co⁺ 电子排布为 (^3F , $3d^8$)^[34], 能量较激发态五重态 (^5F , $3d^7 4s^1$)^[34] 低 6.0 kcal/mol, Co⁺ 以低自旋三重态进入反应通道。Co⁺ 催化 N₂O 与 C₂H₆ 的部分反应路径如图 1 所示。且可以看出,在 Co⁺ 催化 N₂O 与 C₂H₆ 反应生成 C₂H₅OH 以及重要中间产物 CoC₂H₄⁺ 的过程中,存在三个势能面交叉点。交叉点 CP1 位于过渡态 T1 后,过渡态 $^5\text{T1}$ 在 Co⁺ 与 N 成键的过程中,形成势能较低的中间体 ^5II 。CoO⁺ 与 C₂H₆ 反应时,CoO⁺ 对 C₂H₆ 有正上

方和端位两种不同的进攻方式, 分别为路径a与路径b. 路径b中不论是三重态还是五重态, 中间体I2b及过渡态T3b的能量均高于路径a中中间体及过渡态的, 反应趋向于以低能路径a进行, 过渡态T3b前的交叉点不具有研究意义. 在过渡态T3a中, C-H键与Co原子之间存在电子授-受作用, 相互作用的强度可采用二阶微扰能^[35] ($\Delta E(2) = -2 \langle \sigma | \hat{F} | \sigma^* \rangle / \varepsilon \sigma^* - \varepsilon \sigma$) 进行估算. ⁵T3a中, $E(2)_{\text{BD}(\text{C-H}) \rightarrow \text{LP}^*(\text{Co})} = 4.22 \text{ kcal/mol}$. ³T3a中, $E(2)_{\text{BD}(\text{C-H}) \rightarrow \text{LP}^*(\text{Co})} = 15.64 \text{ kcal/mol}$, $E(2)_{\text{BD}(\text{Co-O}) \rightarrow \text{BD}^*(\text{C-H})} = 9.86 \text{ kcal/mol}$, $E(2)_{\text{BD}(\text{C-H}) \rightarrow \text{BD}^*(\text{Co-O})} = 30.67 \text{ kcal/mol}$. 三重态的二级微扰能较高, 表明有更明显的电子转移, C-H键中成键电子减少, 反键电子增多, C-H键的稳定性遭到破坏, 易于断裂. 在T3a后, 存在势能面交叉点CP2, ³I3比⁵I3更稳定. 该部分反应为平行反应, 生成C₂H₅OH与CoC₂H₄⁺的产率之比Y1:Y2约为0.21:0.79^[7].

如图2所示, CoC₂H₄⁺与N₂O发生反应, 在过渡态T8后存在势能面交叉点CP3, 对过渡态T8中Co与N-O间相互作用的二级微扰能进行比较, ³T8中 $E(2)_{\text{LP}(\text{Co}) \rightarrow \text{BD}^*(\text{N-O})} = 3.90 \text{ kcal/mol}$. ⁵T8中 $E(2)_{\text{BD}^*(\text{Co-N}) \rightarrow \text{BD}^*(\text{N-O})} = 11.31 \text{ kcal/mol}$. 五重态的二级微扰能较大, 其中N-O键较三重态中的更易断裂. 中间体⁵I8较³I8势能更低. ⁵CoOC₂H₄⁺继续发生H原子的转移时, 势垒T9前存在势能面交叉点CP4, 反应可重回三重态势能面进行, ³I10为反应势能面最低点, 产物复合物解离需要吸收大量的热, 一般认为会抑制产物的生成.

对于CoC₂H₄⁺与N₂O反应生成CH₃CHO以及CH₂CH₂O的平行反应. 如图3所示, ³T11与⁵T11能量相近, 在过渡态T11之前存在一个前交叉点CP5. 该交叉点处若发生有效系间窜越, 体系会窜越到势能面较低的三重态势能面上. ³T11处势垒较小, 可以降低反应能垒, 促进反应进行.

综上所述, 整个Co⁺催化N₂O与C₂H₆反应历程发生在两个势能面上, 反应中共出现五处势能面的交叉, 是一个典型的两态反应.

3.2. 最低能量交叉点(MECP)及最低能量路径

3.2.1. MECP

根据自旋-轨道耦合定则, 催化循环反应中出现的五个交叉点处总自旋的改变值满足自旋-轨道耦合选择定律($\Delta S = \pm 1$), 具有发生自旋翻转的可能性. 为确定各MECP位置, 本文先运用Yoshizawa的内禀坐标单点垂直激发的方法, 对三重态的IRC反应坐标点所对应的构型进行单点垂直激发计算, 得到了五重态势能面上的垂

直投影. 在两势能面的交叉区域处估算近似CP点位置, 继而采用Harvey等^[36]的Crossing2004程序包, 优化得到MECP. MECP是反应交叉区域处的能量最低点, 本文中的五个交叉点构型参数如图4所示的MECP附近, 三重态与五重态结构近似, 因能量近似相等而发生强烈作用, 形成三重态与五重态的混合态. 在自旋-轨道耦合作用下, 混合态能量发生分裂, 为探讨各MECP附近非绝热跃迁情况, 本文在各MECP构型下, 采用GAMESS程序计算得到各MECP处自旋-轨道耦合常数列于表1.

由表1可知, 在各MECP处, 计算得到的自旋污染均较小, 并无显著的自旋污染, 对能量产生的影响可以忽略. 通过计算, 在5个MECP处均有较大的自旋-轨道耦合作用能 H_{SOC} , 高、低势能面能差 $2H_{\text{SOC}}$ 较大, 由(5)式算得的由低势能面向高势能面的Landau-Zener跃迁几率 P^{LZ} 很小, 说明体系在各MECP处极容易沿低势能面从一势能面到另一势能面, 一次系间几率很高, 二次系间几率均接近于1, 各MECP均为有效交叉点. 因此, 两态反应路径上势能面交叉处的非绝热性不会对低能反应路径造成影响.

3.2.2. 最低能量路径

有效交叉点的出现改变了原本的反应机理, 形成最低能量反应路径以降低能垒或影响产物分布. 综合上文分析, 催化循环的最低能量反应路径为:

3.3. 催化循环反应中TOF的计算

Co⁺催化N₂O与C₂H₆进行反应, 其反应历程中包含有4个催化循环. 为评价Co⁺在反应循环中的催化性能, 本文运用能量跨度模型对反应循环中TOF进行了计算. 反应过程中中间产物CoO⁺与CoC₂H₄⁺既是前一步反应的产物, 又是后一步的反应物, 为计算方便, 本文将其分别作为过渡态T2与T7处理. CoOC₂H₄⁺继续反应需跨越势能更高的过渡态T9, T11, 故选取T9和T11分别作为两中间体之间的势垒. 反应最低能量路径上各驻点的Gibbs自由能图如图5所示, 反应循环生成C₂H₅OH, 反应经历两个过渡态之后的交叉点, 部分反应路径在高自旋五重态势能面上发生. 反应中Gibbs自由能最高的过渡态为³T1, ³I4为Gibbs自由能最低的中间体. 反应的Gibbs自由能变为-51.01 kcal/mol. 根据TOF中关于控制度的

概念, 本文所计算的298 K时该反应循环中各个过渡态和中间体的 X_{TOF} 列于表2. 可以看出, $X_{\text{TOF}, {}^3\text{T1}} \approx 0.99$, $X_{\text{TOF}, {}^3\text{I4}} \approx 1$. 说明该反应循环的决速过渡态(TDTS)和决速中间体(TDI)分别为 ${}^3\text{T1}$ 和 ${}^3\text{I4}$, 它们主要决定了 Co^+ 催化了 N_2O 和 C_2H_6 反应生成 $\text{C}_2\text{H}_5\text{OH}$ 的TOF, 决速过渡态 ${}^3\text{T1}$ 位于决速中间体 ${}^3\text{I4}$ 之前, $i < j$, 循环反应的能量跨度可表示为:

$$\delta E = {}^3\text{T1} - {}^3\text{I4} + \Delta G_r$$

算得 $\delta E = 50.08 \text{ kcal/mol}$, 用近似公式(10)求得反应循环的TOF约为 $1.16 \times 10^{-24} \text{ s}^{-1}$.

在 Co^+ 催化 N_2O 与 C_2H_6 反应生成产物 CH_3CHO 的过程中, Gibbs自由能最高的过渡态为 ${}^3\text{T1}$, 最低的中间体为 ${}^3\text{I13}$, 反应的Gibbs自由能变 ΔG_r 为 -117.22 kcal/mol . 本文计算了TOF值和各态对应的 X_{TOF} , 结果见表3. 结果表明, $X_{\text{TOF}, {}^3\text{T1}} \approx 0.87$, $X_{\text{TOF}, {}^3\text{I10}} \approx 0.88$. 虽然 ${}^3\text{I6}$ 和 ${}^3\text{T8}$ 相对的 X_{TOF} 较大(约0.12), 但仍远小于 ${}^3\text{I13}$. ${}^3\text{T1}$ 和 ${}^3\text{I13}$ 对反应循环的TOF影响最大, 分别为该循环中的TDTS和TDI, 其中前者居前. 该循环反应中的 $\delta E = {}^3\text{T1} - {}^3\text{I10} + \Delta G_r$. 由此算得 $\delta E = 45.36 \text{ kcal/mol}$, 用近似公式(10)求得该反应循环的TOF约为 $3.35 \times 10^{-21} \text{ s}^{-1}$.

反应过程中其余两个循环反应分别生成 $\text{CH}_2\text{CH}_2\text{O}$ 与 CH_2CHOH , 反应 ΔG_r 均小于0; 本文同时估算了它们的TOF, 各态对应的 X_{TOF} 见表4和表5.

计算发现, 对于产物为 $\text{CH}_2\text{CH}_2\text{O}$ 的反应循环, 反应的Gibbs自由能变为 -89.86 kcal/mol . $X_{\text{TOF}, {}^3\text{T1}} \approx 0.59$, $X_{\text{TOF}, {}^3\text{T8}} \approx 0.40$, $X_{\text{TOF}, {}^3\text{I6}} \approx 0.40$, $X_{\text{TOF}, {}^3\text{I12}} \approx 0.56$. 其余态的 X_{TOF} 近似为0. 反应过程中的 ${}^3\text{T1}$, ${}^3\text{T8}$, ${}^3\text{I6}$ 和 ${}^3\text{I12}$ 均对TOF值的影响较大, 有四项 $T_i - I_j$ 值较大, 最大者 ${}^3\text{T1} - {}^3\text{I12} = 136.04 \text{ kcal/mol}$, 因此认为 ${}^3\text{T1}$ 和 ${}^3\text{I12}$ 为决速态, 决定了TOF值的大小, 求得反应 $\delta E = 46.18 \text{ kcal/mol}$, $\text{TOF} = 8.37 \times 10^{-22} \text{ s}^{-1}$.

产物为 CH_2CHOH 的反应循环, 反应的 $\Delta G_r =$

-108.47 kcal/mol . 经计算得到TDTS为 ${}^3\text{T1}$, TDI为 ${}^3\text{I10}$, $\delta E = 54.12 \text{ kcal/mol}$, $\text{TOF} = 1.26 \times 10^{-27} \text{ s}^{-1}$.

综上所述, 根据 δE 值可以间接估算催化剂TOF值. 对于 $\Delta G_r < 0$ 的反应, δE 越小, 相应的TOF值越大. 在 N_2O 与 C_2H_6 整个反应体系中, 反应有多个平行反应, 反应循环的 ΔG_r 均小于0. 其中产物为 CH_3CHO 的反应循环有最小的 δE 值和最大的TOF值. 由于TOF被定义为单位时间内单位催化剂浓度下反应循环发生的次数, 因此可以认为, 该循环中催化剂 Co^+ 的活性最大, 反应生成 $\text{CH}_2\text{CH}_2\text{O}$ 时催化活性次之, Co^+ 在生成 $\text{C}_2\text{H}_5\text{OH}$ 反应中的催化活性小于生成 $\text{CH}_2\text{CH}_2\text{O}$ 中的. 而对于产物为 CH_2CHOH 的反应循环, 反应有最大的 δE , 最小的TOF值, 催化剂 Co^+ 的活性最小. 由此可以认为, Co^+ 催化 N_2O 与 C_2H_6 反应主要生成 CH_3CHO . 这与 CrO^+ , MnO^+ , FeO^+ 与 C_2H_6 反应的实验结果^[37,38]相一致.

4. 结论

采用DFT在UB3LYP/6-311++G(2p, 2d)/DZVP(opt+3f)方法水平上, 对 Co^+ (${}^3\text{F}$, ${}^5\text{F}$)催化 N_2O 与 C_2H_6 的循环反应中出现的反应势能面交叉点处的系间窜越几率以及催化剂 Co^+ 分别在四个循环反应中的催化活性进行了详细研究. 结果表明, 气相中 Co^+ 催化 N_2O 与 C_2H_6 发生的是典型的两态反应. 两个不同自旋态势能面间的五个最低能量交叉点处均有较大的自旋耦合作用能和系间窜越几率, 表明在该点处可以发生有效窜越, 降低反应势能, 使得反应沿最低能量路径进行, 加快反应速率. 经能量跨度模型对 Co^+ 催化剂在反应中转化频率的计算发现, Co^+ 在催化生成 CH_3CHO 反应时活性最高, TOF值最大; 在 CH_2CHOH 生成反应中催化活性最低. Co^+ 催化 N_2O 与 C_2H_6 发生反应主要生成 CH_3CHO .

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