Theoretical Study on the Mechanism of $Ni(d^{10}\,{}^1S)+CO_2+3H_2 \rightarrow NiO+CH_4+H_2O$ Reaction

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Introduction

Ni-based catalyst is very effective in CO_2 hydrogenation, and its reaction mechanism therefore represents a research topic of great interest[1-3]. Some experimental investigations provide evidences for the formation of adsorbed surface acid species in CO_2 hydrogenation on Ni-based catalysts[4,5]. However, no theoretical study regarding co-interaction of H_2 molecule and CO_2 molecule with Ni atom is available so far to our knowledge. It is shown recently, density functional methods yield reasonable molecular geometries at a relatively low computational cost for transition metal system[6-8]. In present work, the co-interaction of H_2 and CO_2 with Ni is studied by using DTF method in order to find possible reaction intermediates and reaction path in CO_2 hydrogenation on Ni-based catalyst.

Computational Details

Full geometry optimizations and ZPE corrected energies of all intermediates and transition states in the above reaction were performed at B3LYP/6-311+G(2d,2p) level using Gaussian 98 programs. The intrinsic reaction coordination (IRC) method is used to track and verify the minimum energy paths from intermediates to intermediates via transition states.

Results and Discussion

The optimized geometries of various species along the predicted reaction path of the titled reaction and their corresponding ZPE corrected relative energies are shown in **Figure 1**.

Our predicted reaction path can be divided into three stages as the following:

1. $CO_2 + H_2 + Ni(d^{101}S) \rightarrow H_2\text{-}NiCO_2 \rightarrow TS1 \rightarrow HNiCOOH \rightarrow TS3 \rightarrow O\text{-}NiCHOH$
2. $O\text{-}NiCHOH + H_2 \rightarrow H_2\text{-}NiOCHOH \rightarrow TS4 \rightarrow HO\text{-}HNiCHOH \rightarrow TS5 \rightarrow H_2O\text{-}NiCHOH \rightarrow NiCHOH + H_2O$
3. $NiCHOH + H_2 \rightarrow H_2\text{-}NiCHOH \rightarrow TS6 \rightarrow H_2\text{-}NiCHOH' \rightarrow TS7 \rightarrow HNiCH_2OH \rightarrow TS8 \rightarrow HNiCH_2OH' \rightarrow TS9 \rightarrow HONiCH_3 \rightarrow TS10 \rightarrow ONiHCH_3 \rightarrow TS11 \rightarrow ONi\text{-}CH_4 \rightarrow CH_4 + NiO$

In stage 1, reactants H_2 and CO_2 molecules first co-interact with the Ni center with formation the precursor complex H_2-$NiCO_2$ before proceeding to transition state. The calculation shows that, for H_2-$NiCO_2$ species, H_2 is undissotiatively interacted with Ni atom and Ni-CO_2 moiety is very close to the singlet η^2_{co} complex which have been found to be the most stable form in four possible different $Ni(CO_2)$ complex modes[9]. The calculated energies place this species 51.0kJ mol^{-1} lower than that of the free H_2 and η^2_{co} mode of $NiCO_2$ complex, which means that the H_2-$NiCO_2$ complex may be a possible intermediate in CO_2 hydrogenation involving Ni atom. From H_2-$NiCO_2$ complex, the reaction proceeds to form intermediate HNiCOOH in which -COOH fragment is much similar to carboxyl. From intermediate HNiCOOH the reaction continues to form intermediate Ni-HCOOH whose HCOOH moiety were very close to formic acid molecule. The above results indicate that the predicted reaction stage 1 involves the formation of adsorbed formic acid intermediates and leads to the cleavage of C-O bond of CO_2 molecule. This is in accordance with previous experimental investigations which provided evidences that the CO_2 hydrogenation on Ni catalyst involves the formation of adsorbed formic acid.[10]

In stage 2, another H_2 molecule attaches the O-NiCHOH species with formation of the H_2-NiOCHOH complex. For this species, H_2 is undissotiatively interacted with Ni. From this complex, the reaction is predicted to the formation of intermediate HO-HNiCHOH in which H-H bond of H_2 molecule is broken. From intermediate HO-HNiCHOH, the reaction continues to proceed and forms intermediate H_2O-NiCHOH in which the adsorbed water molecule forms. The H_2O-NiCHOH may lose one water molecule and completes this reaction stage with the formation of NiCHOH species.

In stage 3, another H_2 molecule continues to attach the NiCHOH species and forms H_2-NiCHOH complex. In this complex, H_2 molecule is still undissotiatively interacted with Ni atom. From this species, the reaction proceeds via a series of transition states and corresponding intermediates to form the intermediates $HNiCH_2OH$ in which the H-H bond of H_2 molecule is broken and the CH_2OH moiety forms. From this species, the reaction continues to proceed and eventually forms the ONi-CH_4 complex which contains an adsorbed methane molecule. This intermediate may lose the adsorbed methane molecule and completes the whole reaction with formation of NiO and CH_4 products.

The overall exothermicity of this reaction is calculated to be 61.1kJmol^{-1}. B3LYP/6-311+G(2d,2p) level gives the energy between intermediate Ni-HCOOH and transition state TS3 is 246.0kJ mol^{-1} which is the largerest in the whole predicted reaction path, the rate-controlling step therefore may be considered to be from intermediate Ni-HCOOH to intermediate O-NiCHOH via TS3.

Conclusion

A detailed reaction mechanism of CO_2 hydrogenation on Ni atom is carried out at B3LYP/6-311+G(2d,2p) level. The calculation predicts that this reaction involves the formation of some sorts of adsorbed formic acid complex, the exothermicity of overall reaction is calculated to be about 61.1kJ mol^{-1}, and the activation energy is calculated to be about 246.0kJ mol^{-1}. The rate-controlling step is predicted to be the step from intermediate Ni-HCOOH to intermediate O-NiCHOH via TS3.

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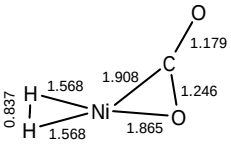
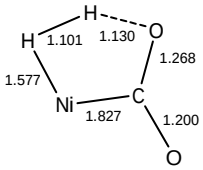
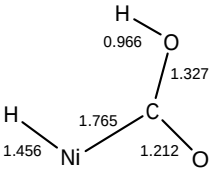


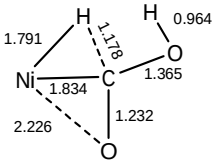
H_2-$NiCO_2$ (-274.7)



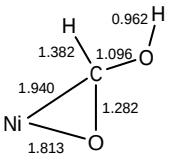
TS1 (-115.8)



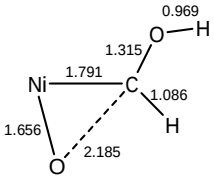
HNiCOOH (-211.0)



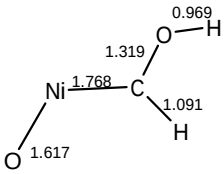
TS2 (-105.8)



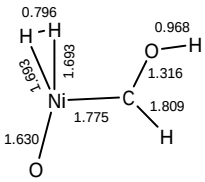
Ni-HCOOH (-162.4)



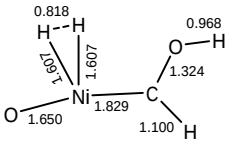
TS3 (83.6)



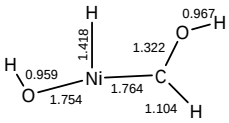
O-NiCHOH (53.9)



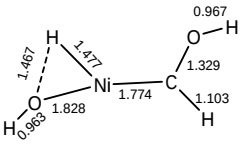
H_2-NiOCHOH (24.0)



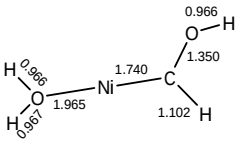
TS4(62.1)



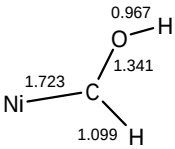
OH-HNiCHOH (-180.5)



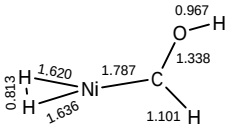
TS5 (-116.5)



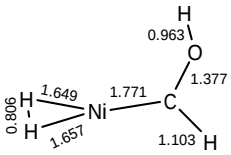
H_2O-NiCHOH (-188.2)



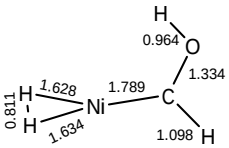
NiCHOH (-104.3)



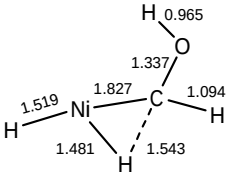
H_2-NiCHOH (-159.5)



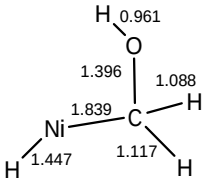
TS6 (-103.7)



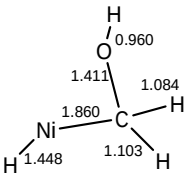
H_2-NiCHOH′
(-174.5)



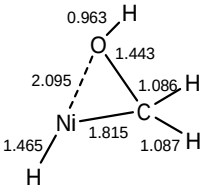
TS7 (-101.8)



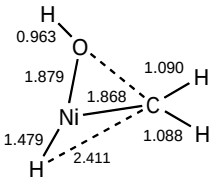
$HNiCH_2OH$ (-207.3)



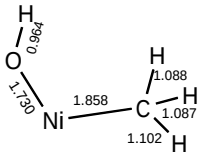
TS8 (-201.7)



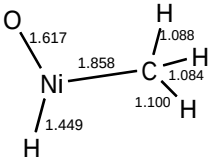
$HNiCH_2OH'$ (-235.0)



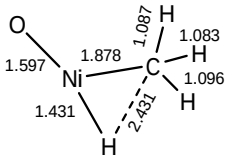
TS9 (-115.7)



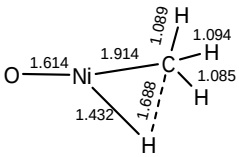
$HONiCH_3$(-318.2)



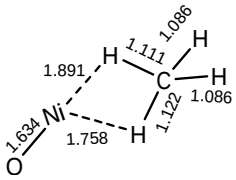
TS10 (-83.5)



$ONiHCH_3$(-92.3)



TS11 (-72.4)



ONi-CH_4 (-121.8)

Products
NiO + CH_4+ H_2O

(-61.0)

Figure 1. Geometries of all species obtained at B3LYP/6-311+G(2d,2p) level along the Ni(d^{10} ^1S)+CO_2+$3H_2$→ NiO+CH_4+H_2O reaction. Bond lengths are in Å, and the ZPE corrected relative energies with respected to reactant [Ni(d^{10} ^1S)+CO_2+$3H_2$] given in kJ mol^{-1} are in parentheses.