Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information

Methanol synthesis from CO_2 hydrogenation promoted by hydrogen dissociation on Ga_3Ni_5(221) surface

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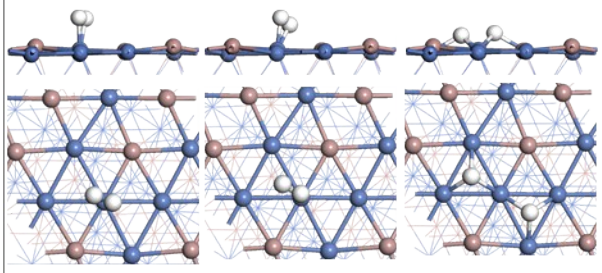
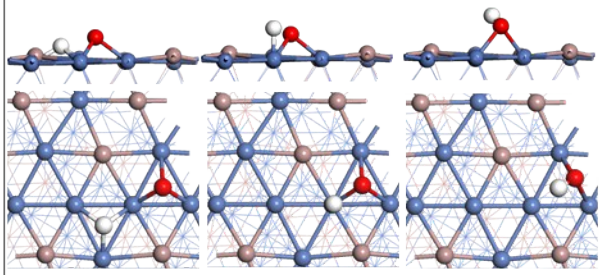
R0-1 $H_2 \rightarrow H+H$



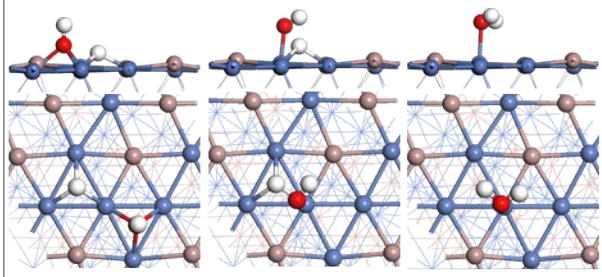
H_2 TS0-1 H+H

R0-2 $O+H \rightarrow OH$



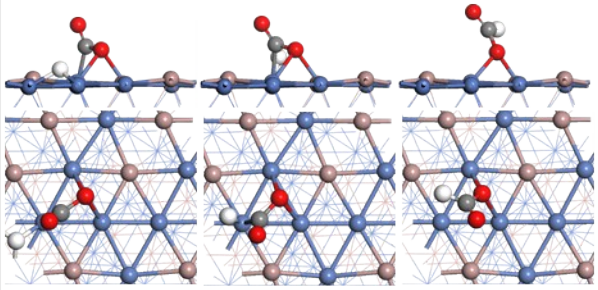
O+H TS0-2 OH

R0-3 $OH+H \rightarrow H_2O$



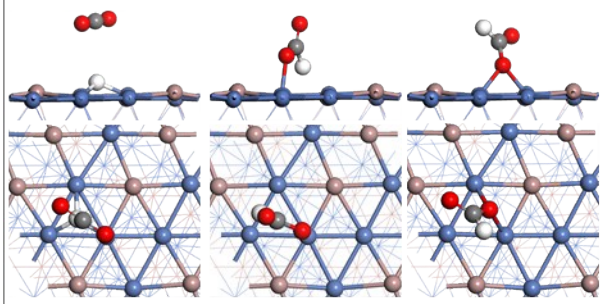
OH+H TS0-3 H_2O

R1-1 $CO_2+H \rightarrow$ *mono*-HCOO



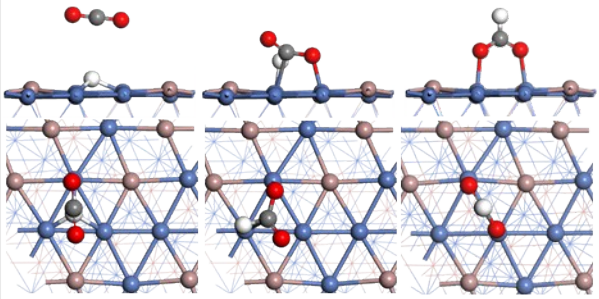
CO_2+H TS1-1 *mono*-HCOO

R1-2 CO_2(g)+H→*mono*-HCOO



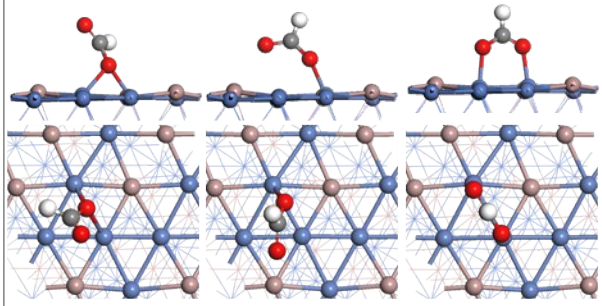
CO_2(g)+H TS1-2 *mono*-HCOO

R1-3 CO_2(g)+H→*bi*-HCOO



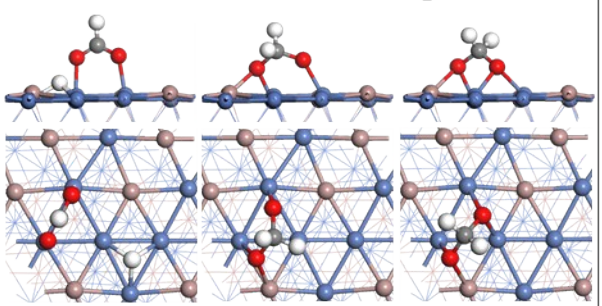
CO_2(g)+H TS1-3 *bi*-HCOO

R1-4 *mono*-HCOO→*bi*-HCOO

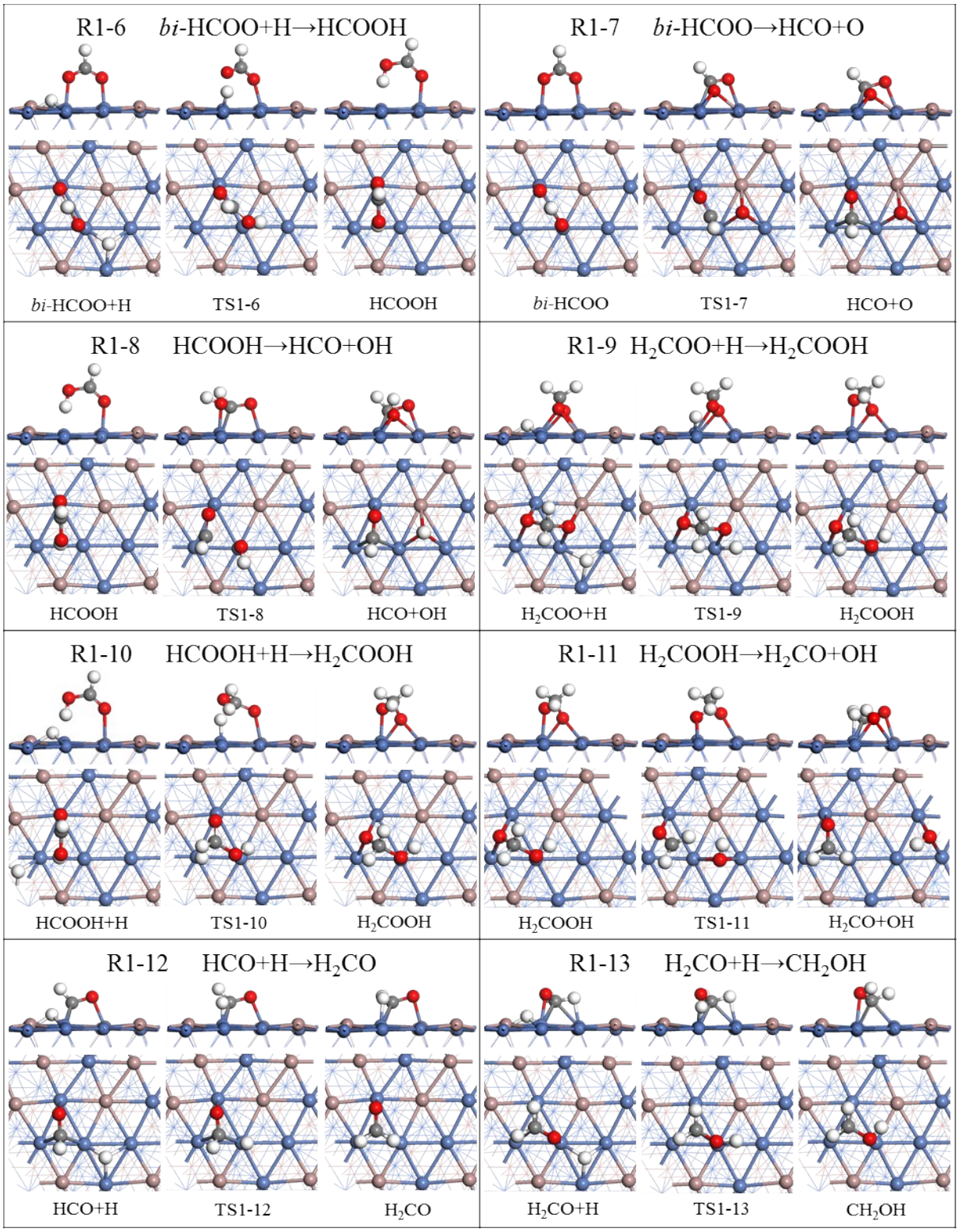


mono-HCOO TS1-4 *bi*-HCOO

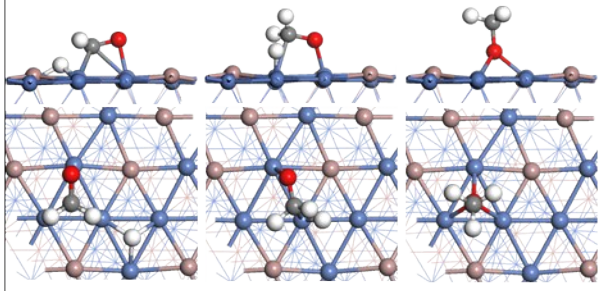
R1-5 *bi*-HCOO+H→H_2COO



bi-HCOO+H TS1-5 H_2COO

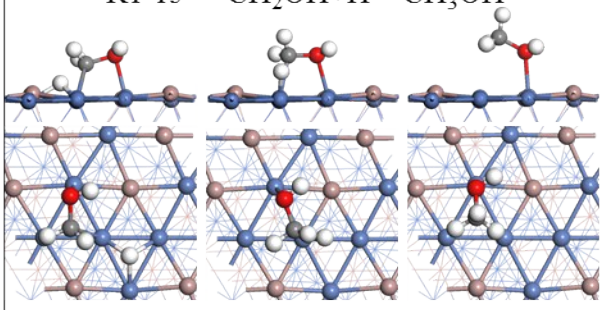

R1-6 bi-HCOO+H→HCOOH
bi-HCOO+H
TS1-6
HCOOH
R1-7 bi-HCOO→HCO+O
bi-HCOO
TS1-7
HCO+O
R1-8 HCOOH→HCO+OH
HCOOH
TS1-8
HCO+OH
R1-9 H2COO+H→H2COOH
H2COO+H
TS1-9
H2COOH
R1-10 HCOOH+H→H2COOH
HCOOH+H
TS1-10
H2COOH
R1-11 H2COOH→H2CO+OH
H2COOH
TS1-11
H2CO+OH
R1-12 HCO+H→H2CO
HCO+H
TS1-12
H2CO
R1-13 H2CO+H→CH2OH
H2CO+H
TS1-13
CH2OH

R1-14 $H_2CO+H \rightarrow CH_3O$



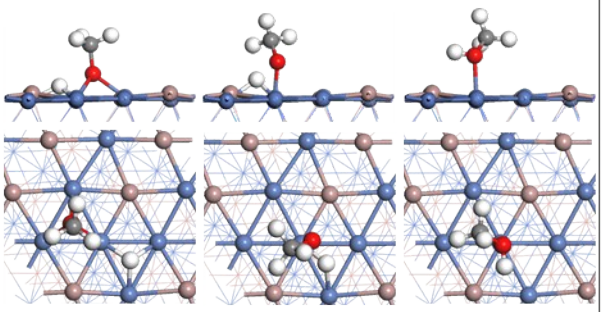
H_2CO+H TS1-14 CH_3O

R1-15 $CH_2OH+H \rightarrow CH_3OH$



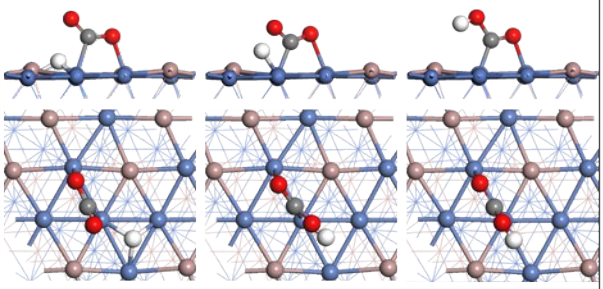
CH_2OH+H TS1-15 CH_3OH

R1-16 $CH_3O+H \rightarrow CH_3OH$



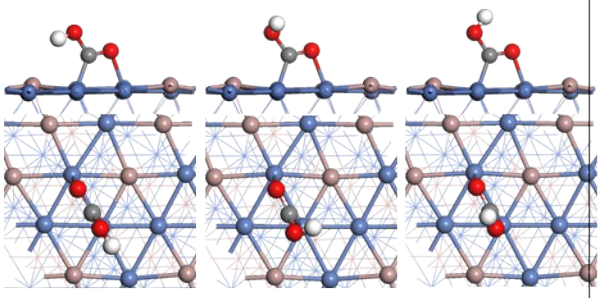
CH_3O+H TS1-16 CH_3OH

R2-1 $CO_2+H \rightarrow$ *trans*-COOH



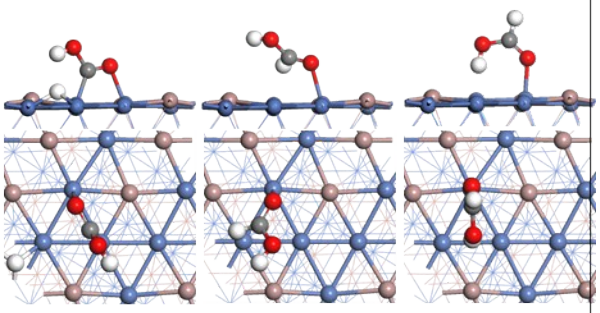
CO_2+H TS2-1 *trans*-COOH

R2-2 *trans*-COOH→*cis*-COOH



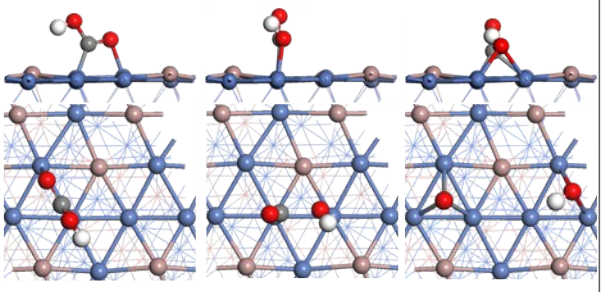
trans-COOH TS2-2 *cis*-COOH

R2-3 *trans*-COOH+H→HCOOH



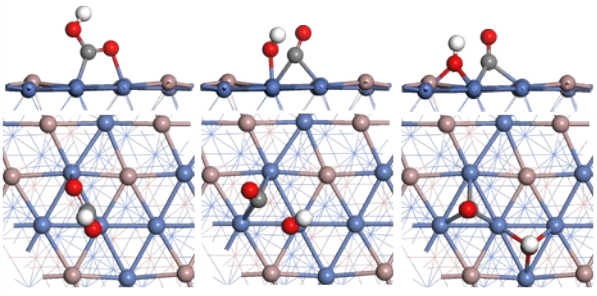
trans-COOH+H TS2-3 HCOOH

R2-4 *trans*-COOH→CO+OH



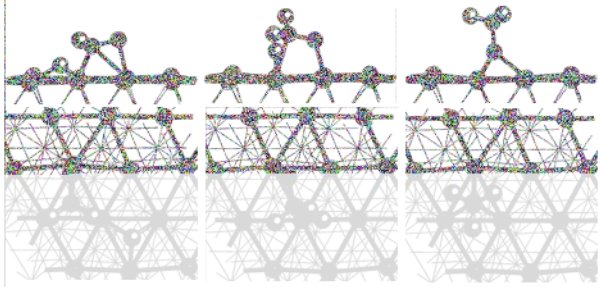
trans-COOH TS2-4 CO+OH

R2-5 *cis*-COOH→CO+OH



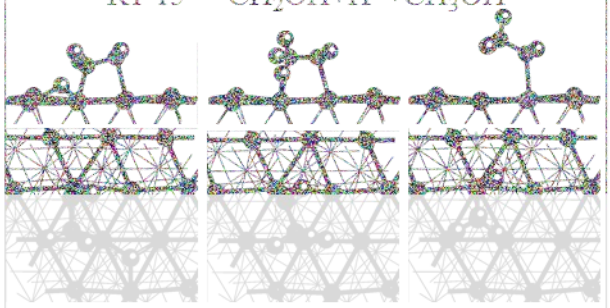
cis-COOH TS2-5 CO+OH

R1-14 $H_2CO+H \rightarrow CH_3O$



H_2CO+H TS1-14 CH_3O

R1-15 $CH_2OH+H \rightarrow CH_3OH$



CH_2OH+H TS1-15 CH_3OH

R1-16 $CH_3O+H \rightarrow CH_3OH$

CH_3O+H TS1-16 CH_3OH

R2-1 $CO_2+H \rightarrow$ *trans*-COOH

CO_2+H TS2-1 *trans*-COOH

R2-2 *trans*-COOH→*cis*-COOH

trans-COOH TS2-2 *cis*-COOH

R2-3 *trans*-COOH+H→HCOOH

trans-COOH+H TS2-3 HCOOH

R2-4 *trans*-COOH→CO+OH

trans-COOH TS2-4 CO+OH

R2-5 *cis*-COOH→CO+OH

cis-COOH TS2-5 CO+OH

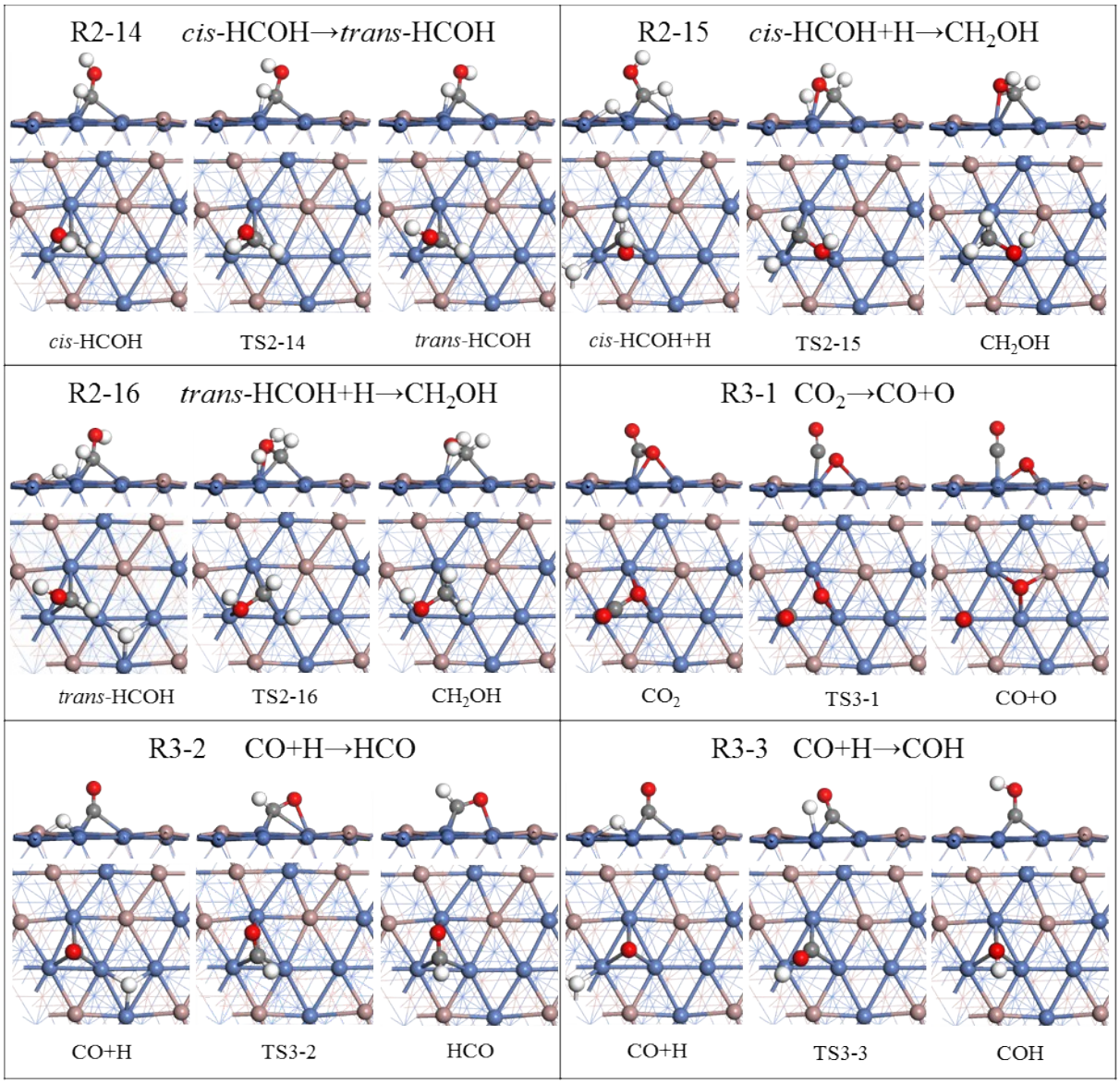


Fig. S1 The side views (top one) and top views (bottom one) of initial states, transition states and final states of all the elementary steps that are considered in the process of CO_2 hydrogenation to CH_3OH on Ga_3Ni_5(221) surface. Here, C, H, O, Ni and Ga atoms are shown in grey, white, red, blue and brown balls, respectively.