Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Hydrodeoxygenation of Acetic Acid over Ni-promoted Cu-based Catalysts: A Theoretical Mechanism and Kinetic Study

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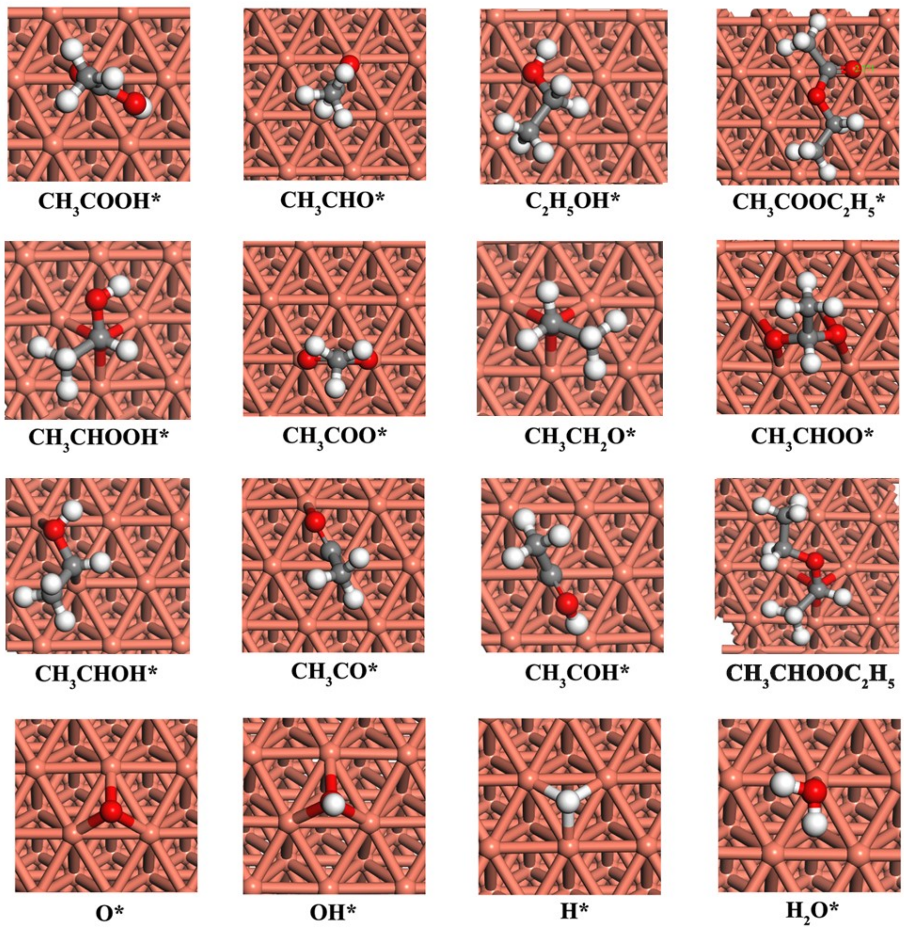
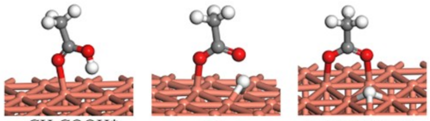
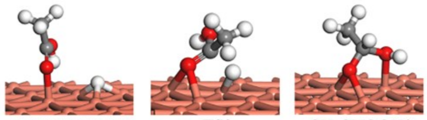


Figure S1. The configuration of adsorbates involved in the HDO process of acetic acid on the Cu (111) surface

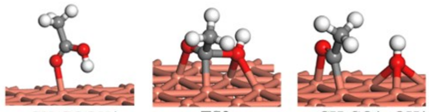
R1 $CH_3COOH^* \rightarrow CH_3COO^* + H^*$



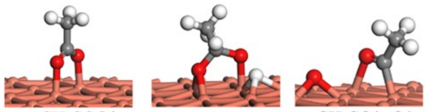
R2 $CH_3COOH^* + H^* \rightarrow CH_3CHOOH^*$



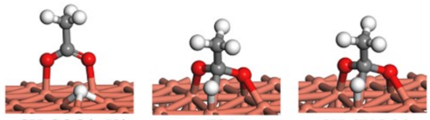
R3 $CH_3COOH^* \rightarrow CH_3CO^* + OH^*$



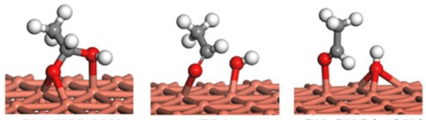
R4 $CH_3COO^* \rightarrow CH_3CO^* + O^*$



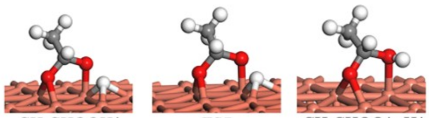
R5 $CH_3COO^* + H^* \rightarrow CH_3CHOO^*$



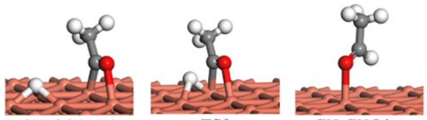
R6 $CH_3CHOOH^* \rightarrow CH_3CHO^* + OH^*$



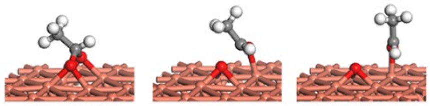
R7 $CH_3CHOOH^* \rightarrow CH_3CHOO^* + H^*$



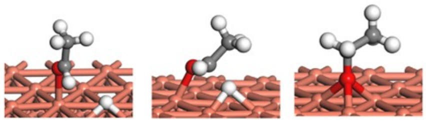
R8 $CH_3CO^* + H^* \rightarrow CH_3CHO^*$



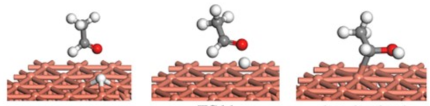
R9 $CH_3CHOO^* \rightarrow CH_3CHO^* + O^*$



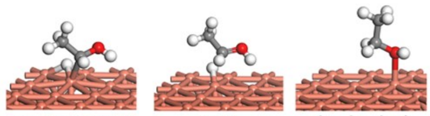
R10 $CH_3CHO^* + H^* \rightarrow CH_3CH_2O^*$



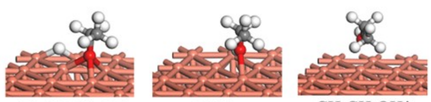
R11 $CH_3CHO^* + H^* \rightarrow CH_3CHOH^*$



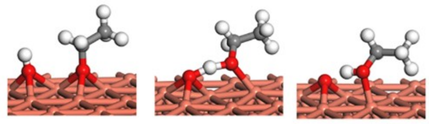
R12 $CH_3CHOH^* + H^* \rightarrow CH_3CH_2OH^*$



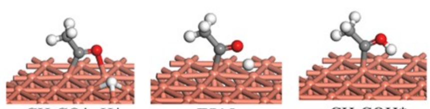
R13 $CH_3CH_2O^* + H^* \rightarrow CH_3CH_2OH^*$



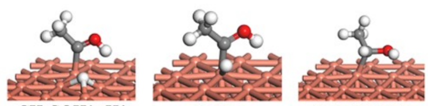
R14 $CH_3CH_2O^* + OH^* \rightarrow CH_3CH_2OH^* + O^*$



R15 $CH_3CO^* + H^* \rightarrow CH_3COH^*$



R16 $CH_3COH^* + H^* \rightarrow CH_3CHOH^*$



R17 $CH_3CO^* + C_2H_5O^* \rightarrow CH_3COOC_2H_5^*$

R18 $CH_3CHO^* + C_2H_5O^* \rightarrow CH_3CHOOC_2H_5^*$

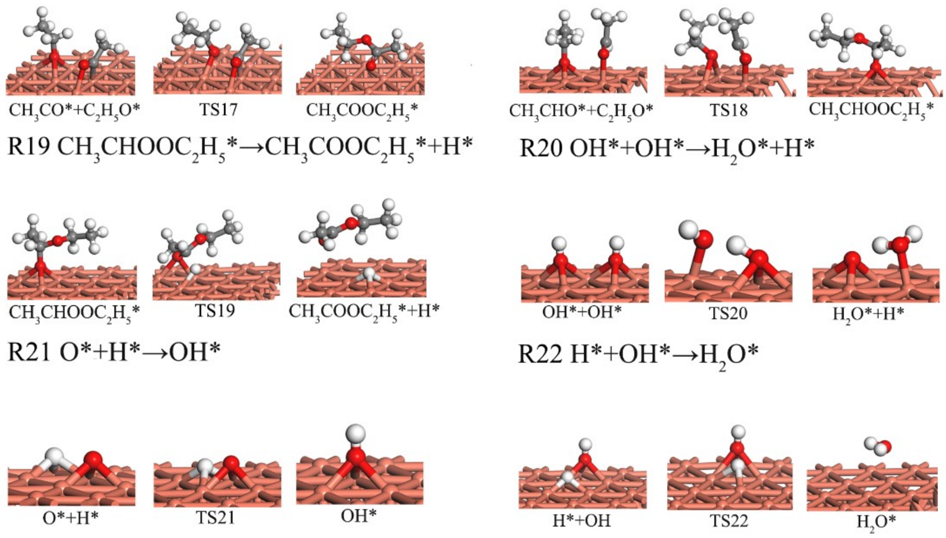


Figure S2. The configuration of IS, TS and FS of the each elementary step involved in the conversion of acetic acid on the Cu (111) surface

Table S1. The relative stability of the several NiCu(111) surface with and without the existence of the adsorbates on the Ni site. The $Ni_{sin}Cu$, $Ni_{sin}Cu$, $Ni_{sin}Cu$ and NiCu-X*was the same meaning as that in the Figure 1. For every chosen species, adsorbate with highest adsorption energies was defined as the zero point of energy for simplicity.

Species	$Ni_{sin}Cu$ (eV)	$Ni_{dim}Cu$ (eV)	$Ni_{tet}Cu$ (eV)
bare	0.00	+0.02	+0.05
H*	+0.36	+0.19	0.00
O*	+0.72	+0.38	0.00
OH*	+0.32	+0.18	0.00

Table S2. The elementary reaction and corresponding rate equation involved in the HDO process of acetic acid. There were 4 kinds of sites in the current system. *, **, *** and **** represented that the most stable site (Ni^3 site), the secondary stable site (usually Ni^2 site), the site for the adsorbed hydrogen atoms on the nickel and the monometallic Cu site, respectively.

Elementary Reaction	Rates equation
$RCOOH^{*} + ^{***} \rightarrow RCOO^{*} + H^{***}$	$r_1 = k_1\theta_{RCOOH*}\theta_{***} - k_{-1}\theta_{RCOO*}\theta_{H***}$
$RCOOH^{*} + H^{***} \rightarrow RCHOOH^{*} + ^{***}$	$r_2 = k_2\theta_{RCOOH*}\theta_{H***} - k_{-2}\theta_{RCHOOH*}\theta_{***}$
$RCOOH^{*} + ^{**} \rightarrow RCO^{*} + OH^{**}$	$r_3 = k_3\theta_{RCOOH*}\theta_{**} - k_{-3}\theta_{RCO*}\theta_{OH**}$
$RCO^{*} + OH^{**} + ^{****} \rightarrow RCO^{*} + ^{**} + OH^{****}$	$r_{31} = k_{31}\theta_{RCO*}\theta_{OH**}\theta_{****} - k_{-31}\theta_{RCO*}\theta_{**}\theta_{OH****}$
$OH^{****} + ^{*} \rightarrow OH^{*} + ^{****}$	$r_{32} = k_{32}\theta_{OH****}\theta_{*} - k_{-32}\theta_{OH*}\theta_{****}$
$RCOO^{*} + ^{**} \rightarrow RCO^{**} + O^{*}$	$r_4 = k_4\theta_{RCOO*}\theta_{**} - k_{-4}\theta_{RCO**+O*}$
$RCO^{**} + O^{*} + ^{****} \rightarrow RCO^{****} + O^{*} + ^{**}$	$r_{41} = k_{41}\theta_{RCO**+O*}\theta_{****} - k_{-41}\theta_{RCO****}\theta_{O*}\theta_{**}$
$RCO^{****} + ^{*} \rightarrow RCO^{*} + ^{****}$	$r_{42} = k_{42}\theta_{RCO****}\theta_{*} - k_{-42}\theta_{RCO*}\theta_{****}$
$RCOO^{*} + H^{***} \rightarrow RCHOO^{*} + ^{***}$	$r_5 = k_5\theta_{RCOO*}\theta_{H***} - k_{-5}\theta_{RCHOO*}\theta_{***}$
$RCHOOH^{*} \rightarrow RCHO\ (g) + OH^{*}$	$r_6 = k_6\theta_{RCHOOH*} - k_{-6}P_{RCHO}/P^0\theta_{OH*}$
$RCHOOH^{*} + ^{***} \rightarrow RCHOO^{*} + H^{***}$	$r_7 = k_7\theta_{RCHOOH*}\theta_{***} - k_{-7}\theta_{RCHOO*}\theta_{H***}$
$RCO^{*} + H^{***} \rightarrow RCHO\ (g) + ^{*} + ^{***}$	$r_8 = k_8\theta_{RCO*}\theta_{H***} - k_{-8}\theta_{*}\theta_{***}P_{RCHO}/P^0$
$RCO^{**} + O^{*} + H^{***} \rightarrow RCHO\ (g) + O^{*} + ^{**} + ^{***}$	$r_{81} = k_{81}\theta_{RCO**+O*}\theta_{H***} - k_{-81}\theta_{O*}\theta_{**}\theta_{***}P_{RCHO}/P^0$
$RCO^{*} + OH^{**} + H^{***} \rightarrow RCHO\ (g) + OH^{*} + ^{**} + ^{***}$	$r_{82} = k_{82}\theta_{RCO*}\theta_{OH**}\theta_{H***} - k_{-82}\theta_{OH*}\theta_{**}\theta_{***}P_{RCHO}/P^0$
$RCHOO^{*} \rightarrow RCHO\ (g) + O^{*}$	$r_9 = k_9\theta_{RCHOO*} - k_{-9}\theta_{O*}P_{RCHO}/P^0$
$RCHO\ (g) + H^{***} + ^{*} \rightarrow RCH_2O^{*} + ^{***}$	$r_{10} = k_{10}\theta_{H***}\theta_{*}P_{RCHO}/P^0 - k_{-10}\theta_{RCH_2O*}\theta_{***}$
$RCHO\ (g) + O^{*} + ^{**} + H^{***} \rightarrow O^{*} + RCH_2O^{**} + ^{***}$	$r_{101} = k_{101}\theta_{O*}\theta_{**}\theta_{H***}P_{RCHO}/P^0 - k_{-101}\theta_{RCH_2O**+O*}\theta_{***}$
$RCHO\ (g) + OH^{*} + ^{**} + H^{***} \rightarrow OH^{*} + RCH_2O^{**} + ^{***}$	$r_{102} = k_{102}P_{RCHO}/P^0\theta_{OH*}\theta_{**}\theta_{H***} - k_{-102}\theta_{RCH_2O**+OH*}\theta_{***}$
$RCH_2O^{**} + O^{*} + ^{****} \rightarrow RCH_2O^{****} + O^{*} + ^{**}$	$r_{103} = k_{103}\theta_{RCH_2O**+O*}\theta_{****} - k_{-103}\theta_{RCH_2O****}\theta_{O*}\theta_{**}$
$RCH_2O^{**} + OH^{*} + ^{****} \rightarrow RCH_2O^{****} + OH^{*} + ^{**}$	$r_{104} = k_{104}\theta_{RCH_2O**+OH*}\theta_{****} - k_{-104}\theta_{RCH_2O****}\theta_{OH*}\theta_{**}$
$RCH_2O\ ^{****} + ^{*} \rightarrow RCH_2O^{*} + ^{****}$	$r_{105} = k_{105}\theta_{RCH_2O****}\theta_{*} - k_{-105}\theta_{RCH_2O*}\theta_{****}$
$RCH_2O^{****}+RCO^{*} + ^{**} \rightarrow RCH_2O^{**} + RCO^{*} + ^{****}$	$r_{106} = k_{106}\theta_{RCH_2O****}\theta_{RCO*}\theta_{**} - k_{-106}\theta_{RCH_2O**+RCO*}\theta_{****}$
$RCH_2O^{*}+RCO^{****} + ^{**} \rightarrow RCH_2O^{*} + RCO^{**} + ^{****}$	$r_{107} = k_{107}\theta_{RCO****}\theta_{RCH_2O*}\theta_{**} - k_{-107}\theta_{RCO**+RCH_2O*}\theta_{****}$
$RCH_2O^{****} + RCO^{*} + OH^{**} + ^{**} \rightarrow RCH_2O^{**} + RCO^{*} + OH^{**} + ^{****}$	$r_{108} = k_{108}\theta_{RCH_2O****}\theta_{RCO*}\theta_{OH**}\theta_{**} - k_{-108}\theta_{OH**}\theta_{RCH_2O**+RCO*}\theta_{****}$
$RCHO\ (g) + H^{***} + ^{*} \rightarrow RCHOH^{*} + ^{***}$	$r_{11} = k_{11}\theta_{H***}\theta_{*}P_{RCHO}/P^0 - k_{-11}\theta_{RCHOH*}\theta_{***}$
$RCHO\ (g) + O^{*} + ^{**} + H^{***} \rightarrow RCHOH^{**} + O^{*} + ^{***}$	$r_{111} = k_{111}\theta_{O*}\theta_{**}\theta_{H***}P_{RCHO}/P^0 - k_{-111}\theta_{RCHOH**+O*}\theta_{***}$
$RCHO(g) + OH^{*} + ^{**} + H^{***} \rightarrow RCHOH^{*} + OH^{**} + ^{***}$	$r_{112} = k_{112}\theta_{OH*}\theta_{**}\theta_{H***}P_{RCHO}/P^0 - k_{-112}\theta_{RCHOH*}\theta_{OH**}\theta_{***}$
$RCHOH^{*} + H^{***} \rightarrow RCH_2OH(g) + ^{*} + ^{***}$	$r_{12} = k_{12}\theta_{RCHOH*}\theta_{H***} - k_{-12}\theta_{*}\theta_{***}P_{RCH_2OH}/P^0$
$RCHOH^{**} + O^{*} + H^{***} \rightarrow RCH_2OH(g) + O^{*} + ^{**} + ^{***}$	$r_{121} = k_{121}\theta_{RCHOH**+O*}\theta_{H***} - k_{-121}\theta_{O*}\theta_{**}\theta_{***}P_{RCH_2OH}/P^0$
$RCHOH^{*} + OH^{**} + H^{***} \rightarrow RCH_2OH(g) + OH^{*} + ^{**} + ^{***}$	$r_{122} = k_{122}\theta_{RCHOH*}\theta_{OH**}\theta_{H***} - k_{-122}\theta_{OH*}\theta_{**}\theta_{***}P_{RCH_2OH}/P^0$
$RCH_2O^{*} + H^{***} \rightarrow RCH_2OH\ (g) + ^{*} + ^{***}$	$r_{13} = k_{13}\theta_{RCH_2O*}\theta_{H***} - k_{-13}\theta_{*}\theta_{***}P_{RCH_2OH}/P^0$

$RCH_2O^{**} + O^{*} + H^{***} \rightarrow RCH_2OH\ (g) + O^{*} + {}^{**} + {}^{***}$	$r_{131} = k_{131}\theta_{RCH_2O^{**}+O^{*}}\theta_{H^{***}} - k_{-131}\theta_{O^{*}}\theta_{**}\theta_{***}P_{RCH_2OH}/P^0$
$RCH_2O^{**} + OH^{*} + H^{***} \rightarrow RCH_2OH\ (g) + OH^{*} + {}^{**} + {}^{***}$	$r_{132} = k_{132}\theta_{RCH_2O^{**}+OH^{*}}\theta_{H^{***}} - k_{-132}\theta_{OH^{*}}\theta_{**}\theta_{***}P_{RCH_2OH}/P^0$
$RCH_2O^{**} + OH^{*} \rightarrow RCH_2OH\ (g) + O^{*} + {}^{**}$	$r_{14} = k_{14}\theta_{RCH_2O^{**}+OH^{*}} - k_{-14}\theta_{O^{*}}\theta_{**}P_{RCH_2OH}/P^0$
$RCO^{*} + H^{***} \rightarrow RCOH^{*} + {}^{***}$	$r_{15} = k_{15}\theta_{RCO^{*}}\theta_{H^{***}} - k_{-15}\theta_{RCOH^{*}}\theta_{***}$
$RCO^{**} + O^{*} + H^{***} \rightarrow RCOH^{**} + O^{*} + {}^{***}$	$r_{151} = k_{151}\theta_{RCO^{**}+O^{*}}\theta_{H^{***}} - k_{-151}\theta_{RCOH^{**}+O^{*}}\theta_{***}$
$RCO^{*} + OH^{**} + H^{***} \rightarrow RCOH^{*} + OH^{**} + {}^{***}$	$r_{152} = k_{152}\theta_{RCO^{*}}\theta_{OH^{**}}\theta_{H^{***}} - k_{-152}\theta_{RCOH^{*}}\theta_{OH^{**}}\theta_{***}$
$RCOH^{*} + H^{***} \rightarrow RCHOH^{*} + {}^{***}$	$r_{16} = k_{16}\theta_{RCOH^{*}}\theta_{H^{***}} - k_{-16}\theta_{RCHOH^{*}}\theta_{***}$
$RCOH^{**} + O^{*} + H^{***} \rightarrow RCHOH^{**} + O^{*} + {}^{***}$	$r_{161} = k_{161}\theta_{RCOH^{**}+O^{*}}\theta_{H^{***}} - k_{-161}\theta_{RCHOH^{**}+O^{*}}\theta_{***}$
$RCOH^{*} + OH^{**} + H^{***} \rightarrow RCHOH^{*} + OH^{**} + {}^{***}$	$r_{162} = k_{162}\theta_{RCOH^{*}}\theta_{OH^{**}}\theta_{H^{***}} - k_{-162}\theta_{RCHOH^{*}}\theta_{OH^{**}}\theta_{***}$
$RCO^{**} + RCH_2O^{*} \rightarrow RCOOC_2H_5\ (g) + {}^{*} + {}^{**}$	$r_{170} = k_{170}{*}\theta_{RCO^{**}+RCH_2O^{*}} - k_{-170}P_{RCOOC_2H_5}/P^0\theta_{*}\theta_{**}$
$RCO^{*} + RCH_2O^{**} \rightarrow RCOO\ C_2H_5\ (g) + {}^{*} + {}^{**}$	$r_{17} = k_{17}\theta_{RCH_2O^{**}+RCO^{*}} - k_{-17}\theta_{*}\theta_{**}P_{RCOOC_2H_5}/P^0$
$RCO^{**} + O^{*} + RCH_2O^{****} \rightarrow RCOOC_2H_5\ (g) + O^{*} + {}^{**} + {}^{****}$	$r_{171} = k_{171}\theta_{RCO^{**}+O^{*}}\theta_{RCH_2O^{****}} - k_{-171}\theta_{O^{*}}\theta_{**}\theta_{****}P_{RCOOC_2H_5}/P^0$
$RCH_2O^{**} + RCO^{*} + OH^{**} \rightarrow RCOOC_2H_5\ (g) + OH^{*} + 2^{**}$	$r_{172} = k_{172}\theta_{OH^{**}}\theta_{RCH_2O^{**}+RCO^{*}} - k_{-172}\theta_{OH^{*}}\theta_{**}2P_{RCOOC_2H_5}/P^0$
$RCHO\ (g) + RCH_2O^{*} \rightarrow RCHOOC_2H_5^{*}$	$r_{180} = k_{180}\theta_{RCH_2O^{*}}P_{RCHO}/P^0 - k_{-180}\theta_{RCHOOC_2H_5^{*}}$
$RCHO\ (g) + RCH_2O^{**} + O^{*} \rightarrow RCHOOC_2H_5^{**} + O^{*}$	$r_{181} = k_{181}\theta_{RCH_2O^{**}+O^{*}}P_{RCHO}/P^0 - k_{-181}\theta_{RCHOOC_2H_5^{**}+O^{*}}$
$RCHO\ (g) + RCH_2O^{**} + OH^{*} \rightarrow RCHOOC_2H_5^{**} + OH^{*}$	$r_{182} = k_{182}\theta_{RCH_2O^{**}+OH^{*}}P_{RCHO}/P^0 - k_{-182}\theta_{RCHOOC_2H_5^{**}+OH^{*}}$
$RCHOOC_2H_5^{**} + O^{*} + {}^{****} \rightarrow RCHOOC_2H_5^{****} + O^{*} + {}^{**}$	$r_{183} = k_{183}\theta_{RCHOOC_2H_5^{**}+O^{*}}\theta_{****} - k_{-183}\theta_{RCHOOC_2H_5^{****}}\theta_{O^{*}}\theta_{**}$
$RCHOOC_2H_5^{**} + OH^{*} + {}^{****} \rightarrow RCHOOC_2H_5^{****} + OH^{*} + {}^{**}$	$r_{184} = k_{184}\theta_{RCHOOC_2H_5^{**}+OH^{*}}\theta_{****} - k_{-184}\theta_{RCHOOC_2H_5^{****}}\theta_{OH^{*}}\theta_{**}$
$RCHOOC_2H_5^{****} + {}^{*} \rightarrow RCHOOC_2H_5^{*} + {}^{****}$	$r_{185} = k_{185}\theta_{RCHOOC_2H_5^{****}}\theta_{*} - k_{-185}\theta_{RCHOOC_2H_5^{*}}\theta_{****}$
$RCHOOC_2H_5^{*} + {}^{***} \rightarrow CH3COOC_2H_5(g) + {}^{*} + H^{***}$	$r_{19} = k_{19\theta RCHOOC_2H_5^{*}}\theta_{***} - k_{-19}\theta_{*}\theta_{H^{***}}P_{RCOOC_2H_5}/P^0$
$RCHOOC_2H_5^{**} + O^{*} + {}^{***} \rightarrow RCOOC_2H_5\ (g) + O^{*} + {}^{**} + H^{***}$	$r_{191} = k_{191}\theta_{RCHOOC_2H_5^{**}+O^{*}}\theta_{***} - k_{-191}\theta_{O^{*}}\theta_{**}\theta_{H^{***}}P_{RCOOC_2H_5}/P^0$
$RCHOOC_2H_5^{**} + OH^{*} + {}^{***} \rightarrow RCOOC_2H_5\ (g) + OH^{*} + {}^{**} + H^{***}$	$r_{192} = k_{192}\theta_{RCHOOC_2H_5^{**}+OH^{*}}\theta_{***} - k_{-192}\theta_{OH^{*}}\theta_{**}\theta_{H^{***}}P_{RCOOC_2H_5}/P^0$
$2OH^{*} \rightarrow H_2O\ (g) + O^{*} + {}^{*}$	$r_{20} = k_{20}\theta 2\ OH^{*} - k_{-20}\theta_{O^{*}}\theta_{*}P_{H_2O}/P^0$
$O^{*} + H^{***} \rightarrow OH^{*} + {}^{***}$	$r_{21} = k_{21}\theta_{O^{*}}\theta_{H^{***}} - k_{-21}\theta_{OH^{*}}\theta_{***}$
$OH^{*} + H^{***} \rightarrow H_2O\ (g) + {}^{*} + {}^{***}$	$r_{22} = k_{22}\theta_{OH^{*}}\theta_{H^{***}} - k_{-22}\theta_{*}\theta_{***}P_{H_2O}/P^0$
$RCOOH\ (g) + {}^{*} \rightarrow RCOOH^{*}$	$r_{23} = k_{23}\theta_{*}P_{RCOOH}/P^0 - k_{-23}\theta_{RCOOH^{*}}$
$H2(g) + 2^{***} \rightarrow 2H^{***}$	$r_{24} = k_{24}\theta 2\ {***}P_{H_2}/P^0 - k_{-24}\theta 2\ H^{***}$
$RCOOH^{****} + {}^{****} \rightarrow RCOO^{****} + H^{****}$	$r_{01} = k_{01}\theta_{RCOOH^{****}}\theta_{****} - k_{-01}\theta_{RCOO^{****}}\theta_{H^{****}}$
$RCOOH^{****} + H^{****} \rightarrow RCHOOH^{****} + {}^{****}$	$r_{02} = k_{02}\theta_{RCOOH^{****}}\theta_{H^{****}} - k_{-02}\theta_{RCHOOH^{****}}\theta_{****}$
$RCHOOH^{****} \rightarrow RCHO\ (g) + OH^{****}$	$r_{03} = k_{03}\theta_{RCHOOH^{****}} - k_{-03}\theta_{OH^{****}}P_{RCHO}/P^0$
$RCO^{****} + H^{****} \rightarrow RCHO\ (g) + 2^{****}$	$r_{04} = k_{04}\theta_{RCO^{****}}\theta_{H^{****}} - k_{-04}\theta_{****}P_{RCHO}/P^0$
$RCHO\ (g) + H^{****} \rightarrow RCH_2O^{****}$	$r_{05} = k_{05}\theta_{H^{****}}P_{RCHO}/P^0 - k_{-05}\theta_{RCH2O^{****}}$
$RCH_2O^{****} + H^{****} \rightarrow RCH_2OH\ (g) + 2^{****}$	$r_{06} = k_{06}\theta_{RCH2O^{****}}\theta_{H^{****}} - k_{-06}\theta_{****}P_{RCH_2OH}/P^0$
$RCO^{****} + RCH_2O^{****} \rightarrow RCOOC_2H_5\ (g) + 2^{****}$	$r_{07} = k_{07}\theta_{RCO^{****}}\theta_{RCH2O^{****}} - k_{-07}\theta 2\ {****}P_{RCOOC_2H_5}/P^0$
$RCHO\ (g) + RCH_2O^{****} \rightarrow RCHOOC_2H_5^{****}$	$r_{08} = k_{08}\theta_{RCH2O^{****}}\ P_{RCHO}/P^0 - k_{-08}\theta_{RCHOOC2H5^{****}}$
$RCHOOC_2H_5\ {}^{****} \rightarrow RCOOC_2H_5\ (g) + H^{****}$	$r_{09} = k_{09}\theta_{RCHOOC_2H_5^{****}} - k_{-09}\theta_{H^{****}}\ P_{RCOOC_2H_5}/P^0$
$OH^{****} + H^{****} \rightarrow H_2O\ (g) + 2^{****}$	$r_{010} = k_{010}\theta_{OH^{****}}\theta_{H^{****}} - K_{-010}\theta 2\ {****}P_{H_2O}/P^0$
$RCOOH\ (g) + {}^{****} \rightarrow RCOOH^{****}$	$r_{011} = k_{011}\theta_{****}P_{RCOOH}/P^0 - k_{-011}\theta_{RCOOH^{****}}$
$H_2\ (g) + 2^{****} \rightarrow 2H^{****}$	$r_{012} = k_{012}\theta 2\ {****}P_{H_2}/P^0 - k_{-012}\theta 2\ H^{****}$

Table S3. The barrier, reaction energies in Gibbs free energy and corresponding rates of every elementary reaction involved in the HDO process of acetic acid. The barrier of the migration of species between different sites was set as big as the reaction energies in the endothermic reaction and zero in exothermic reaction, respectively. The relevant energetic values of the R01 ~ R012 step occurred on the Cu site was assumed the same as that on the Cu (111) surface.

Elementary Reaction	Ga (eV)	△G (eV)	Rates (s^{-1})
R1: $RCOOH^{*} + {}^{***} \rightarrow RCOO^{*} + H^{***}$	0.20	-0.50	1.23E+00
R2: $RCOOH^{*} + H^{***} \rightarrow RCHOOH^{*} + {}^{***}$	0.97	0.49	4.01E-02
R3: $RCOOH^{*} + {}^{**} \rightarrow RCO^{*} + OH^{**}$	0.77	0.03	9.18E-01
R31: $RCO^{*} + OH^{**} + {}^{****} \rightarrow RCO^{*} + {}^{**} + OH^{****}$	0.00	-0.03	9.10E-01
R32: $OH^{****} + {}^{*} \rightarrow OH^{*} + {}^{****}$	0.00	-0.41	-1.24E+00
R4: $RCOO^{*} + {}^{**} \rightarrow RCO^{**} + O^{*}$	0.88	0.44	1.14E+00
R41: $RCO^{**} + O^{*} + {}^{****} \rightarrow RCO^{****} + O^{*} + {}^{**}$	0.52	0.52	1.14E+00
R42: $RCO^{****} + {}^{*} \rightarrow RCO^{*} + {}^{****}$	0.00	-1.16	9.58E-01
R5: $RCOO^{*} + H^{***} \rightarrow RCHOO^{*} + {}^{***}$	1.21	0.99	8.18E-02
R6: $RCHOOH^{*} \rightarrow RCHO\ (g) + OH^{*}$	0.55	-0.46	4.01E-02
R7: $RCHOOH^{*} + {}^{***} \rightarrow RCHOO^{*} + H^{***}$	0.67	0.00	-2.52E-05
R8: $RCO^{*} + H^{***} \rightarrow RCHO\ (g) + {}^{*} + {}^{***}$	0.67	0.44	1.86E+00
R81: $RCO^{**} + O^{*} + H^{***} \rightarrow RCHO\ (g) + O^{*} + {}^{**} + {}^{***}$	0.78	-0.20	1.28E-03
R82: $RCO^{*} + OH^{**} + H^{***} \rightarrow RCHO\ (g) + OH^{*} + {}^{**} + {}^{***}$	0.54	0.00	7.91E-03
R9: $RCHOO^{*} \rightarrow RCHO\ (g) + O^{*}$	0.26	-0.75	8.18E-02
R10: $RCHO\ (g) + H^{***} + {}^{*} \rightarrow RCH_2O^{*} + {}^{***}$	0.64	0.03	-2.26E+01
R101: $RCHO\ (g) + O^{*} + {}^{**} + H^{***} \rightarrow O^{*} + RCH_2O^{**} + {}^{***}$	1.21	0.53	-3.80E-05
R102: $RCHO\ (g) + OH^{*} + {}^{**} + H^{***} \rightarrow OH^{*} + RCH_2O^{**} + {}^{***}$	0.99	0.50	-9.05E-05
R103: $RCH_2O^{**} + O^{*} + {}^{****} \rightarrow RCH_2O^{****} + O^{*} + {}^{**}$	0.06	0.06	-1.01E-04
R104: $RCH_2O^{**} + OH^{*} + {}^{****} \rightarrow RCH_2O^{****} + OH^{*} + {}^{**}$	0.04	0.04	-9.51E-01
R105: $RCH_2O\ {}^{****} + {}^{*} \rightarrow RCH_2O^{*} + {}^{****}$	0.00	-0.56	2.27E+01
R106: $RCH_2O^{****} + RCO^{*} + {}^{**} \rightarrow RCH_2O^{**} + RCO^{*} + {}^{****}$	0.00	-0.02	3.24E-02
R107: $RCH_2O^{*} + RCO^{****} + {}^{**} \rightarrow RCH_2O^{*} + RCO^{**} + {}^{****}$	0.00	-0.38	3.94E-02
R108: $RCH_2O^{****} + RCO^{*} + OH^{**} + {}^{**} \rightarrow RCH_2O^{**} + RCO^{*} + OH^{**} + {}^{****}$	0.16	0.16	-2.21E-02
R11: $RCHO\ (g) + H^{***} + {}^{*} \rightarrow RCHOH^{*} + {}^{***}$	1.16	0.71	5.45E-04
R111: $RCHO\ (g) + O^{*} + {}^{**} + H^{***} \rightarrow RCHOH^{**} + O^{*} + {}^{***}$	1.75	1.33	-3.78E-05
R112: $RCHO(g) + OH^{*} + {}^{**} + H^{***} \rightarrow RCHOH^{*} + OH^{**} + {}^{***}$	1.48	1.00	4.94E-09
R12: $RCHOH^{*} + H^{***} \rightarrow RCH_2OH(g) + {}^{*} + {}^{***}$	0.36	-0.43	4.86E-04
R121: $RCHOH^{**} + O^{*} + H^{***} \rightarrow RCH_2OH(g) + O^{*} + {}^{**} + {}^{***}$	0.89	-0.25	-1.06E-05

R122: $RCHOH^{*} + OH^{**} + H^{***} \rightarrow RCH_2OH(g) + OH^{*} + {}^{**} + {}^{***}$	0.31	-0.74	-1.63E-06
R13: $RCH_2O^{*} + H^{***} \rightarrow RCH_2OH\ (g) + {}^{*} + {}^{***}$	1.15	0.25	7.00E-02
R131: $RCH_2O^{**} + O^{*} + H^{***} \rightarrow RCH_2OH\ (g) + O^{*} + {}^{**} + {}^{***}$	0.89	-0.19	6.61E-05
R132: $RCH_2O^{**} + OH^{*} + H^{***} \rightarrow RCH_2OH\ (g) + OH^{*} + {}^{**} + {}^{***}$	0.94	-0.22	1.73E-06
R14: $RCH_2O^{**} + OH^{*} \rightarrow RCH_2OH\ (g) + O^{*} + {}^{**}$	0.26	-0.50	9.51E-01
R15: $RCO^{*} + H^{***} \rightarrow RCOH^{*} + {}^{***}$	1.20	0.84	-3.27E-05
R151: $RCO^{**} + O^{*} + H^{***} \rightarrow RCOH^{**} + O^{*} + {}^{***}$	0.97	0.17	2.72E-05
R152: $RCO^{*} + OH^{**} + H^{***} \rightarrow RCOH^{*} + OH^{**} + {}^{***}$	1.08	0.70	3.02E-07
R16: $RCOH^{*} + H^{***} \rightarrow RCHOH^{*} + {}^{***}$	0.88	0.41	-3.25E-05
R161: $RCOH^{**} + O^{*} + H^{***} \rightarrow RCHOH^{**} + O^{*} + {}^{***}$	0.48	0.44	2.72E-05
R162: $RCOH^{*} + OH^{**} + H^{***} \rightarrow RCHOH^{*} + OH^{**} + {}^{***}$	0.65	0.09	7.39E-09
R170: $RCO^{**} + RCH_2O^{*} \rightarrow RCOOC_2H_5\ (g) + {}^{*} + {}^{**}$	0.54	-0.67	3.94E-02
R17: $RCO^{*} + RCH_2O^{**} \rightarrow RCOO\ C_2H_5\ (g) + {}^{*} + {}^{**}$	0.78	-0.43	1.04E-02
R171: $RCO^{**} + O^{*} + RCH_2O^{****} \rightarrow RCOOC_2H_5\ (g) + O^{*} + {}^{**} + {}^{****}$	0.89	-0.98	1.16E-07
R172: $RCH_2O^{**} + RCO^{*} + OH^{**} \rightarrow RCOOC_2H_5\ (g) + OH^{*} + 2^{**}$	0.73	-0.76	3.39E-08
R180: $RCHO\ (g) + RCH_2O^{*} \rightarrow RCHOOC_2H_5^{*}$	1.23	0.65	-5.50E-03
R181: $RCHO\ (g) + RCH_2O^{**} + O^{*} \rightarrow RCHOOC_2H_5^{**} + O^{*}$	1.15	0.71	-2.69E-06
R182: $RCHO\ (g) + RCH_2O^{**} + OH^{*} \rightarrow RCHOOC_2H_5^{**} + OH^{*}$	1.49	0.87	-2.56E-07
R183: $RCHOOC_2H_5^{**} + O^{*} + {}^{****} \rightarrow RCHOOC_2H_5^{****} + O^{*} + {}^{**}$	0.09	0.09	-2.69E-06
R184: $RCHOOC_2H_5^{**} + OH^{*} + {}^{****} \rightarrow RCHOOC_2H_5^{****} + OH^{*} + {}^{**}$	0.31	0.31	-2.47E-07
R185: $RCHOOC_2H_5^{****} + {}^{*} \rightarrow RCHOOC_2H_5^{*} + {}^{****}$	0.00	-0.67	5.62E-03
R19: $RCHOOC_2H_5^{*} + {}^{***} \rightarrow CH3COOC_2H_5(g) + {}^{*} + H^{***}$	0.50	-0.97	1.25E-04
R191: $RCHOOC_2H_5^{**} + O^{*} + {}^{***} \rightarrow RCOOC_2H_5\ (g) + O^{*} + {}^{**} + H^{***}$	0.37	-1.37	8.73E-09
R192: $RCHOOC_2H_5^{**} + OH^{*} + {}^{***} \rightarrow RCOOC_2H_5\ (g) + OH^{*} + {}^{**} + H^{***}$	0.80	-1.31	3.59E-11
R20: $2OH^{*} \rightarrow H_2O\ (g) + O^{*} + {}^{*}$	0.60	-0.27	2.61E-02
R21: $O^{*} + H^{***} \rightarrow OH^{*} + {}^{***}$	0.96	0.29	2.20E+00
R22: $OH^{*} + H^{***} \rightarrow H_2O\ (g) + {}^{*} + {}^{***}$	1.05	0.02	1.06E-02
R23: $RCOOH\ (g) + {}^{*} \rightarrow RCOOH^{*}$	0.10	0.10	2.18E+00
R24: $H_2\ (g) + 2^{***} \rightarrow 2H^{***}$	0.20	-0.29	-9.81E+00
R01: $RCOOH^{****} + {}^{****} \rightarrow RCOO^{****} + H^{****}$	0.47	-0.33	0E+00
R02: $RCOOH^{****} + H^{****} \rightarrow RCHOOH^{****} + {}^{****}$	1.10	0.49	1.13E-01
R03: $RCHOOH^{****} \rightarrow RCHO\ (g) + OH^{****}$	0.52	-0.55	1.13E-01
R04: $RCO^{****} + H^{****} \rightarrow RCHO\ (g) + 2^{****}$	0.50	-0.87	1.44E-01
R05: $RCHO\ (g) + H^{****} \rightarrow RCH_2O^{****}$	1.19	0.32	2.45E+01
R06: $RCH_2O^{****} + H^{****} \rightarrow RCH_2OH\ (g) + 2^{****}$	0.96	-0.43	7.46E-01
R07: $RCO^{****} + RCH_2O^{****} \rightarrow RCOOC_2H_5\ (g) + 2^{****}$	0.67	-1.49	5.04E-07
R08: $RCHO\ (g) + RCH_2O^{****} \rightarrow RCHOOC_2H_5^{****}$	1.13	0.61	5.93E-03
R09: $RCHOOC_2H_5\ {}^{****} \rightarrow RCOOC_2H_5\ (g) + H^{****}$	0.59	-1.15	3.01E-04
R010: $OH^{****} + H^{****} \rightarrow H_2O\ (g) + 2^{****}$	0.91	-0.59	2.26E+00
R011: $RCOOH\ (g) + {}^{****} \rightarrow RCOOH^{****}$	0.42	0.42	1.13E-01
R012: $H_2\ (g) + 2^{****} \rightarrow 2H^{****}$	0.80	0.07	1.39E+01
r_{RCHO} = r8 + r81 + r82 - r10 - r101 - r102 + r003 + r004 - r005 - r008 - r11 - r111 - r112 – r180 - r181 - r182			3.01E-01
r_{RCH2OH} = r13 + r131 + r132 + r14 + r006 + r12 + r121 + r122			1.77E+00

$r_{RCOOC2H5}$ = r170 + r17 + r171 + r172 + r007 + r009 + r19 + r191 + r192	5.02E-02

Table S4. Coverage of surface species in HDO process of acetic acid on the NiCu (111) surface. (R=CH_3)

Species	Coverage	Species	Coverage	Species	Coverage
θ_{RCOOH*}	2.18E-05	$\theta_{RCO**+O*}$	1.54E-08	θ_{H***}	4.945E-02
θ_{RCOO*}	5.80E-03	$\theta_{RCO**+RCH_2O*}$	1.79E-10	θ_{***}	5.466E-04
$\theta_{RCHOOH*}$	5.87E-10	θ_{OH**}	1.20E-06	$\theta_{RCOOH****}$	6.884E-05
θ_{RCO*}	1.33E-03	$\theta_{RCH_2O**+OH*}$	5.68E-10	$\theta_{RCOO****}$	2.248E-02
θ_{OH*}	3.08E-05	$\theta_{RCH_2O** + O*}$	1.10E-08	$\theta_{RCHOOH****}$	3.977E-10
θ_{O*}	1.09E-03	$\theta_{RCH_2O**+RCO*}$	5.99E-09	$\theta_{RCO****}$	7.948E-10
θ_{RCHOO*}	3.83E-11	$\theta_{RCHOOC_2H_5*+OH*}$	5.85E-15	θ_{OH****}	2.903E-05
θ_{RCH_2O*}	1.60E-03	$\theta_{RCHOOC_2H_5*+O*}$	2.46E-15	θ_{RCH_2O**}	3.979E-05
$\theta_{RCHOOC_2H_5*}$	4.64E-10	$\theta_{RCHOH**+O*}$	2.78E-11	θ_{H****}	6.328E-01
θ_{RCHOH*}	1.86E-10	$\theta_{RCOH**+O*}$	2.21E-09	$\theta_{RCHOOC_2H_5****}$	4.862E-12
θ_{RCOH*}	1.95E-09	θ_{**}	2.00E-02	θ_{****}	2.646E-01
θ_{*}	1.31E-04				

Table S5. The barrier, reaction energies in Gibbs free energy and corresponding rates of every elementary reaction involved in the HDO process of acetic acid on Cu (111) surface. The X* represented the adsorbed on the Cu site.

Elementary Reaction	Ga (eV)	△G (eV)	Rates (s^{-1})
R1: $RCOOH^* + {}^* \rightarrow RCOO^* + H^*$	0.47	0.80	1.82E-03
R2: $RCOOH^* + H^* \rightarrow RCHOOH^* + {}^*$	1.10	0.61	1.34E-01
R3: $RCOOH^* + {}^* \rightarrow RCO^* + OH^*$	1.46	0.65	4.09E-05
R4: $RCOO^* + {}^* \rightarrow RCO^* + O^*$	1.96	0.30	5.53E-07
R5: $RCOO^* + H^* \rightarrow RCHOO^* + {}^*$	1.60	0.48	1.82E-03
R6: $RCHOOH^* \rightarrow RCHO\ (g) + OH^*$	0.52	1.12	1.34E-01
R7: $RCHOOH^* + {}^* \rightarrow RCHOO^* + H^*$	1.10	0.80	5.39E-08
R8: $RCO^* + H^* \rightarrow RCHO\ (g) + 2^*$	0.50	1.42	4.10E-05
R9: $RCHOO^* \rightarrow RCHO\ (g) + O^*$	0.38	0.76	1.82E-03
R10: $RCHO\ (g) + H^* \rightarrow RCH_2O^*$	1.24	0.87	1.29E-01
R11: $RCHO\ (g) + H^* \rightarrow RCHOH^*$	1.54	0.23	2.34E-03
R12: $RCHOH^* + H^* \rightarrow RCH_2OH(g) + 2^*$	0.09	1.50	2.34E-03
R13: $RCH_2O^* + H^* \rightarrow RCH_2OH\ (g) + 2^*$	0.96	1.45	1.31E-01
R14: $RCH_2O^* + OH^* \rightarrow RCH_2OH\ (g) + O^* + {}^*$	0.64	0.58	-2.22E-03
R15: $RCO^* + H^* \rightarrow RCOH^* + {}^*$	0.81	0.37	4.43E-07
R16: $RCOH^* + H^* \rightarrow RCHOH^* + {}^*$	0.54	0.59	4.43E-07
R17: $RCO^* + RCH_2O^* \rightarrow RCOOC_2H_5\ (g) + 2^*$	0.67	2.16	1.45E-09
R18: $RCHO\ (g) + RCH_2O^* \rightarrow RCHOOC_2H_5^*$	1.18	0.52	8.45E-06
R19: $RCHOOC_2H_5^* \rightarrow CH3COOC_2H_5(g) + H^*$	0.59	1.74	8.45E-06
R20: $2OH^* \rightarrow H_2O\ (g) + O^* + {}^*$	0.32	0.44	4.23E-04
R21: $O^* + H^* \rightarrow OH^* + {}^*$	0.91	1.43	2.89E-05
R22: $OH^* + H^* \rightarrow H_2O\ (g) + 2^*$	0.91	1.55	1.35E-01
R23: $RCOOH\ (g) + {}^* \rightarrow RCOOH^*$	0.42	0.00	1.36E-01
R24: $H_2\ (g) + 2^* \rightarrow 2H^*$	0.80	0.73	2.67E-01
$r_{RCHO} = r6 + r8 + r9 - r10 - r11 - r18$			4.51E-03
$r_{RCH2OH} = r11 + r12 + r13 + r14$			1.31E-01
$r_{RCOOC2H5} = r17 + r19$			8.46E-06

To corroborate the conclusion from DFT results and gain more quantitative activities of HDO process of acetic acid, the micro-kinetic analysis was used in this paper. The rate equation of every elementary step was summarized in Table S2. Simply, the rate constant $k_i(k_{-i})$ of the step i was calculated based on the transition state theory (TST):

$$k = \frac{k_b T}{h} e^{-\frac{\Delta G}{k_b T}}$$

where the h, k_b and T was the Planck constant, Boltzmann constant and chosen temperature. The △G was the standard molar Gibbs free energy change between the IS (FS) and TS. The Gibbs free energies of all gaseous species (CH_3COOH, CH_3CHO, C_2H_5OH, $CH_3COOC_2H_5$, H_2 and H_2O) was obtained by the following equation:

$G(T,p) = E_{tot} + ZPE + \triangle G(0 \rightarrow T, p) = E_{tot} + ZPE + \triangle G(0 \rightarrow T, P0) – RT\ln(P/P^0)$

where the E_{tot}, ZPE, $\triangle G(0 \rightarrow T, P^0)$ represented the DFT energies, zero point energies, the free energies change from the 0 K and standard to the current temperature T and partial pressure P. Both of the ZPE and $\triangle G(0 \rightarrow T, p)$ could be obtained based on frequency calculation and the details could be found in VASPKIT code. In addition, the Gibbs free energies of adsorbates was calculated by:

$G(T) = E_{tot} + ZPE + \triangle G(0 \rightarrow T)$

where the E_{tot}, ZPE, $\triangle G(0 \rightarrow T)$ represented the DFT energies, zero point energies, the thermal correction. The ZPE and required thermal correction could be obtained with the help of the vibrational frequency. As shown in the next two equations:

$$ZPE = \sum_i \left(\frac{v_i h}{2} \right)$$

$$\Delta G_i(0 \rightarrow T) = \sum_i \left(-k_b T \ln \frac{1}{1 - \exp\left(-\frac{v_i h}{k_b T}\right)} \right)$$

where the vi, h, k_b and T was the frequency, Planck constant, Boltzmann constant and temperature.

The reaction conditions was set as T=573 K, p=2.5 MPa, H_2/CH_3COOH = 20 and which was used in the experimental evaluations. The conversion of acetic acid was set to be 70%. The steady-state approximation was applied here to treat the micro-kinetic model where the coverage of the adsorbates was assumed unchanged (dX/dt ≈ 0, X = adsorbates) in the steady state, leading to a set of equations as shown below:

Table S6. The steady-state equations of the each species X involved in the HDO process of acetic acid

X species : dX/dt = 0
X = $RCOOH^*$: $r_1 + r_2 + r_3 – r_{23} = 0$
X = $RCOO^*$: $r_1 - r_4 - r_5 = 0$
X = RCHOOH: $^*r_2 - r_6 - r_7 = 0$
X = RCO^*: $r_3 + r_{42} - r_8 - r_{82} - r_{106} - r_{108} = 0$
X = OH^*: $r_{32} + r_{82} + r_6 - r_{102} + r_{104} + r_{132} + r_{172} + r_{184} + r_{192} – 2*r_{20} + r_{21} - r_{22} = 0$
X = O^*: $r_{41} + r_{81} + r_9 - r_{101} + r_{103} - r_{111} + r_{121} + r_{131} + r_{14} + r_{171} + r_{183} + r_{191} + r_{20} - r_{21} = 0$
X = $RCHOO^*$: $r_5 + r_7 - r_9 = 0$
X = RCH_2O^*: $r_{10} + r_{105} - r_{107} - r_{13} = 0$
X = $RCHOH^*$: $r_{11} + r_{112} - r_{12} - r_{122} + r_{16} + r_{162} = 0$
X = $RCOH^*$: $r_{15} + r_{152} - r_{16} - r_{162} = 0$
X = $RCHOOC_2H_5{}^*$: $r_{180} + r_{185} - r_{19} = 0$
X = $RCO^{**} + O^*$: $r_4 - r_{41} - r_{81} - r_{151} - r_{171} = 0$
X = $RCO^{**} + C_2H_5O^*$: $r_{107} - r_{170} = 0$
X = OH^{**}: $r_3 - r_{31} - r_{82} - r_{172} = 0$
X = $CH_2O^{**} + OH^*$: $r_{102} - r_{104} - r_{14} - r_{132} - r_{182} = 0$
X = $RCH_2O^{**} + O^*$: $r_{101} - r_{103} - r_{131} - r_{181} = 0$
X = $RCH_2O^{**} + RCO^*$: $r_{106} + r_{108} - r_{17} - r_{172} = 0$
X = $RCHOH^{**} + O^*$: $r_{111} - r_{121} + r_{161} = 0$
X = $RCOH^{**} + O^*$: $r_{151} - r_{161} = 0$
X = $RCHOOC_2H_5{}^{**} + OH^*$: $r_{182} - r_{184} - r_{192} = 0$
X = $RCHOOC_2H_5{}^{**} + O^*$: $r_{181} - r_{183} - r_{191} = 0$
X = H^{***}: $r_1 - r_2 - r_5 + r_7 - r_8 - r_{81} - r_{82} - r_{10} - r_{101} - r_{102} - r_{11} - r_{111} - r_{112} - r_{12} - r_{121} - r_{122} - r_{13} - r_{131} - r_{132} - r_{15} - r_{151} - r_{152} - r_{16} - r_{161} - r_{162} + r_{19} + r_{191} + r_{192} - r_{21} - r_{22} + 2^*r_{24} = 0$
X = $RCOOH^{****}$: $- r_{01} - r_{02} + r_{011} = 0$
X = $RCOO^{****}$: $r_{01} = 0$
X = $RCHOOH^{****}$: $r_{02} - r_{03} = 0$
X = RCO^{****}: $r_{41} - r_{42} - r_{81} - r_{107} - r_{04} - r_{07} = 0$
X = OH^{****}: $r_{31} - r_{32} + r_{03} - r_{010} = 0$
X = RCH_2O^{****}: $r_{103} + r_{104} - r_{105} - r_{106} - r_{108} - r_{181} + r_{05} - r_{06} - r_{07} - r_{08} = 0$
X = H^{****}: $r_{01} - r_{02} - r_{04} - r_{05} - r_{06} + r_{09} - r_{010} + 2^*r_{012} = 0$
X = $RCHOOC_2H_5{}^{****}$: $r_{183} + r_{184} - r_{185} + r_{08} - r_{09} = 0$

There were 4 kinds of sites in the current system. *, **, *** and **** represented that the most stable site (Ni^3 site), the secondary stable site (usually Ni^2 site), the site for the adsorbed hydrogen atoms on the nickel and the monometallic Cu site, respectively. The Ni3 site was assumed to occupy 1% of surface sites which was low enough to match the experimental preparations. In addition, the normalization equations of 4 kinds of sites should by satisfied by eq S6-S9:

$$\theta_{RCOOH*} + \theta_{RCOO*} + \theta_{RCHOOH*} + \theta_{RCO*} + \theta_{RCO**+O*} + \theta_{RCO**+RCH_2O*} + \theta_{OH*} + \theta_{O**} + \theta_{RCHOO**} + \theta_{RCH_2O**} + \theta_{RCHOH**} + \theta_{RCOH**} + \theta_{RCHOOC_2H_5*} + \theta_{RCH_2O**+OH*} + \theta_{RCH_2O**+O*} + \theta_{RCH_2O**+RCO*} + \theta_{RCHOH**+O*} + \theta_{RCOH**+O*} + \theta_{RCHOOC_2H_5*+OH*} + \theta_{RCHOOC_2H_5*+O*} + \theta_{*} = 0.01 \quad \text{S6}$$

$$\theta_{RCO**+O*} + \theta_{RCO**+RCH_2O*} + \theta_{OH**} + \theta_{RCH_2O**+OH*} + \theta_{RCH_2O**+O*} + \theta_{RCH_2O**+RCO*} + \theta_{RCHOOC_2H_5*+OH*} + \theta_{RCHOOC_2H_5*+O*} + \theta_{**} = 0.02 \quad \text{S7}$$

$$\theta_{H***} + \theta_{***} = 0.05 \quad \text{S8}$$

$$\theta_{RCOOH****} + \theta_{RCOO****} + \theta_{RCHOOH****} + \theta_{RCO****} + \theta_{OH****} + \theta_{RCH_2O**} + \theta_{H****} + \theta_{RCHOOC_2H_5****} + \theta_{****} = 0.92 \quad \text{S9}$$

Note that the secondary stable (Ni^2) site was considered independent during the adsorption and reaction which could accommodate carbonaceous ($C_xH_yO_z$) species only if the neighboring Ni^3 site had been occupied by the other species. Taking the co-adsorbed CH_3CO** and O* species as an example, the two species was taken as a whole instead of the sum of individual acetyl and oxygen species. The (CH_3CO** + O*) occupied the Ni^2 and Ni^3 sites simultaneously and existed on the two normalization equations ($\theta_{RCO**+O*}$ in the eq S6 and S9). Other dual species such as RCH_2O**+OH* and RCH_2O**+O* species were treated as similar methods. Due to the complexity of the reaction network (70 elementary reactions in total), some simplification was performed to enable the HDO process more understandable through omitting some unnecessary steps. The deleted reactions should exhibited relatively low reaction rates and degree of rate control (X_{RC}) and the production rates of the products should be almost unchanged after the simplification. Finally, the reactions reduced from 70 to 37 with the CH_3COH-, CH_3CHOH- and $CH_3CHOOC_2H_5$-assistant steps omitted and the activity surged by less than 2%, meaning that CH_3COH, CH_3CHOH and $CH_3CHOOC_2H_5$ had little contribution to the generation of ethanol and ethyl acetate, in accordance with the experimental results.