Theoretical Design of Diatomic Catalysts for Intermolecular Hydrogen Transfer between Crotonaldehyde and Hydrazine

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Calculation details

To simulate the behavior of catalysts and reactant molecules in electrolyte solution during electrochemical reactions, an implicit solvation model was employed in this work to account for solvation effects.

All solvation energies were calculated using the VASPsol code. [1, 2], In this model, the solvent environment is represented by a dielectric continuum surrounding the system, and the Poisson–Boltzmann equation is solved self-consistently to correct the electrostatic interactions. In the calculations, the relative dielectric constant of water was set to ε = 80.0 to mimic an aqueous electrolyte environment. The ionic concentration of the solution was set to 0.1 M, corresponding to a Debye screening length of about 10 Å. The dielectric constant of the cavity and the Thomas–Fermi screening length were kept at their default values.

The Gibbs free energy (G) of each reaction intermediate consists of the following contributions:

$$G = E_{DFT} + E_{ZPE} + \int C_v dT - TS + \Delta E_{solv} \qquad (1)$$

where E_{DFT} is the total energy obtained from DFT calculations, E_{ZPE} is the zero-point energy, $\int C_v dT$ is the enthalpy correction from 0 K to 298.15 K (usually obtained from thermodynamic tables within the ideal-gas approximation), TS is the entropy contribution, and ΔE_{solv} is the solvation-energy correction term described above. The Gibbs free energies of gas-phase molecules are taken directly from the NIST database or calculated using the ideal-gas approximation[3], and their solvation energies are usually already implicit in the reference energy of the standard hydrogen electrode (SHE) model, or are evaluated separately in an analogous manner.

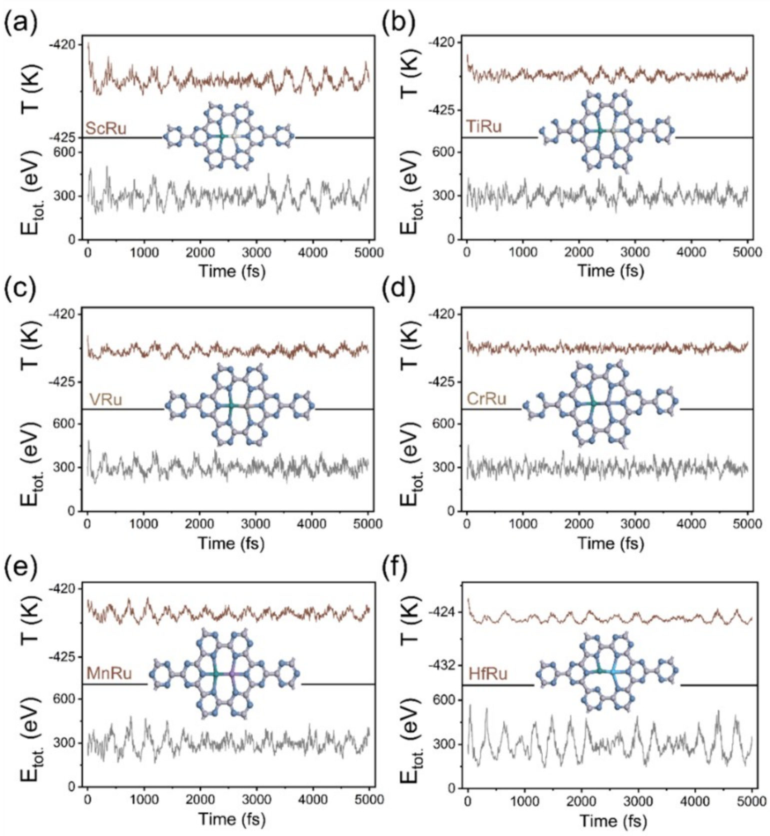

Figure S1. AIMD trajectories of TM–Ru (TM = Sc, Ti, V, Cr, Mn, Hf) dual-atom catalysts at 298 K.

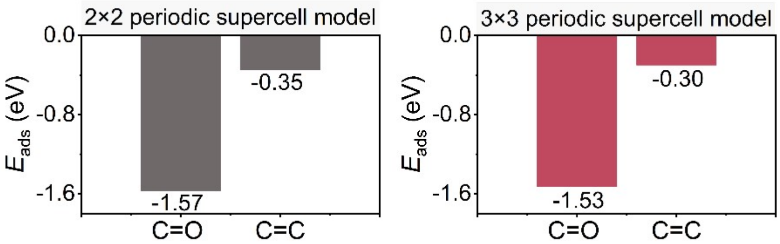

Figure S2. Comparison of crotonaldehyde adsorption energies on the ScRu catalyst with different supercell sizes. The 3×3 supercell model is used as an example to verify the reliability of the 2×2 supercell computational model. Under vacuum conditions, the adsorption energies of the C=O and C=C groups of crotonaldehyde on the 3×3 supercell are -1.57 eV and -0.35 eV, respectively, which show minimal differences compared to the corresponding results for the 2×2 supercell (-1.53 eV and -0.30 eV). This indicates that the 2×2 supercell model used in this study can reasonably reflect the adsorption characteristics of the system while ensuring computational efficiency.

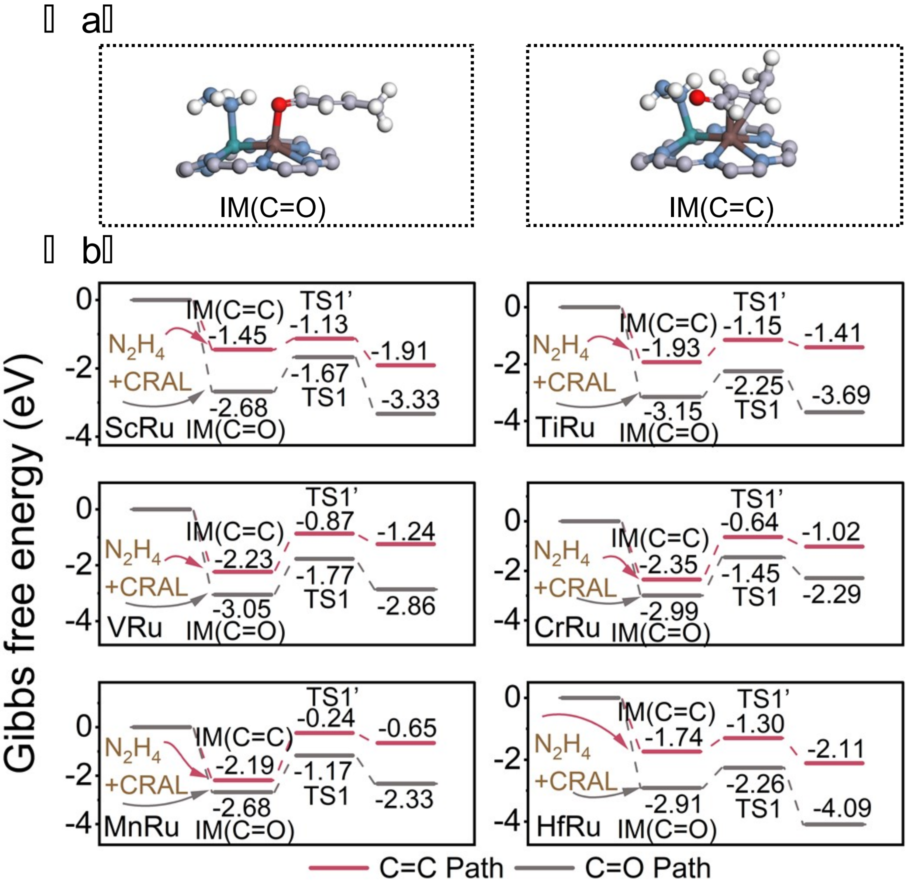

Figure S3. Co-adsorption configurations on the surfaces of TM–Ru catalysts. (a) Co-adsorption configurations of the C=O group, C=C group, and hydrazine. (b) Comparison of the first hydrogenation step of the C=O group and the C=C group.

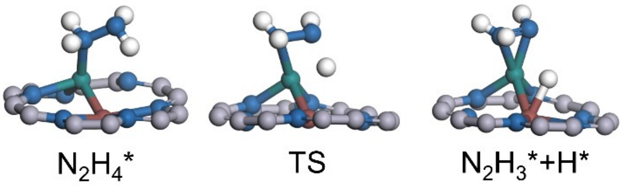

Figure S4. Schematic diagram of hydrazine adsorption and dissociation on TM-Ru.

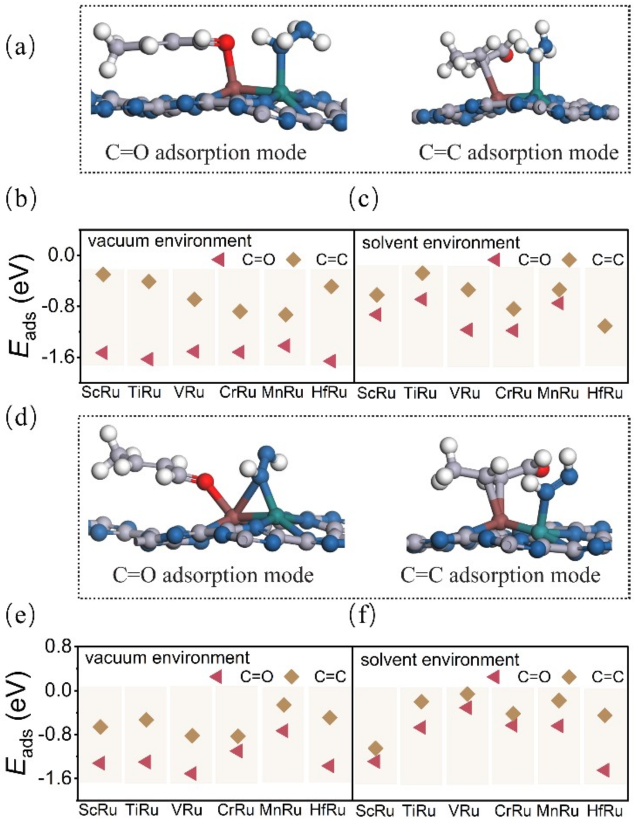

Figure S5. Adsorption behavior of crotonaldehyde at different catalytic reaction stages. (a) At the initial reaction stage, adsorption configurations of crotonaldehyde on the catalyst surface via the C=O group and the C=C group, respectively. (b, c) Comparison of the adsorption energies of these two adsorption modes at the initial stage under vacuum (b) and in a solvent environment (c). (d) After the formation of the first crotyl alcohol molecule, re-adsorption configurations of newly introduced crotonaldehyde on the catalyst surface via the C=O and C=C groups. (e, f) Differences in the adsorption energies of the C=O and C=C groups during (e)the re-adsorption process under vacuum and (f)under solvent conditions.

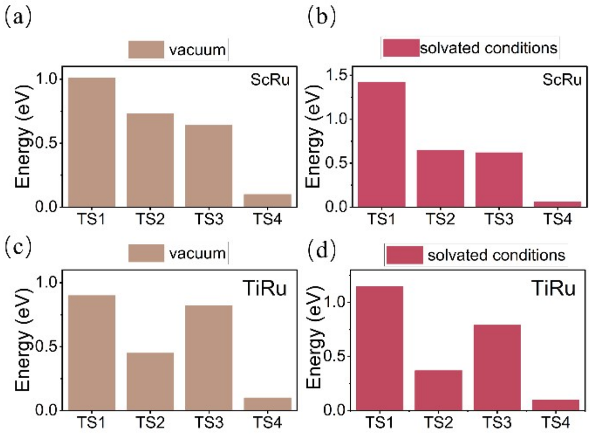

Figure S6. Summary of the reaction energy barriers for the key hydrogenation steps on ScRu and TiRu catalysts under vacuum and in solvent. (a) Reaction energy barriers of TS1, TS2, TS3, and TS4 on the ScRu catalyst under vacuum. (b) Reaction energy barriers of the corresponding steps on the ScRu catalyst under solvent conditions. (c) Reaction energy barriers of TS1–TS4 on the TiRu catalyst under vacuum. (d) Reaction energy barriers of the corresponding steps on the TiRu catalyst under solvent conditions.

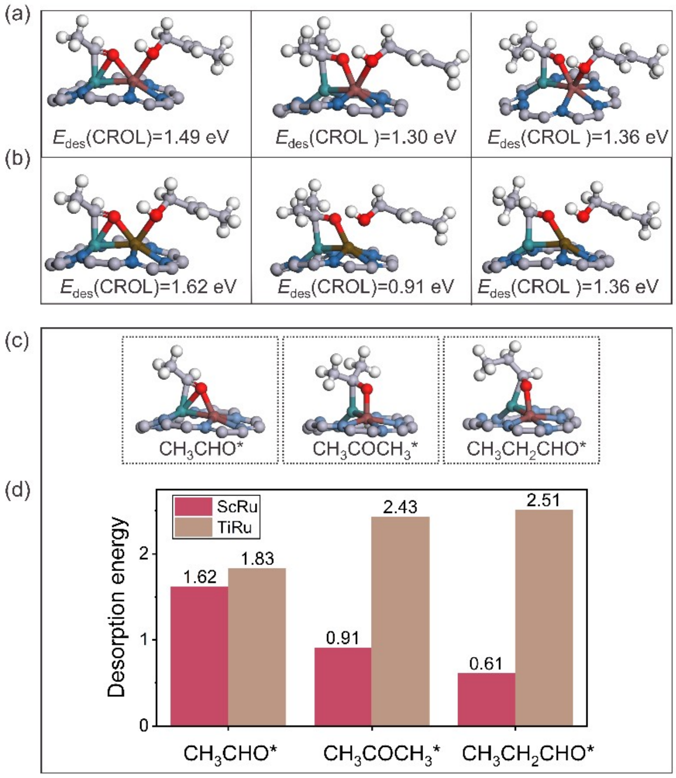

Figure S7. Desorption energies of crotyl alcohol formed by hydrogenating crotonaldehyde using ethanol, isopropanol, and propanol as hydrogen donors on (a) ScRu and (b) TiRu diatomic catalysts. (c) Schematic structures of adsorbed acetaldehyde (CH_3CHO^*), acetone ($CH_3COCH_3^*$), and propionaldehyde ($CH_3CH_2CHO^*$) on ScRu and TiRu catalysts. (d) summary plot of their desorption energies on ScRu and TiRu.

Table S1. Key parameters of the elementary steps for the reaction between crotonaldehyde and hydrazine on TM–Ru diatomic catalysts, including the reaction energy (ΔE) of each step, the activation barrier (Ea) of the rate-determining step, and the barrier (E_{TS}) of the first dehydrogenation step of N_2H_4 ($N_2H_4 \rightarrow N_2H_3 + H$); all values are given in eV.

Catalyst	E_{TS}(eV)	ΔE(eV)	E_a(eV)
Sc-Ru	1.18	0.78	1.15
Ti-Ru	1.25	0.50	1.21
V-Ru	1.62	0.51	1.28

Cr-Ru	1.56	0.88	1.54
Mn-Ru	1.45	0.40	1.53
Hf-Ru	1.65	-0.08	1.57

Table S2. Calculated energy barriers (eV) for the main reaction and competing side reactions, including deoxygenation, decarbonylation, and isomerization, on different TM-Ru diatomic catalysts. Values in regular font represent the activation barriers of the rate-determining step for each pathway, while italic values denote the reaction energies (Δ*E*) of the corresponding reactions.

DACs	Main reaction	Side reaction		
		Deoxygenation Pathway	*Decarbonylation Pathway*	Isomerization reaction
Sc-Ru	1.15	1.83	*1.70*	1.57
Ti-Ru	1.21	1.35	*1.28*	1.42
V-Ru	1.28	1.38	1.28	—
Cr-Ru	1.54	1.37	*0.80*	—
Mn-Ru	1.53	1.40	1.47	—
Hf-Ru	1.57	2.00	1.16	—

Table S3. Calculated Bader charges (|e|) of the relevant atoms on the clean catalyst surface. “Catalyst” denotes the catalyst system under investigation; “Charge state” refers to the charge state of the surface transition-metal atom (TM, e.g., Ti denotes a titanium atom); Ea is the activation barrier (eV) of the rate-determining step for the reaction of crotonaldehyde on the catalyst when hydrazine is used as the hydrogen source.

Catalyst	*Charge State（TM）*	*Bader Charge*	*Charge State（Ru）*	*Bader Charge*	E_a
Sc-Ru	Sc	1.52	Ru	0.49	1.15
Ti-Ru	Ti	1.51	Ru	0.53	1.21
V-Ru	V	1.35	Ru	0.60	1.28
Cr-Ru	Cr	1.19	Ru	0.66	1.54
Mn-Ru	Mn	1.11	Ru	0.75	1.53

References

1. K. Mathew, V. S. C. Kolluru, S. Mula, S. N. Steinmann and R. G. Hennig, Implicit self-consistent electrolyte model in plane-wave density-functional theory, *The Journal of Chemical Physics*, 2019, **151**, 234101.

2. K. Mathew, R. Sundararaman, K. Letchworth-Weaver, T. A. Arias and R. G. Hennig, Implicit solvation model for density-functional study of nanocrystal surfaces and reaction pathways, *The Journal of Chemical Physics*, 2014, **140**, 084106.

3. H. Oberhofer, in *Handbook of Materials Modeling: Applications: Current and Emerging Materials*, eds. W. Andreoni and S. Yip, Springer International Publishing, Cham, 2020, DOI: 10.1007/978-3-319-44680-69, pp. 1505-1537.