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

Supplementary Information

Pinpointing the Active Site and Reaction Mechanism of CO Oxidation on NiO

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Table S1 Surface energies of NiO surfaces

NiO surface	100	110	111	311
Surface energy（J/m^2）	0.38	0.82	1.14	1.33

Data from *New J. Chem*., 2018, 42, 10791

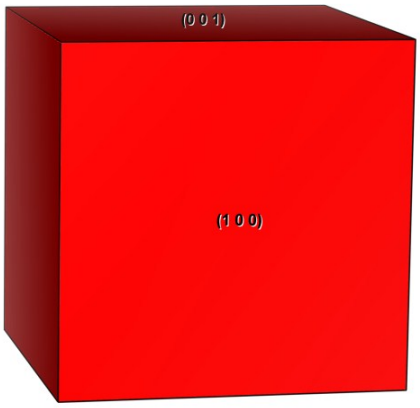

Fig. S1 Morphology of NiO samples predicted by Wulff construction

TS searching Method and main parameters of lasp.in

Global pathway searching of CO oxidation on NiO catalysts by stochastic surface walking method was carried out by LASP package. The double-ended surface walking was adopted to connect the initial and the final structures obtained by DFT optimization. The transition state location method in LASP does not compute Hessian matrix explicitly, and requires only energy and force to identify transition state. All possible reaction pathways and the transition state location was set as 0.05e V/Å for the maximal force and 0.05 GPa for the maximal stress. The Brillouin zone was sampled using 2×2×1 Monkhorst-Pack k-points. The reaction barrier was calculated on the basis of the energy difference between the initial and transition states. Frequency analysis was carried out to verify a single imaginary one for the transition state structure.

The main parameters of the input file lasp.in were set as follows:

```
potential vasp                  #   energy calculated by VASP package
explore_type ssw                #   select the PES sampling method
Run_type 2                      #    2 for DESW
DESW.task optpath               #   optimizing pathway followed by TS search
SSW.ftol          0.05          #   maximal force of geometry convergence criteria
CBD.TSftol        0.05          #   maximal force for TS
SSW.Rotftol       0.05          #   final rotation accuracy
```