SUPPLEMENTARY INFORMATION:

Theoretical determination of a model molecule for

the catalytic upcycling of polyethylene and

polypropylene

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S-1. Reaction energies for the C-H cleavage of polyethylene oligomer with and without the vdW correction enabled for the lattice constant optimization of bulk platinum



Figure S1. Reaction energies for the C-H cleavage (referred to as RE1 since the initial state is the clean metal slab and gas-phase hydrocarbon) as a function of the number of monomers in the polyethylene oligomers over Pt(211) when the platinum bulk lattice constant was optimized without vdW correction and with vdW correction.

S-2. Cell size effect



Figure S2. (a) Adsorption energy of polypropylene trimer (three monomers) over Pt(211) as a function of the reciprocal of the surface area of the slab. The surface area was obtained by multiplying the supercell lattice vectors *a* and *b* parallel to the XY plane. The metal slabs tested consisted of 3x4, 6x4, 9x4, 6x8, and 9x8 atoms. (b) Adsorption energy as a function of the number of polypropylene monomers for two different metal slab sizes consisting of 12x3 and 9x8 atoms.

S-3. Fine-tuning of the machine learning model

The fine-tuning of the machine learning model for the Open Catalyst Project (OCP) calculator was done by feeding more data in the training process, using the pre-trained weights and bias as a starting point. The initial checkpoint for the machine learning model was the GemNet-OC OC20+OC22. First, an ASE database was created containing 2005 trajectories from the OUTCAR files of several DFT geometry optimizations for the final state of C-H and C-C bond cleavage of PE and PP oligomers over Pt(211). An 80/10/10 training/validation/test split was selected, since the total number of images for the training is small compared to the checkpoint model number of parameters (38 million parameters), so 80% provides more data than other traditional splitting ratios as 70/15/15 and 60/20/20. Since more data is provided for the training there may be overfitting, however the validation data was used as a control to stop the training; the number of epochs used is very small (10 epochs), which makes overfitting less likely.

The hyperparameters used for fine tuning this model were a learning rate of 0.0005 with a loss function of mean absolute error (MAE) combining the error in the energies and forces, the maximum number of epochs was fixed to 10 epochs. The activation function used was SiLu, which is similar to a ReLu function, however it is smoother and differentiable at the point of argument equal 0. The optimization method was AdamW, a modification of classical Adam method by including weight decay for prevent overfitting by penalizing large weights. Finaly the batch size was fixed to 8 images.



Figure S3. (a) Training and validation loss as a function of epochs. (b) Training and validation energy mean absolute error (MAE) as a function of epochs. (c) Training and validation forces MAE as a function of epochs.

Figure S1 shows the MAE for energies, forces and the loss that combine both metrics, the finetuning process shows a spike increase in the error for the beginning of the training, after the spike the loss decrease and converge in the first epoch, it is also clear the majority of the loss is composed by the energy MAE and the forces have a small improvement for the MAE metric. The reason for higher deviation for each step for the training compared to validation metric, is because the validation data has broad sample size, the MAE for each step is calculated for 8 images and for the validation 201 images.

S-4. Reaction energies for the C-H cleavage calculated without van der Waals correction



Figure S4. Reaction energies for the C-H cleavage (referred to as RE1 since the initial state is the clean metal slab and gas-phase hydrocarbon) as a function of the number of monomers in the polyethylene oligomers calculated omitting the van der Waals correction (Grimme's DFT-D3 method).



S-5. Reaction energies and adsorption energies for the C-H cleavage over different metals

Figure S5. (a) Reaction energies for the C-H cleavage (referred to as RE1 since the initial state is the clean metal slab and gas-phase hydrocarbon) and adsorption energies as a function of the number of monomers in the polyethylene oligomers over Ag(211). (b) Reaction energies for the C-H cleavage (RE2 since the initial state is the adsorbed hydrocarbon) as a function of the number of monomers in the polyethylene oligomers over Ag(211).



Figure S6. (a) Reaction energies for the C-H cleavage (referred to as RE1 since the initial state is the clean metal slab and gas-phase hydrocarbon) and adsorption energies as a function of the number of monomers in the polyethylene oligomers over Cu(211). (b) Reaction energies for the C-H cleavage (RE2 since the initial state is the adsorbed hydrocarbon) as a function of the number of monomers in the polyethylene oligomers over Cu(211).



Figure S7. (a) Reaction energies for the C-H cleavage (referred to as RE1 since the initial state is the clean metal slab and gas-phase hydrocarbon) and adsorption energies as a function of the

number of monomers in the polyethylene oligomers over Rh(211). (b) Reaction energies for the C-H cleavage (RE2 since the initial state is the adsorbed hydrocarbon) as a function of the number of monomers in the polyethylene oligomers over Rh(211).



Figure S8. (a) Reaction energies for the C-H cleavage (referred to as RE1 since the initial state is the clean metal slab and gas-phase hydrocarbon) and adsorption energies as a function of the number of monomers in the polyethylene oligomers over Pd(211). (c) Reaction energies for the C-H cleavage (RE2 since the initial state is the adsorbed hydrocarbon) as a function of the number of monomers in the polyethylene oligomers over Pd(211).

S-6. Energy barriers for the C-H with the adsorbed hydrocarbon as the initial state



Figure S9. Energy barriers for the C-H cleavage (the initial state is the adsorbed hydrocarbon) as a function of the number of carbons in the n-alkane over Pt(211). The energy barriers were calculated in two different ways: by the difference between the data points and by the difference between linear trends.

S-7. Transition state search: C-C breaking before contacting the metal surface



Figure S10. Geometries of the initial state (1), converged transition state (2), and final state (3). The transition state was obtained through the NEB method.

S-8. Reaction energies for the C-H cleavage of polypropylene oligomers with the adsorbed hydrocarbon as the initial state



Figure S11. Reaction energies for the C-H cleavage (RE2 since the initial state is the adsorbed hydrocarbon) as a function of the number of monomers in the polypropylene oligomers. The RE2s were calculated in two different ways: by the difference between the data points and by the difference between linear trends.