Electronic Supplementary Information

A High Performance Catalyst for Methane Conversion to Methanol: Graphene Supported Single Atom Co

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Computational Methods and Models

All periodic calculations were performed with spin unrestricted density functional theory implemented in DMol³ of Materials Studio package.^{1, 2} A great number of investigations have confirmed that Perdew-Burke-Ernzerhof (PBE)³ functional can give reasonable results for similar catalytic systems to this work.⁴⁻⁶ Thus, the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) functional is used in this work. Due to including dispersion interactions, Grimme's method (DFT-D2) was considered for all calculations. Double- ζ numerical basis set with polarization functions (DNP) and DFT semi-core pseudopotentials (DSPPs) were employed in all calculations. In the DSPPs scheme, all electrons are treated explicitly for C, O and H atoms and a relativistic effective potential is used to describe the core electrons of the Co atom. The transition state searches were performed with the synchronous transit methods (complete LST/QST).⁷ In order to eliminate excrescent imaginary frequencies, transition state optimizations were further carried out and each transition state structure was confirmed to have only one imaginary vibrational frequency.

A hexagonal graphene supercell with 6×6 supercell containing 64 atoms is used as the model. The cell parameters a and b in the graphene plane of 14.82 Å are used,⁸ in which one carbon atom at the center was deleted to model single vacant defect. The Co was placed on the top of the single vacant defect and optimized to the local minimum. The Brillouin zone integration was performed with the Monkhorst-Pack $2 \times 2 \times 1$ *k*-point sampling for structure optimizations and transition state searches. The vacuum layer was set to 20 Å in order to confirm the negligible interaction between two the neighbor layers. A real-space cutoff of 4.5 Å and a thermal smearing of 0.005 Hartree were used. For static calculations, a more precise orbital cutoff of 4.6 Å and the Monkhorst-Pack 7 \times 7 \times 1 *k*-point samplings were used.

The reactants, intermediates, transition states and products in the doublet state are all lower in energy than

those in the quartet state, indicative of the spin crossing not taking place along the reaction pathway. By combining infrared multiple photon dissociation with theoretical calculations, Metz group also concluded the reaction occurring on the lower spin state for CoO⁺ catalyzing methane oxidation to methanol.⁹ Therefore the reaction pathways in doublet states are discussed in this work.

N₂O as the oxidant

The N₂-oxygen affinity of N₂O is as low as 40 kcal/mol,¹⁰ therefore, it is easy to provide active species O. Besides, N₂O comes from agriculture ecosystem, wastewater treatment, sewerage and sludge treatment, the combustion of fossil fuels and biomass, and so on.¹¹⁻¹² It indicates that producing N₂O is easy and N₂O is a renewable resource. In addition, CH₄ and N₂O are produced simultaneously in these systems, and their global warming are 28 and 265 times higher than CO₂ in a 100-year period. Thus, direct conversion CH₄ using N₂O as an oxidant is not only useful for methane conversion into fuels, but also useful for air pollution control. N2O is known as giggle gas, and is a poison gas, thus it may be difficult to use it in the large scale industrial processes at present.

N₂O decomposition on Co/Gr

N₂O is adsorbed on Co/Gr forming an intermediate (IN1-N₂O). The adsorption energy of N₂O on Co/Gr is only 0.11 eV, indicative of a weak interaction between N₂O and Co/Gr. The Co–O and N–O bond distances of IN1-N₂O are 2.27 Å and 1.21 Å, respectively. The IN1-N₂O will decompose into IN2-N₂O via TS1-2-N₂O. This elementary reaction is nearly no energy barrier (0.1 eV). The Co–O and N–O bond distances of TS1-2-N₂O are 1.88 and 1.37 Å, respectively. IN2-N₂O consists of N₂ adsorbed on CoO/Gr. The adsorption energy of N₂ on CoO/Gr is only 0.1 eV. The energy barrier and adsorption energies are too low to tolerate computational deviation and sensitive to dispersion correction. Once dispersion corrections are carried out, the energy barrier is a negative value. Thus dispersion corrections are not included for this elementary reaction.

After the first N2O dissociation, one single O atom is adsorbed on the Co. In order to investigate if another N2O can dissociate on the same site or directly react with the O to form an O2 molecules, the adsorptions of the second N2O on CoO/Gr were calculated. After optimization, N2O got away from Co or O. The Co---ON2 and CoO---ON2 bond distances are more than 3.6 Å and 3.2 Å, far longer than Co-O (1.82 Å) and O-O (1.32 Å) covalent bonds. The tested adsorption configurations indicate another N2O will not dissociate on CoO/Gr.

The stability of Co/Gr and CoO/Gr

In order to confirm the stability of Co atom embedded in the graphene and during the reaction, the formation energies of Co and CoO embedded in single vacant graphene were calculated to be -7.57 eV and -7.53 eV, respectively. It shows that the interaction between the support and active center is very strong. Additionally, we calculated the configurations of Co and CoO locating at the hollow sites of C6 ring (adjacent to the vacant) to be 6.13 eV and 5.85 eV higher than those of Co and CoO locating at the vacant, respectively. It reveals that the diffusion energies of Co and CoO are higher than 6.13 eV and 5.85 eV, respectively. The high formation energies and the high diffusion energies confirm that single atom Co embedded in the graphene and during the reaction are very stable. The formation energies were calculated according to the equation: $E_f = E_{graphene-M} - E_{graphene} - E_M$ (M= Co, CoO), in which $E_{graphene-M}$, $E_{graphene}$, E_M are the energies of single vacant graphene supported M, single vacant graphene, and M, respectively.

Comparison of CoO⁺ and CoO/Gr as the catalyst

Firstly, in their work, ⁹ energy barrier of hydrogen abstraction to HO-Co-CH₃ insertion intermediate is 0.71 eV. The elementary reaction from HO-Co-CH₃ to Co-CH₃OH has an energy barrier of 0.91 eV. Thus, the second step is the rate-limiting step for methane conversion into methanol. In this work, taking CoO/Gr as the catalyst, the energy barrier of the first step (0.7 eV) is much higher than that of the second step (0.18 eV). Therefore, the rate-limiting step is the first step for methane conversion into methanol. It is different from that of CoO⁺ as the catalyst. Secondly, the energy barrier of the second step elementary reaction catalyzed by CoO/Gr (0.18 eV) is lowered by 0.73 eV due to the support of graphene. In addition, energy barrier from HO-Co-CH₃ to carbene is 0.71 higher than that to produce methanol taking CoO⁺ as the catalyst, while it is 0.69 eV higher than that to produce methanol for CoO/Gr catalyst. This predicts CoO/Gr also has the high selectivity for methane conversion into methanol. As a whole, taking graphene as a support of CoO in this work, it not only prevents CoO from aggregation, provides more active centers, lowers the energy barrier of the rating-determine step, but also keeps excellent reaction selectivity for methane conversion to methanol. Thus, Gr/Co as the catalyst and N₂O as oxidant is high reactivity and selectivity for methane conversion into methanol at mild condition. Meanwhile, it eliminates air pollution of N₂O and CH₄, which are both serious gas to greenhouse effect.

Table S1. The Hirshfeld charges on graphene for each species in the reaction processes.

Hirshfeld	IN1	TS1-2	IN2/IN2n	TS2-3/TS2n-3n	IN3/IN3n
charge (e)	0.0028	0.0006	0.0002/0.0018	-0.0017/-0.0020	-0.0049/-0.0056

The C-H bond activation on CoO embedded in single/double vacant graphene

For comparison, we also tested methane conversion to methanol on double vacant graphene supported Co. It is found that the barrier for C-H activation on double vacant graphene supported CoO (1.27 eV) is much higher than that on single vacant graphene supported CoO (0.81 eV) in the radical pathway. Thus, single vacant graphene supported CoO is more suitable for methane conversion at mild conditions. It also shows that different models have different catalytic performance. To save calculation time, the energy barrier values here are directly from transition state search calculations, therefore, a little different from the more accurate values in the main text. But the relative trends are reliable.

Notes and references

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