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# An automated reaction route mapping for the reaction of NO and active species on Ag<sub>4</sub> clusters in zeolites†

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A computational investigation of the catalytic reaction on multinuclear sites is very challenging. Here, using an automated reaction route mapping method, the single-component artificial force induced reaction (SC-AFIR) algorithm, the catalytic reaction of NO and OH/OOH species over the Ag<sub>4</sub><sup>2+</sup> cluster in a zeolite is investigated. The results of the reaction route mapping for H<sub>2</sub> + O<sub>2</sub> reveal that OH and OOH species are formed over the Ag<sub>4</sub><sup>2+</sup> cluster *via* an activation barrier lower than that of OH formation from H<sub>2</sub>O dissociation. Then, reaction route mapping is performed to examine the reactivity of the OH and OOH species with NO molecules over the Ag<sub>4</sub><sup>2+</sup> cluster, resulting in the facile reaction path of HONO formation. With the aid of the automated reaction route mapping, the promotion effect of H<sub>2</sub> addition on the SCR reaction was computationally proposed (boosting the formation of OH and OOH species). In addition, the present study emphasizes that automated reaction route mapping is a powerful tool to elucidate the complicated reaction pathway on multi-nuclear clusters.

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## 1. Introduction

Automated reaction route mapping is considered a powerful method for elucidating the mechanism of chemical reactions.<sup>1–10</sup> Maeda *et al.* developed an artificial force-induced reaction (AFIR) method implemented in the global reaction route mapping (GRRM) program as an efficient reaction path-searching method; additionally, they demonstrated the rational design of chemical reactions in homogeneous systems.<sup>11–16</sup> Investigating the reaction mechanism over multinuclear clusters in heterogeneous systems is challenging<sup>17–21</sup> because various active sites are present in one cluster (*e.g.*, on-top, bridge, and hollow sites) and their shapes change during the reaction.<sup>22–25</sup> Thus, the exploration of the reaction mechanism over the clusters, based on transition state calculations, focuses typically only on some critical steps expected from previous results and experiences, which hinders the identification of more plausible reaction pathways.<sup>26–33</sup> Gao *et al.* employed the AFIR method to investigate the structural transformation of neutral Au<sub>x</sub> clusters (*x* = 3–12) induced by O<sub>2</sub> adsorption and reported that the transformation of Au clusters was promoted by O<sub>2</sub> adsorption.<sup>34</sup> Similarly, Iwasa *et al.* investigated the

relationship between the structural transformation of a Cu<sub>13</sub> cluster and NO dissociation using the AFIR method.<sup>35</sup> Although the aforementioned studies reveal the nature of metal clusters and adsorbed molecules by the AFIR method, the detailed reaction mechanism in the catalytic processes over metal clusters has not been reported.

Ag-loaded Al<sub>2</sub>O<sub>3</sub> and Ag-exchanged zeolites have been studied for the selective catalytic reduction of NO to N<sub>2</sub> (SCR).<sup>36–39</sup> Interestingly, adding a small amount of H<sub>2</sub> improved the SCR performance of these catalysts; many researchers have intensively studied the reaction mechanism of H<sub>2</sub>-assisted SCR on Ag-loaded Al<sub>2</sub>O<sub>3</sub> and unraveled that the oxidized Ag species was promoted to be reduced into the metallic state by H<sub>2</sub>.<sup>40–48</sup> In the case of Ag-exchanged zeolite, in the presence of H<sub>2</sub>, the formed Ag<sub>n</sub><sup>δ+</sup> clusters improved the SCR performance.<sup>49–53</sup> Shibata *et al.* performed UV-vis and XAS measurements, which revealed that the average structure of the formed cluster in the zeolite was Ag<sub>4</sub><sup>2+</sup>.<sup>54</sup> Using *in situ* IR measurements, Shimizu *et al.* reported that the formed Ag<sub>n</sub><sup>δ+</sup> cluster activates O<sub>2</sub> and H<sub>2</sub> to yield OOH species that are responsible for the drastic improvement in ammonia- (NH<sub>3</sub>-) and hydrocarbon-(HC-) SCR performance.<sup>52,55</sup> For decades, numerous experimental<sup>50–52,55,56</sup> and theoretical<sup>53</sup> investigations have been reported on the characterization of active Ag clusters and plausible SCR mechanisms. However, these studies still lack a molecular-level understanding of the reaction pathways based on computational techniques.

In this study, using automated reaction route mapping, the reaction of H<sub>2</sub> and O<sub>2</sub> was investigated over Ag<sub>4</sub><sup>2+</sup> clusters

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confined in CHA zeolite (a relatively small number of atoms are required to describe its periodic model). The formation of OOH and OH species from  $\text{H}_2 + \text{O}_2$  requires a lower activation barrier than OH formation from  $\text{H}_2\text{O}$  dissociation over the  $\text{Ag}_4^{2+}$  cluster. Subsequently, the reactivity of NO with the active species formed on  $\text{Ag}_4^{2+}$  was assessed. The results indicated that minimal activation barrier was required to produce the HONO intermediate, which then migrated into the Brønsted acid sites to give  $\text{N}_2 + \text{H}_2\text{O}$  via reaction with  $\text{NH}_3$  (discussed in our previous reports<sup>57</sup>). Similarly, the  $\text{NO} + \text{H}_2$  reaction required a relatively high activation barrier to produce  $\text{NH}_3$ , thus indicating that NO preferentially reacts with the active species, OH, and OOH species on the  $\text{Ag}_4^{2+}$  cluster. The present study demonstrates the effective use of an automated reaction path-searching method to explore catalytic reactions in multi-nuclear clusters.

## 2. Computational details

Spin-polarized density functional theory (DFT) calculations were performed using the Vienna Ab initio Simulation Package (VASP).<sup>58,59</sup> In particular, the projected augmented wave (PAW) method<sup>60,61</sup> was employed for the Kohn–Sham equations<sup>62,63</sup> with a plane-wave energy cutoff of 400 eV. The generalized gradient approximated Perdew–Burke–Ernzerhof (GGA-PBE) functional<sup>64</sup> was employed to describe the electron exchange–correlation. The Brillouin zone sampling was restricted to the  $\Gamma$  point (convergence tests of cutoff energy and k-point mesh are shown in Table S1 and S2, ESI†).<sup>65</sup> van der Waals interactions were considered using the dispersion-corrected DFT-D3 (BJ) method.<sup>66,67</sup> The periodic model of the CHA zeolite, utilized as the model zeolite for reducing the computational cost for the reaction mapping, was obtained from the International Zeolite Association (IZA) database ( $a = b = 13.7 \text{ \AA}$ ,  $c = 14.8 \text{ \AA}$ ,  $\alpha = \beta = 90.0^\circ$ , and  $\gamma = 120^\circ$ ).<sup>68</sup> The lattice constants were fixed at the initial values during the calculations (comparison before/after the optimization of the lattice constants is shown in Table S3, ESI†). CHA zeolite is composed of only one crystallographically inequivalent  $T$  site,<sup>69</sup> and the third-nearest-neighbor in a six-membered ring site (6MR3NN site) in CHA was considered a model paired Al site in this study (Fig. 1).<sup>26,70,71</sup> Reaction route mapping was performed using the single-component artificial force induced reaction (SC-AFIR) method, as implemented in the GRRM17 program.<sup>16</sup> In this method, a structural deformation is induced by pushing or pulling a pair of target atoms with the applied artificial force using the following AFIR function.<sup>16</sup>

$$F^{\text{AFIR}}(Q) = E(Q) + \rho\alpha \frac{\sum_{i \in A} \sum_{j \in B} \omega_{ij} r_{ij}}{\sum_{i \in A} \sum_{j \in B} \omega_{ij}}$$

$E(Q)$  represents the potential energy surface (PES) of geometrical parameters  $Q$ . In the second term, the artificial force is applied to the system, and the strength of the artificial force is controlled by  $\alpha$ , where  $\rho$  is set to either 1 or  $-1$ .  $r_{ij}$  represents

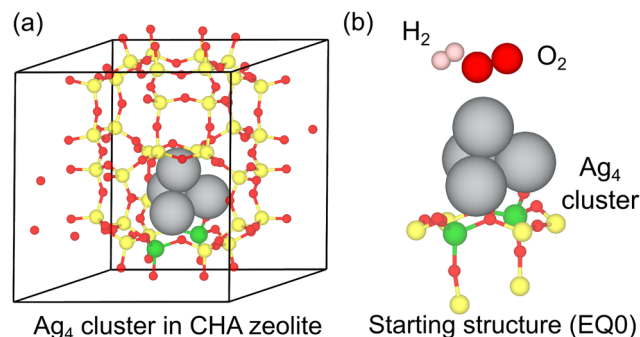


Fig. 1 (a) Utilized periodic model of CHA zeolite including the  $\text{Ag}_4$  cluster and (b) the starting structure (EQ0) for the reaction route mapping with the SC-AFIR method.

the interatomic distance of atoms  $i$  and  $j$  in fragments  $A$  and  $B$ , respectively. The weight  $\omega_{ij}$  is described as,

$$\omega_{ij} = \left[ \frac{R_i + R_j}{r_{ij}} \right]^6$$

where  $R_i$  and  $R_j$  represent each covalent radius.

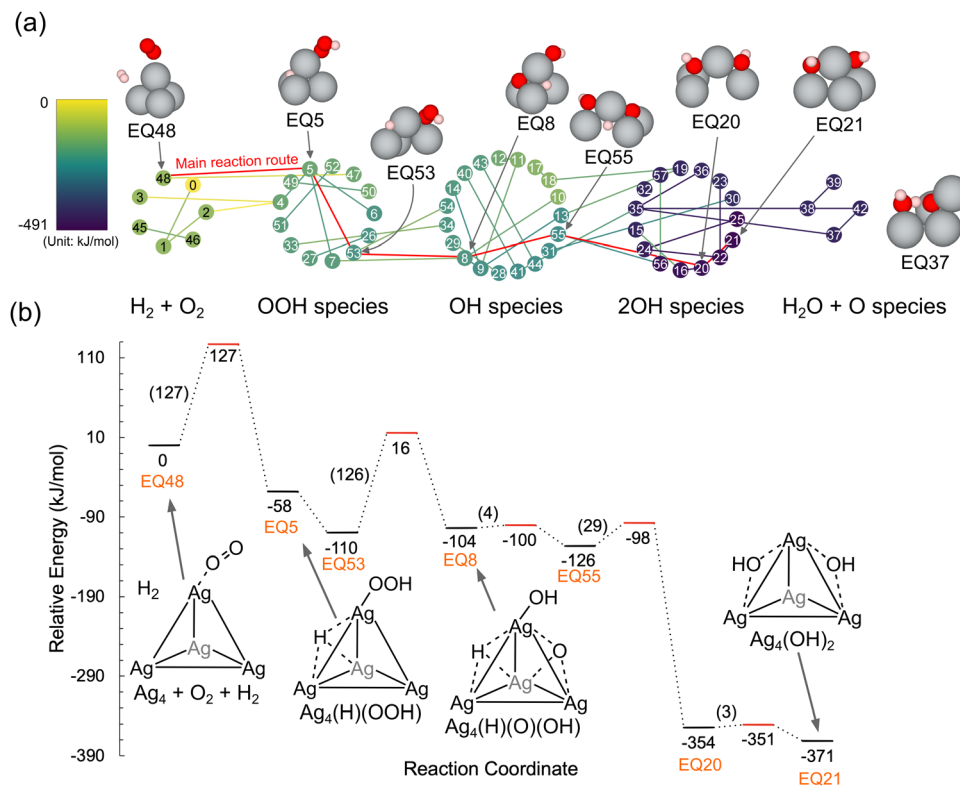
A model collision energy parameter of  $1000 \text{ kJ mol}^{-1}$  was used for all calculations. The obtained AFIR path was subsequently optimized by the locally updated plane (LUP) method to obtain the approximate equilibrium structures (EQs) and path top (PT) points, which were subsequently re-optimized by the following intrinsic reaction coordinate (IRC) calculation to determine the transition state (TS) structures and their connectivity.<sup>72</sup> The structures are treated to be optimized when the difference in their electronic energies, the RMS error in interatomic distances, and the maximum error in interatomic distances are all smaller than  $6.0 \text{ kJ mol}^{-1}$ , 3%, and 6%, respectively. Only a positive force was applied to the SC-AFIR calculations. Reactants in the gas phase ( $\text{H}_2$ ,  $\text{O}_2$ , and NO molecules) of the initial structures were considered the target atoms of the SC-AFIR algorithm. During the calculations, the positions of the atoms in the zeolite framework were fixed at the initial positions, except for the Al atoms, the Si atoms around the Al atoms, and the O atoms connected to the Al and Si atoms (Fig. 1b).<sup>73</sup> All the structures predicted in this study can be found in the ESI.†

## 3. Results and discussion

### 3.1 Reaction route mapping of the $\text{H}_2 + \text{O}_2$ reaction to produce an OH group over the $\text{Ag}_4$ cluster in CHA zeolite

Our group previously reported the mechanism of  $\text{NH}_3$ -SCR, wherein the OH species bound to transition metal cations oxidizes NO into HONO species ( $\text{M}^{n+}(\text{OH}) + \text{NO} \rightarrow \text{M}^{(n-1)+} + \text{HONO}$ ;  $\text{M}^{n+}$  describes metal cations) that then migrate into Brønsted acid sites (BAS) to form  $\text{H}_2\text{O}$  and  $\text{NO}^+$  species ( $\text{HONO} + \text{H}^+\text{O}_z^- \rightarrow \text{NO}^+\text{O}_z^- + \text{H}_2\text{O}$ ;  $\text{H}^+\text{O}_z^-$  represents BAS) that easily react with  $\text{NH}_3$  to produce  $\text{N}_2$  and  $\text{H}_2\text{O}$  ( $\text{NO}^+\text{O}_z^- + \text{NH}_3 \rightarrow \text{H}^+\text{O}_z^- + \text{N}_2 + \text{H}_2\text{O}$ ).<sup>57,74–77</sup> Thus, the generation of OH groups on active metal cations is a crucial step in the SCR reaction.

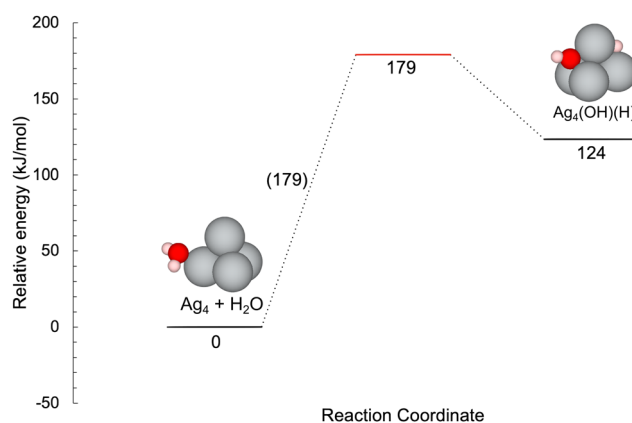




**Fig. 2** (a) Reaction route network for  $\text{H}_2 + \text{O}_2$  on a  $\text{Ag}_4$  cluster in CHA zeolite. Nodes and edges describe obtained structures and paths connecting them (TS and PT, determined by GRRM program<sup>16</sup>). The color of the nodes and edges represents the relative energy (the color bar is shown on the left side). The representative structures are displayed together (only the  $\text{Ag}_4$  cluster and reactants are shown for clarity). (b) Energy profile for the main reaction route toward EQ21. The relative energies of each structure and the activation barriers are shown below the bar and in brackets, respectively. Schematic views of the structures are displayed together.

Here, the  $\text{H}_2 + \text{O}_2$  reaction was explored to assess the feasibility of generating OH groups on the  $\text{Ag}_n^{\delta+}$  cationic cluster. Shibata *et al.* reported that in the presence of  $\text{H}_2$ ,  $\text{Ag}_4^{2+}$  clusters were generated within the zeolite framework and acted as active sites for the SCR reaction.<sup>54</sup> Encouraged by their study, the  $\text{Ag}_4^{2+}$  cluster at the 2Al site was used as the initial structure. Fig. 1a shows the periodic model of CHA zeolites obtained from the IZA database. In this study, two *T* sites in the six-membered ring of CHA were replaced by Al.<sup>70</sup> As a starting structure,  $\text{O}_2$  and  $\text{H}_2$  molecules were added to the periodic model, including the  $\text{Ag}_4^{2+}$  cluster (Fig. 1b), and the reaction route was explored by the SC-AFIR method. Fig. 2a shows the results of the reaction route mapping, and the relative energies along the main reaction coordinates are shown in Fig. 2b. 57 of the structures, which showed different shapes of  $\text{Ag}_4^{2+}$  clusters, and 57 of their connections (TS and PT) were found by the aid of the SC-AFIR method. In the first step,  $\text{H}_2$  molecules were dissociated to give OOH species and H atoms on the  $\text{Ag}_4$  cluster *via* an activation barrier (*Ea*) of 127  $\text{kJ mol}^{-1}$ . Sawabe *et al.* also performed DFT calculations to reveal that OOH species on the  $\text{Ag}_4^{2+}$  cluster are potential active species for the SCR reaction while  $\text{H}_2$  dissociation took place as the first step in their reaction path (activation barrier of OOH formation was not shown).<sup>53</sup> Next, the formed OOH species dissociated into OH and O species on the cluster with an *Ea* of 125  $\text{kJ mol}^{-1}$ . Subsequently, the O atom combined with

the H atom to give another OH species *via* low *Eas* (4, 29, and 3  $\text{kJ mol}^{-1}$ ) with an exothermicity of 371  $\text{kJ mol}^{-1}$ . The dissociation of  $\text{H}_2\text{O}$  molecules to form OH species on the  $\text{Ag}_4$  cluster was also examined (Fig. 3). The results revealed that the formation of OH species from  $\text{H}_2 + \text{O}_2$  required a lower *Ea* than the  $\text{H}_2\text{O}$



**Fig. 3** Energy profile for  $\text{H}_2\text{O}$  dissociation reaction to yield OH species and a H atom over a  $\text{Ag}_4$  cluster. The relative energies of each structure and the activation barriers are shown below the bar and in brackets, respectively. The structures are displayed together (only the  $\text{Ag}_4$  cluster and reactants are shown for clarity).



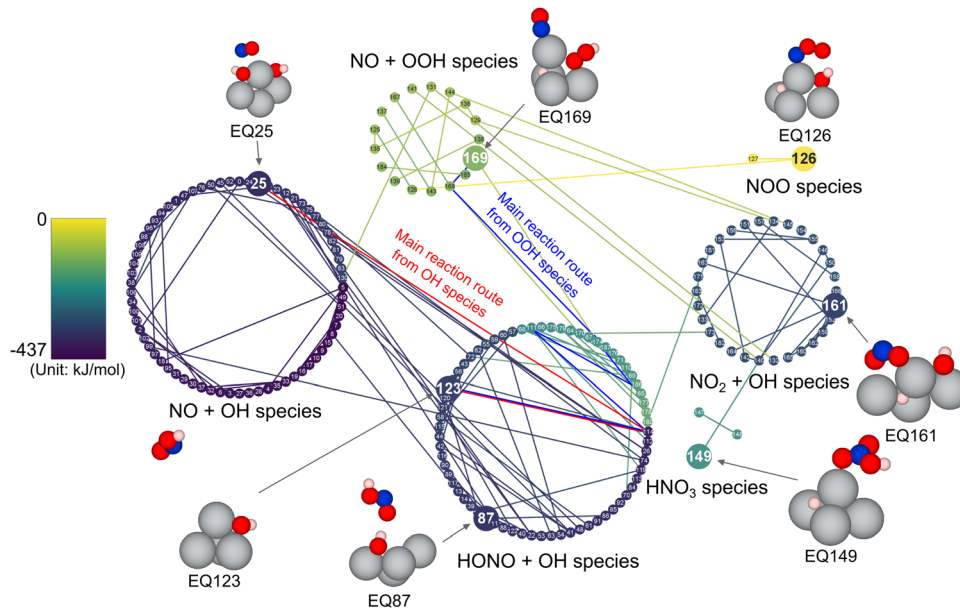


Fig. 4 Reaction route network for a NO molecule and  $\text{Ag}_4(\text{OH})_2$  in CHA zeolite (EQ21 in Fig. 2a). Nodes and edges describe obtained structures and paths connecting them (TS and PT, determined by GRRM program<sup>16</sup>). The color of the nodes and edges describes the relative energy (color bar is shown on the left side). The representative structures are displayed together (only  $\text{Ag}_4$  cluster and reactants are shown for clarity).

dissociation ( $127 \text{ kJ mol}^{-1}$  vs.  $179 \text{ kJ mol}^{-1}$ ). These results indicated that the  $\text{H}_2 + \text{O}_2$  mixture more facily dissociates on the  $\text{Ag}_4$  cluster than  $\text{H}_2\text{O}$  dissociation. The following section discusses the reactivity of OOH and OH species with NO molecules over the  $\text{Ag}_4$  cluster.

### 3.2 Reactivity of OOH and OH species with a NO molecule to produce a HONO intermediate on a $\text{Ag}_4$ cluster

The reactivity of OOH and OH species previously formed on the  $\text{Ag}_4$  cluster with an NO molecule was examined by the SC-AFIR method. One NO molecule was added to the structure of EQ21, as shown in Fig. 2a ( $\text{Ag}_4(\text{OH})_2$  species). Fig. 4 shows the results of the reaction route mapping, and Fig. 5a shows the relative energy along the main reaction route of the OH and NO molecules on the  $\text{Ag}_4$  cluster. The adsorbed NO on the  $\text{Ag}_4$  cluster reacted with OH species to form HONO species as a facile process ( $E_a = 13 \text{ kJ mol}^{-1}$ ). Subsequently, the formed HONO species was desorbed from the cluster *via* an  $E_a$  of  $70 \text{ kJ mol}^{-1}$ . With the same starting structure (EQ21 in Fig. 2a), the reaction of the OOH species and NO molecules was also explored. Fig. 5b shows the relative energies along the main reaction route for OOH + NO. To form the HONO species, the O–O bond in the OOH species was cleaved to provide an OH fragment, which subsequently reacted with adsorbed NO *via* an  $E_a$  of  $47 \text{ kJ mol}^{-1}$ . The formed HONO achieved the same structure as the case of OH species (EQ114) through relatively small  $E_a$ s ( $31$  and  $27 \text{ kJ mol}^{-1}$ ) before detaching through an  $E_a$  of  $70 \text{ kJ mol}^{-1}$  (EQ123). The formation of  $\text{NO}_2$  species on the  $\text{Ag}_4$  cluster was predicted as another reaction route from OOH + NO, and the evaluated  $E_a$  was low ( $17 \text{ kJ mol}^{-1}$ ). Our previous study demonstrated that  $\text{N}_2\text{O}_4$  species, formed *via* the dimerization of  $\text{NO}_2$ , also produced  $\text{NO}^+$  species at the Al site in the

zeolite.<sup>57</sup> Besides, Bader charge analysis<sup>78</sup> was performed to evaluate the charge of the  $\text{Ag}_4$  cluster before/after NO adsorption (Fig. S1, ESI<sup>†</sup>), and the result showed that the total charge of the cluster was not changed by NO adsorption while that of the NO molecule slightly decreased.

In summary, OH and OOH species, formed *via* the  $\text{H}_2 + \text{O}_2$  reaction, easily oxidize NO to HONO or  $\text{NO}_2$  species. Thus,  $\text{H}_2$  addition promotes the formation of the highly active species OH and OOH on the  $\text{Ag}_4$  cluster.

### 3.3 Reaction of NO + $\text{H}_2$ on the $\text{Ag}_4$ cluster toward $\text{NH}_3$ formation.

Three  $\text{H}_2$  and one NO molecules were added to the periodic system, including the  $\text{Ag}_4$  cluster (Fig. 1a), and reaction route mapping was carried out using the SC-AFIR method. Fig. 6 shows the reaction route for the  $3\text{H}_2 + \text{NO}$  reaction; the adsorbed NO was exothermically hydrogenated in a step-by-step manner to yield  $\text{NH}_3$  and  $\text{H}_2\text{O}$ . Fig. 7 shows the energy profile along the main reaction route toward  $\text{NH}_3$  and  $\text{H}_2\text{O}$ . First, the N atom of the adsorbed NO molecule is hydrogenated by the adjacent adsorbed  $\text{H}_2$  molecule toward  $\text{NH}_2\text{O}$  species. This step has an exothermicity of  $126 \text{ kJ mol}^{-1}$  through a relatively high  $E_a$  ( $138 \text{ kJ mol}^{-1}$ ). Subsequently, the O atom in the formed  $\text{NH}_2\text{O}$  species was hydrogenated to give hydroxylamine ( $\text{NH}_2\text{OH}$ ) and adsorbed H atoms with an  $E_a$  of  $90 \text{ kJ mol}^{-1}$ . Finally, the N–O bond in the formed  $\text{NH}_2\text{OH}$  is cleaved by the addition of  $\text{H}_2$  molecules to give molecular  $\text{NH}_3$  and  $\text{H}_2\text{O}$  with a high exothermicity ( $329 \text{ kJ mol}^{-1}$ ) through an  $E_a$  of  $111 \text{ kJ mol}^{-1}$ . The first process in the entire reaction pathway to give the  $\text{NH}_2\text{O}$  species exhibited the highest  $E_a$ . Considering the  $E_a$  for the formation of OH and OOH species



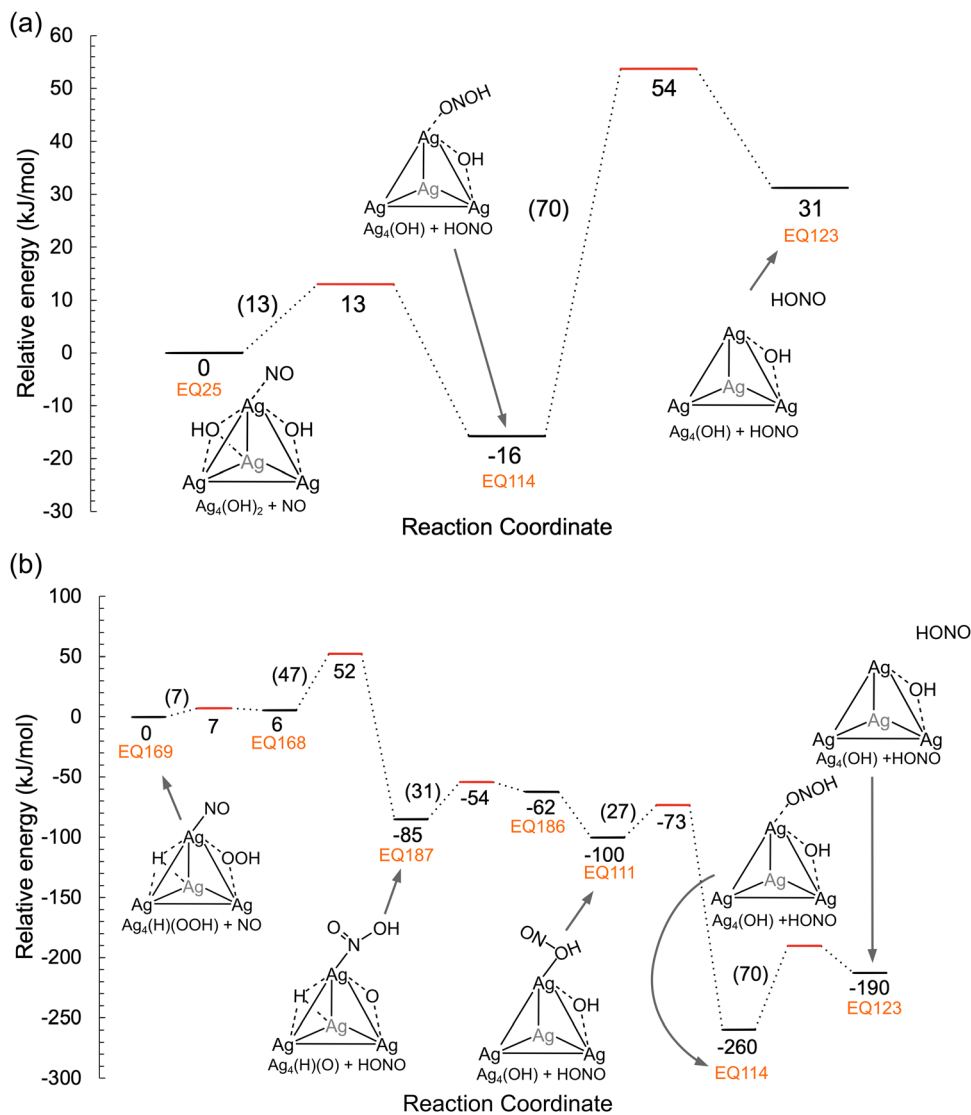


Fig. 5 Energy profile for the main reaction route toward EQ123 from (a) OH species and (b) OOH species. The relative energies of each structure and the activation barriers are shown below each bar and in brackets, respectively. A schematic view of the structures is displayed together.

(127 kJ mol<sup>-1</sup>), the direct hydrogenation of NO with H<sub>2</sub> toward NH<sub>3</sub> is less plausible for the SCR reaction.

Fig. 8 shows the proposed reaction routes in this study, combined with previous reports.<sup>56,57</sup> In the presence of H<sub>2</sub> and O<sub>2</sub>, OH and OOH species were generated on the Ag<sub>4</sub> cluster with an *Ea* of 127 kJ mol<sup>-1</sup>. Moreover, the generation of OH species from adsorbed H<sub>2</sub>O molecules required an *Ea* of 179 kJ mol<sup>-1</sup>. The active species formed on the Ag<sub>4</sub> cluster, OH, and OOH species, easily reacted with the NO molecule to yield the HONO intermediate. As another possible reaction, the direct hydrogenation of NO with H<sub>2</sub> was assessed; the *Ea* for NH<sub>3</sub> formation was evaluated to be 138 kJ mol<sup>-1</sup>, which is higher than that for the H<sub>2</sub> + O<sub>2</sub> reaction. The proposed contribution of H<sub>2</sub> addition to NH<sub>3</sub>-SCR by zeolite-based catalysts is to boost the formation of active OH and OOH species on the Ag<sub>4</sub> cluster. Previous research on H<sub>2</sub>-assisted SCR over Ag-loaded Al<sub>2</sub>O<sub>3</sub> proposes that the main contribution of H<sub>2</sub> addition is stabilizing nitrate

(NO<sub>3</sub><sup>-</sup>) on the Al<sub>2</sub>O<sub>3</sub> surface to prevent poisoning active Ag species, which is different from our result on zeolite-based catalysts.<sup>40,42,45,79</sup> For HC-SCR, the previous study using *in situ* spectroscopy proposed that C<sub>3</sub>H<sub>8</sub> reacted with active species (*e.g.* OOH species) to form NH<sub>3</sub> (by the reaction with NO<sub>2</sub>) through CH<sub>3</sub>COO<sup>-</sup>, CH<sub>3</sub>NO<sub>2</sub>, and NCO<sup>-</sup> intermediates on the Ag<sub>4</sub> cluster.<sup>52,55</sup> According to this result, the formed HONO species is probably decomposed into N<sub>2</sub> and H<sub>2</sub>O at Brønsted acid sites by the formed NH<sub>3</sub>. Thus, the present study demonstrated the effective utilization of automated reaction route mapping to explore the reactions over multinuclear clusters confined in zeolites.

## 4. Conclusion

Automated reaction route mapping was carried out to explore the catalytic reaction over the Ag<sub>4</sub><sup>2+</sup> cluster confined in the zeolite. The H<sub>2</sub> + O<sub>2</sub> reaction over the Ag<sub>4</sub><sup>2+</sup> cluster indicated



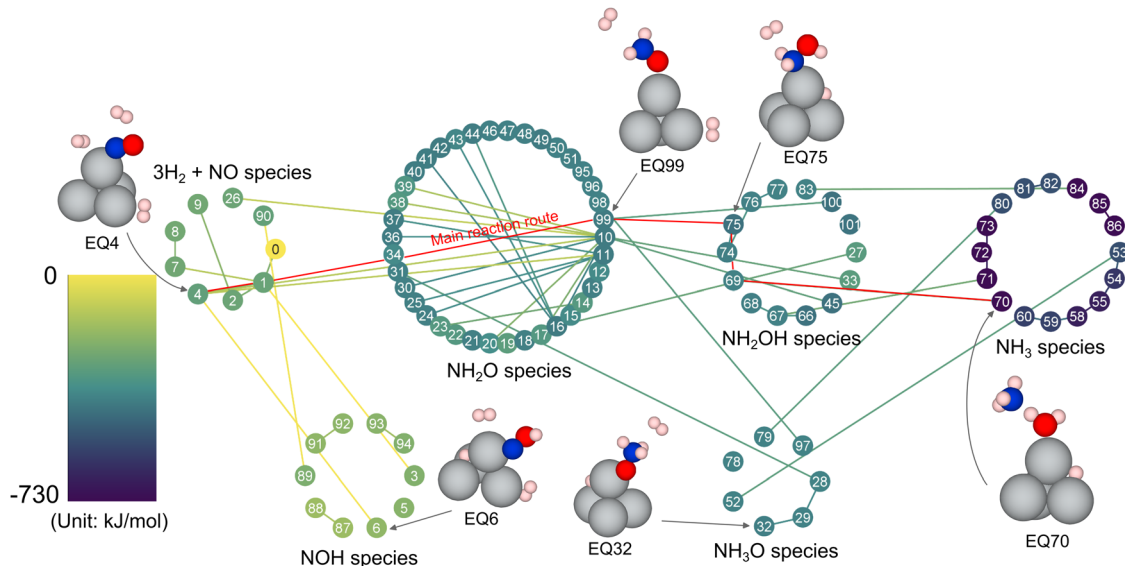


Fig. 6 Reaction route network for one NO and three H<sub>2</sub> molecules and the Ag<sub>4</sub> cluster in CHA zeolite. Nodes and edges describe obtained structures and paths connecting them (TS and path top (PT), determined by GRRM program<sup>16</sup>). The color of the nodes and edges describes the relative energy (color bar is shown on the left side). The representative structures are displayed together (only the Ag<sub>4</sub> cluster and reactants are shown for clarity).

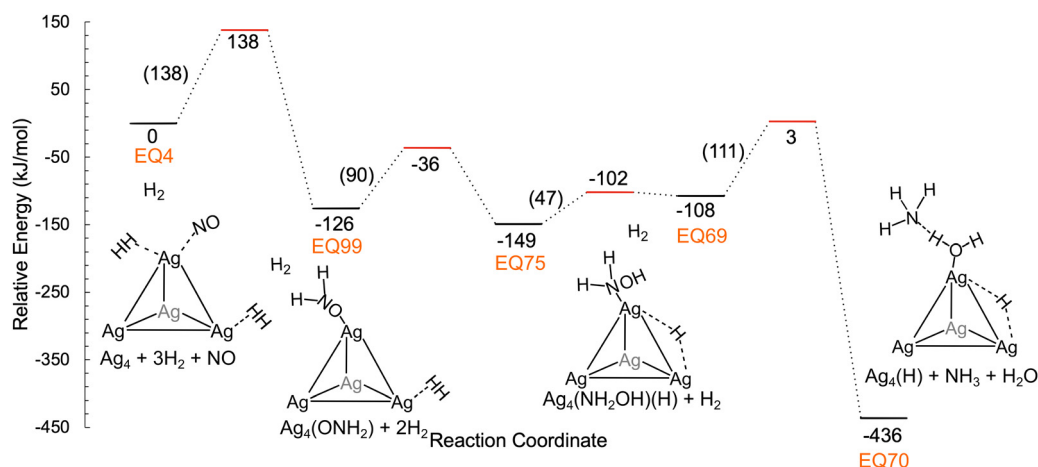


Fig. 7 Energy profile for the main reaction route (NO + 3H<sub>2</sub> → NH<sub>3</sub> + H<sub>2</sub>O + H) over the Ag<sub>4</sub> cluster. The relative energies of each structure and the activation barriers are shown below the bar and in brackets, respectively. A schematic view of the structures is displayed together.

that the generation of active species, OH and OOH species, required lower activation energy than that for the formation of OH species from the dissociative adsorption of H<sub>2</sub>O (127 kJ mol<sup>-1</sup> vs. 179 kJ mol<sup>-1</sup>). The formed OH species were highly reactive with NO molecules to yield HONO species (*E<sub>a</sub>* = 13 kJ mol<sup>-1</sup>), whereas the reaction of NO and OOH species gave HONO or NO<sub>2</sub> species *via Eas* of 47 and 17 kJ mol<sup>-1</sup>, respectively. Additionally, the reactivity of H<sub>2</sub> with NO over the Ag<sub>4</sub> clusters was examined. This result revealed that the formation of NH<sub>3</sub> from NO + H<sub>2</sub> required an *E<sub>a</sub>* as high as 138 kJ mol<sup>-1</sup>, thus indicating that the NO molecule preferentially reacted with OH or OOH species formed on the Ag<sub>4</sub> cluster to give HONO. The present study demonstrated that the automated reaction route-searching method is suitable for

investigating the catalytic reaction over multinuclear clusters with structural changes during the reaction.

## Conflicts of interest

The authors declare no conflicts of interest.

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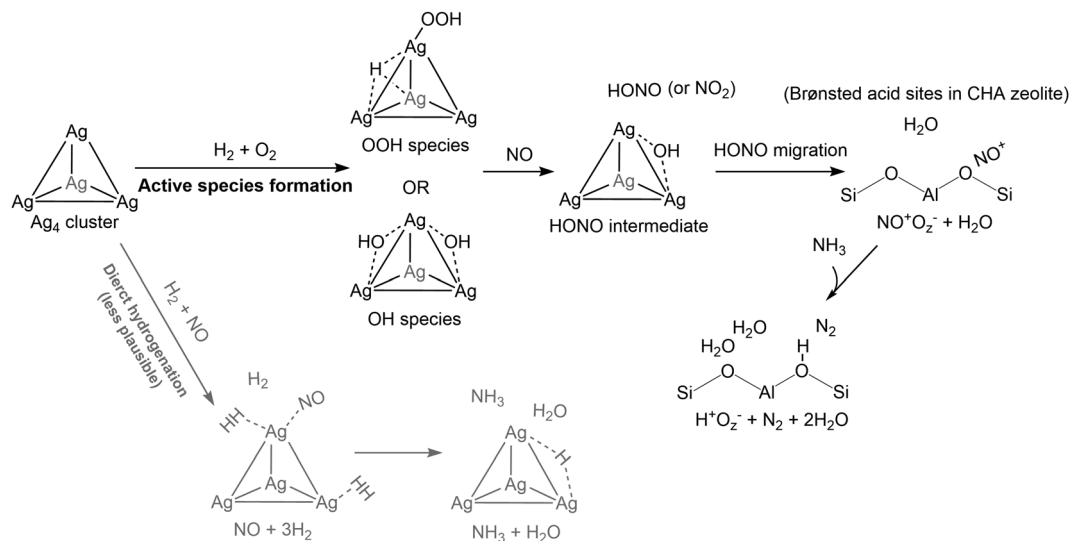


Fig. 8 Whole view of H<sub>2</sub>-assisted NH<sub>3</sub>-SCR over the Ag<sub>4</sub> cluster in CHA zeolite proposed in this study, combined with the reactions on Brønsted acid sites of CHA zeolite described in our previous reports.<sup>57,75</sup>

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## References

- S. Stocker, G. Csányi, K. Reuter and J. T. Margraf, *Nat. Commun.*, 2020, **11**, 5505.
- B. Kreitz, K. Sargsyan, K. Blöndal, E. J. Mazeau, R. H. West, G. D. Wehinger, T. Turek and C. F. Goldsmith, *JACS Au*, 2021, **1**, 1656–1673.
- T. Lan and Q. An, *J. Am. Chem. Soc.*, 2021, **143**, 16804–16812.
- J. Xu, X. M. Cao and P. Hu, *Phys. Chem. Chem. Phys.*, 2021, **23**, 11155–11179.
- X. Fu, J. Li, J. Long, C. Guo and J. Xiao, *ACS Catal.*, 2021, **11**, 12264–12273.
- R. T. Hannagan, G. Giannakakis, R. Réocreux, J. Schumann, J. Finale, Y. Wang, A. Michaelides, P. Deshlahra, P. Christopher, M. Flytzani-Stephanopoulos, M. Stamatakis and E. C. H. Sykes, *Science*, 2021, **372**, 1444–1447.
- Z. W. Ulissi, A. J. Medford, T. Bligaard and J. K. Nørskov, *Nat. Commun.*, 2017, **8**, 14621.
- A. A. Latimer, A. R. Kulkarni, H. Aljama, J. H. Montoya, J. S. Yoo, C. Tsai, F. Abild-Pedersen, F. Studt and J. K. Nørskov, *Nat. Mater.*, 2017, **16**, 225–229.
- J.-M. Schweitzer, J. Rey, C. Bignaud, T. Bučko, P. Raybaud, M. Moscovici-Mirande, F. Portejoie, C. James, C. Bouchy and C. Chizallet, *ACS Catal.*, 2022, **12**, 1068–1081.
- A. Bruix, J. T. Margraf, M. Andersen and K. Reuter, *Nat. Catal.*, 2019, **2**, 659–670.
- K. Ohno and S. Maeda, *J. Phys. Chem. A*, 2006, **110**, 8933–8941.
- S. Maeda, K. Ohno and K. Morokuma, *Phys. Chem. Chem. Phys.*, 2013, **15**, 3683–3701.
- S. Maeda, T. Taketsugu, K. Ohno and K. Morokuma, *J. Am. Chem. Soc.*, 2015, **137**, 3433–3445.
- S. Maeda, S. Komagawa, M. Uchiyama and K. Morokuma, *Angew. Chem., Int. Ed.*, 2011, **50**, 644–649.
- S. Maeda, Y. Harabuchi, Y. Ono, T. Taketsugu and K. Morokuma, *Int. J. Quantum. Chem.*, 2015, **115**, 258–269.
- S. Maeda, Y. Harabuchi, M. Takagi, K. Saita, K. Suzuki, T. Ichino, Y. Sumiya, K. Sugiyama and Y. Ono, *J. Comput. Chem.*, 2018, **39**, 233–250.
- K. Sugiyama, Y. Sumiya, M. Takagi, K. Saita and S. Maeda, *Phys. Chem. Chem. Phys.*, 2019, **21**, 14366–14375.
- S. Maeda, K. Sugiyama, Y. Sumiya, M. Takagi and K. Saita, *Chem. Lett.*, 2018, **47**, 396–399.
- K. Sugiyama, K. Saita and S. Maeda, *J. Comput. Chem.*, 2021, **42**, 2163–2169.
- M. Gao, A. Lyalin, M. Takagi, S. Maeda and T. Taketsugu, *J. Phys. Chem. C*, 2015, **119**, 11120–11130.
- M. Gao, A. Lyalin, S. Maeda and T. Taketsugu, *J. Chem. Theory Comput.*, 2014, **10**, 1623–1630.
- L. Liu, M. Lopez-Haro, J. A. Perez-Omil, M. Boronat, J. J. Calvino and A. Corma, *Nat. Commun.*, 2022, **13**, 821.
- T. Yumura, A. Oda, H. Torigoe, A. Itadani, Y. Kuroda, T. Wakasugi and H. Kobayashi, *J. Phys. Chem. C*, 2014, **118**, 23874–23887.
- Y. Chai, W. Shang, W. Li, G. Wu, W. Dai, N. Guan and L. Li, *Adv. Sci.*, 2019, **6**, 1900299.
- S. Wu, X. Yang and C. Janiak, *Angew. Chem.*, 2019, **131**, 12468–12482.
- S. Yasumura, M. Huang, X. Wu, C. Liu, T. Toyao, Z. Maeno and K. Shimizu, *Catal. Today*, 2020, **352**, 118–126.
- Z. Maeno, S. Yasumura, C. Liu, T. Toyao, K. Kon, A. Nakayama, J. Hasegawa and K. Shimizu, *Phys. Chem. Chem. Phys.*, 2019, **21**, 13415–13427.



- 28 G. Li and E. A. Pidko, *ChemCatChem*, 2019, **11**, 134–156.
- 29 S. Grundner, M. A. C. Markovits, G. Li, M. Tromp, E. A. Pidko, E. J. M. Hensen, A. Jentys, M. Sanchez-Sanchez and J. A. Lercher, *Nat. Commun.*, 2015, **6**, 7546.
- 30 G. Li, P. Vassilev, M. Sanchez-Sanchez, J. A. Lercher, E. J. M. Hensen and E. A. Pidko, *J. Catal.*, 2016, **338**, 305–312.
- 31 M. H. Mahyuddin, A. Staykov, A. G. Saputro, M. K. Agusta, H. K. Dipojono and K. Yoshizawa, *J. Phys. Chem. C*, 2020, **124**, 18112–18125.
- 32 M. H. Mahyuddin, Y. Shiota, A. Staykov and K. Yoshizawa, *Acc. Chem. Res.*, 2018, **51**, 2382–2390.
- 33 M. H. Mahyuddin and K. Yoshizawa, *Catal. Sci. Technol.*, 2018, **8**, 5875–5885.
- 34 M. Gao, D. Horita, Y. Ono, A. Lyalin, S. Maeda and T. Taketsugu, *J. Phys. Chem. C*, 2017, **121**, 2661–2668.
- 35 T. Iwasa, T. Sato, M. Takagi, M. Gao, A. Lyalin, M. Kobayashi, K. Shimizu, S. Maeda and T. Taketsugu, *J. Phys. Chem. A*, 2019, **123**, 210–217.
- 36 J. P. Breen and R. Burch, *Top. Catal.*, 2006, **39**, 53–58.
- 37 K. Theinnoi, S. Sitshebo, V. Houel, R. R. Rajaram and A. Tsolakis, *Energy Fuels*, 2008, **22**, 4109–4114.
- 38 R. Bartolomeu, A. N. Mendes, A. Fernandes, C. Henriques, P. da Costa and M. F. Ribeiro, *Catal. Sci. Technol.*, 2016, **6**, 3038–3048.
- 39 F. Schuricht and W. Reschetilowski, *Microporous Mesoporous Mater.*, 2012, **164**, 135–144.
- 40 Y. Yu, H. He, X. Zhang and H. Deng, *Catal. Sci. Technol.*, 2014, **4**, 1239–1245.
- 41 F. Wang, G. He, B. Zhang, M. Chen, X. Chen, C. Zhang and H. He, *ACS Catal.*, 2019, **9**, 1437–1445.
- 42 G. Xu, H. Wang, Y. Yu and H. He, *J. Catal.*, 2021, **395**, 1–9.
- 43 P. S. Kim, M. K. Kim, B. K. Cho, I. S. Nam and S. H. Oh, *J. Catal.*, 2013, **301**, 65–76.
- 44 J. P. Breen, R. Burch, C. Hardacre, C. J. Hill, B. Krutzsch, B. Bandl-Konrad, E. Jobson, L. Cider, P. G. Blakeman, L. J. Peace, M. V. Twigg, M. Preis and M. Gottschling, *Appl. Catal. B*, 2007, **70**, 36–44.
- 45 S. Tamm, N. Vallim, M. Skoglundh and L. Olsson, *J. Catal.*, 2013, **307**, 153–161.
- 46 S. T. Korhonen, A. M. Beale, M. A. Newton and B. M. Weckhuysen, *J. Phys. Chem. C*, 2011, **115**, 885–896.
- 47 H. Kubota, S. Mine, T. Toyao, Z. Maeno and K. Shimizu, *ACS Catal.*, 2021, **3**, 544–559.
- 48 J. Shibata, K. Shimizu, S. Satokawa, A. Satsuma and T. Hattori, *Phys. Chem. Chem. Phys.*, 2003, **5**, 2154–2160.
- 49 J. Shibata, Y. Takada, A. Shichi, S. Satokawa, A. Satsuma and T. Hattori, *J. Catal.*, 2004, **222**, 368–376.
- 50 A. Satsuma, J. Shibata, K. Shimizu and T. Hattori, *Catal. Surv. Asia*, 2005, **9**, 75–85.
- 51 K. Shimizu, K. Sugino, K. Kato, S. Yokota, K. Okumura and A. Satsuma, *J. Phys. Chem. C*, 2007, **111**, 1683–1688.
- 52 K. Shimizu, K. Sawabe and A. Satsuma, *Catal. Sci. Technol.*, 2011, **1**, 331–341.
- 53 K. Sawabe, T. Hiro, K. Shimizu and A. Satsuma, *Catal. Today*, 2010, **153**, 90–94.
- 54 J. Shibata, K. Shimizu, Y. Takada, A. Shichi, H. Yoshida, S. Satokawa, A. Satsuma and T. Hattori, *J. Catal.*, 2004, **227**, 367–374.
- 55 K. Shimizu, K. Sugino, K. Kato, S. Yokota, K. Okumura and A. Satsuma, *J. Phys. Chem. C*, 2007, **111**, 6481–6487.
- 56 K. Shimizu and A. Satsuma, *Appl. Catal., B*, 2007, **77**, 202–205.
- 57 S. Yasumura, C. Liu, T. Toyao, Z. Maeno and K. Shimizu, *J. Phys. Chem. C*, 2021, **125**, 1913–1922.
- 58 G. Kresse and J. Furthmüller, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1996, **54**, 11169–11186.
- 59 G. Kresse and J. Furthmüller, *Comput. Mater. Sci.*, 1996, **6**, 15–50.
- 60 P. E. Blöchl, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1994, **50**, 17953–17979.
- 61 D. Kresse, G. Joubert, G. Kresse and D. Joubert, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1999, **59**, 1758–1775.
- 62 P. Honnenberg and W. Kohn, *Phys. Rev. [Sect.] B*, 1964, **136**, B864–B871.
- 63 W. Kohn and L. J. Sham, *Phys Rev A*, 1965, **140**, A1133–A1138.
- 64 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865–3868.
- 65 H. J. Monkhorst and J. D. Pack, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1976, **13**, 5188–5192.
- 66 S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.*, 2011, **32**, 1456–1465.
- 67 S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.
- 68 C. Baerlocher; L. B. McCusker; and H. van Koningsveld Database of Zeolite Structures; <http://www.iza-structure.org/databases/> (accessed Jun. 2021).
- 69 Z. Zhao, Y. Xing, S. Li, X. Meng, F. S. Xiao, R. McGuire, A. N. Parvulescu, U. Müller and W. Zhang, *J. Phys. Chem. C*, 2018, **122**, 9973–9979.
- 70 S. Yasumura, T. Ueda, H. Ide, K. Otsubo, C. Liu, N. Tsunoji, T. Toyao, Z. Maeno and K. Shimizu, *Phys. Chem. Chem. Phys.*, 2021, **23**, 22273–22282.
- 71 C. Paolucci, A. A. Parekh, I. Khurana, J. R. di Iorio, H. Li, J. D. Albarracin Caballero, A. J. Shih, T. Anggara, W. N. Delgass, J. T. Miller, F. H. Ribeiro, R. Gounder and W. F. Schneider, *J. Am. Chem. Soc.*, 2016, **138**, 6028–6048.
- 72 K. Fukui, *Acc. Chem. Res.*, 1981, **14**, 363.
- 73 S. Yasumura, K. Saita, T. Miyakage, T. Toyao, Z. Maeno, T. Taketsugu and K. Shimizu, *ChemRxiv*, 2022, preprint, DOI: [10.26434/chemrxiv-2022-w9fjz](https://doi.org/10.26434/chemrxiv-2022-w9fjz).
- 74 S. Yasumura, Y. Qian, T. Toyao, Z. Maeno and K. Shimizu, *J. Phys. Chem. C*, 2022, **126**, 11082–11090.
- 75 S. Yasumura, Y. Qian, T. Kato, S. Mine, T. Toyao, Z. Maeno and K. Shimizu, *ACS Catal.*, 2022, **12**, 9983–9993.
- 76 H. Kubota, T. Toyao, Z. Maeno, Y. Inomata, T. Murayama, N. Nakazawa, S. Inagaki, Y. Kubota and K. Shimizu, *ACS Catal.*, 2021, **11**, 11180–11192.
- 77 C. Liu, S. Yasumura, T. Toyao, Z. Maeno and K. Shimizu, *J. Phys. Chem. C*, 2022, **126**, 11594–11601.
- 78 W. Tang, E. Sanville and G. Henkelman, *J. Phys.: Condens. Matter*, 2009, **21**, 084204.
- 79 G. Xu, J. Ma, L. Wang, Z. Lv, S. Wang, Y. Yu and H. He, *ACS Catal.*, 2019, **9**, 10489–10498.

