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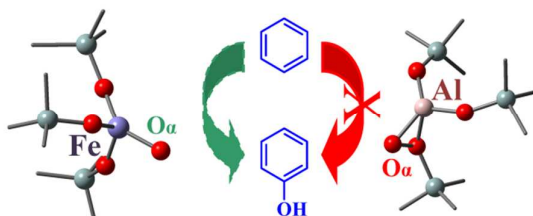
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Framework Fe rather than Al Lewis acidic sites in zeolites are demonstrated to show superior catalysis for benzene hydroxylation.

## COMMUNICATION

## A DFT study on the direct benzene hydroxylation catalyzed by framework Fe and Al sites in zeolites

Cite this: DOI: 10.1039/x0xx00000x

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Received 00th March 2014,

Accepted 00th March 2014

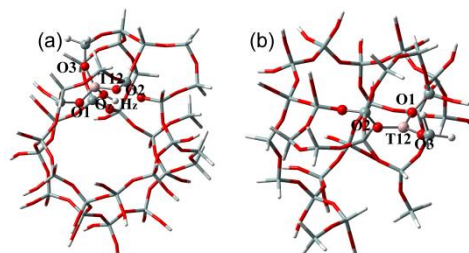
DOI: 10.1039/x0xx00000x

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Three-coordinated framework Fe sites in zeolites were theoretically demonstrated to show Lewis acidity and superior catalysis for titled reaction compared with extra-framework Fe sites that were generally considered as active species, while corresponding Al sites are not reactive. Such catalytic distinctness is ascribed to their divergent  $\alpha$ -oxygen structures.

Owing to peculiar adsorption and catalytic effects, the isomorphous incorporation and cation exchange in zeolites have recently been given enough attention.<sup>1</sup> Zeolites modified with iron show pronounced activity for the selective oxidation of benzene to phenol.<sup>2-4</sup> It is generally believed that the catalytic performance of such materials stems from the high reactivity of extra-framework iron sites stabilized in zeolite micropores.<sup>2,3,5-9</sup> The exact structure of such species is still under debate.<sup>7,10</sup>

Notwithstanding, zeolites with framework Fe sites were also detected to show catalysis for this reaction.<sup>11-15</sup> At a given Fe content, zeolites synthesized with framework Fe sites are significantly more catalytically active than those only with cation exchange (extra-framework Fe),<sup>11,14</sup> an indication that the framework Fe sites are also involved in the catalysis. The tetrahedral framework Fe sites with Brønsted acidity (Fig. 1a) are known not catalytically active for the selective benzene oxidation reaction,<sup>14,16</sup> and it thus drives us to speculate that the superior catalysis is caused by three-coordinated framework Fe sites (Fig. 1b) resulting from the pretreatment by steaming or at high temperatures in He.



**Fig. 1.** The Brønsted (a) and Lewis (b) acidic sites in [M]-ZSM-5 zeolites (M = Al, Fe), where the metal centers are tetrahedrally ( $M_B$ ) and three-coordinated ( $M_L$ ), respectively.

Actually, the three-coordinated Al sites in zeolites that are kept in the framework have been observed experimentally when pretreated similarly,<sup>17,18</sup> and the amount increases with elevation of pretreatment temperatures. Such Al species show Lewis acidity and catalytic performance for a variety of chemical reactions,<sup>18-20</sup> and the Fe analogue is assumed to have resembling Lewis acidity and catalytic effects. Here, density functional calculations were employed with aim to demonstrate the Lewis acidity of [Fe]-ZSM-5 zeolite and catalytic effects for the selective oxidation of benzene. The Lewis acidity and catalysis of [Al]-ZSM-5 zeolite were also explored, and no similar catalytic effects have been detected. The catalytic distinctness of the three-coordinated framework Al and Fe sites was then clarified.

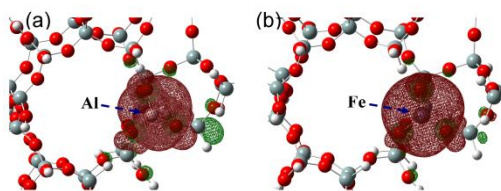
The tetrahedral framework Al and Fe sites in zeolites ( $M_B$ , Fig. 1a) are found to have consistent structures with the previously calculated and experimental results. For the three-coordinated framework Al and Fe sites ( $M_L$ , Fig. 1b), M atoms and three O neighbours interact more strongly than in the case of tetrahedral sites resulting in shorter M-O distances (Table S1). The Al configuration in  $Al_L$  deviates from planar triangle by  $11.71^\circ$ , probably due to the strain force exhibited by associated zeolite frameworks. As a result of larger M-O bond distances, a more configurational distortion from planar triangle is evidenced for the Fe center in  $Fe_L$ , see the supporting information (S2). The three-coordinated Al sites, whether at the framework or extra-framework, are known to show Lewis acidity resulting mainly from the non-bonding  $3p_z$  orbital.<sup>17</sup> The lowest-unoccupied molecular orbital (LUMO) that is often used to

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† Electronic Supplementary Information (ESI) available: Computational methods (S1), Configurational distortions (S2),  $O_3$  decomposition (S3), stability of the  $\alpha$ -oxygen species (S4), Figures of  $N_2O$  adsorption on the Lewis Brønsted and acidic sites as well as benzene adsorption on the  $\alpha$ -oxygen site of framework Al Lewis acidic site. See DOI: 10.1039/c000000x/

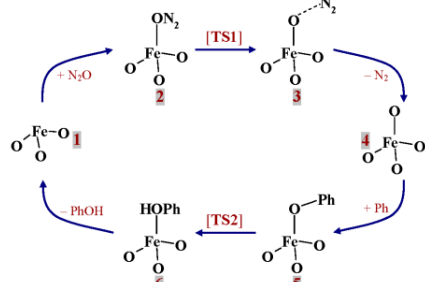
characterize Lewis acidity predominates at the Al center, see Fig. 2a.



**Fig. 2.** The lowest-unoccupied molecular orbitals (LUMO) of Lewis acidic sites in [Al]- (a) and [Fe]- (b) ZSM-5 zeolites.

For the three-coordinated framework Fe sites ( $\text{Fe}_L$ ), the LUMO is principally localized at the Fe center (Fig. 2b) and resembles the scenario of  $\text{Al}_L$ . The presence of Lewis acidity in  $\text{Fe}_L$  is in that the non-bonding  $3d$  orbitals of Fe center are good electron acceptors as the Ti centers in zeolites.<sup>21,22</sup> As a matter of fact,  $\text{FeCl}_3$  has been widely used as a Lewis acidic catalyst.<sup>23</sup> The LUMO energies that should be used cautiously for different metal centers<sup>24,25</sup> are respectively calculated at  $-0.035$  and  $-0.026$  eV for  $\text{Fe}_L$  and  $\text{Al}_L$ , implying the comparable Lewis acid strengths. This is supported by close  $\text{N}_2\text{O}$  adsorption energies ( $-13.8$  and  $-16.9$  kcal mol<sup>-1</sup> on  $\text{Fe}_L$  and  $\text{Al}_L$ , respectively). In both adsorption cases, direct bonds form between metal centers and  $\text{N}_2\text{O}$ , see Fig. S3. The O4-N1 bonds (bond orders) in  $\text{Al}_L$  and  $\text{Fe}_L$  are respectively equal to 1.226 (1.362) and 1.218 (1.412) Å and show slight elongations than gas-phase at 1.195 Å (1.543), which resemble the scenarios of  $\text{N}_2\text{O}$  adsorption on extra-framework Fe sites<sup>5,8,9,10,26</sup> and  $\text{N}_2$  adsorption on framework Al Lewis acidic sites<sup>19</sup>. In contrast,  $\text{N}_2\text{O}$  shows very weak H-bonding interaction with tetrahedral framework Al and Fe sites and the O4-N1 and N1-N2 bonds remain almost intact (Fig. S4).

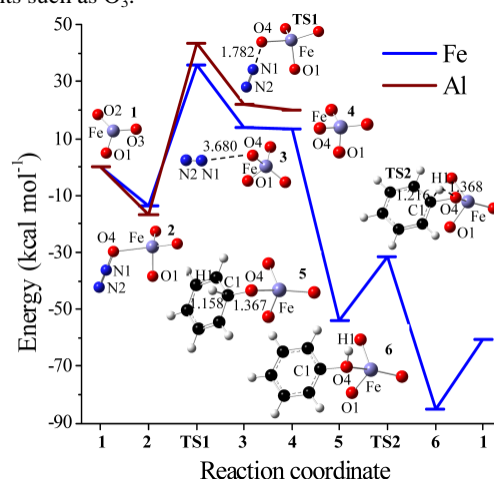
The reaction mechanisms for  $\text{N}_2\text{O}$  decomposition and benzene hydroxylation on the Fe Lewis acidic site are proposed on basis of DFT-calculated results, see Scheme 1. The reaction is initiated by  $\text{N}_2\text{O}$  adsorption (Step 1, **1**  $\rightarrow$  **2**), followed by decomposition (Step 2, **2**  $\rightarrow$  **3**) via the first transition state (**TS1**). Then the weakly interacted  $\text{N}_2$  detaches and the  $\alpha$ -oxygen site (**4**) is released that gets ready for subsequent catalysis. To our surprise, the approach of benzene to the  $\alpha$ -oxygen site (Step 4, **4**  $\rightarrow$  **5**) results in the direct O4-C1 bond formation without any energy barrier. This is distinct from the extra-framework Fe sites where this step has to experience a high-energy transition state.<sup>5,8,9,10,26</sup> Then phenol is produced as a result of an intra-molecular proton transfer from C1 to O1 (Step 5, **5**  $\rightarrow$  **6**), and the reaction is closed by desorption of phenol.



**Scheme 1.** The catalytic cycle of  $\text{N}_2\text{O}$  decomposition and benzene hydroxylation over the Lewis acidic site of [Fe]-ZSM-5 zeolite.

As Fig. 3 indicates, the energy barrier for  $\text{N}_2\text{O}$  decomposition (Step 2) equals 49.9 kcal mol<sup>-1</sup> and exceeds those of extra-framework Fe sites.<sup>5,8,9,10,26</sup> With use of 5-T cluster models, an energy barrier of 44.6 kcal mol<sup>-1</sup> has been predicted for the extra-framework mononuclear-Fe site,<sup>5</sup> and similar computational methodologies as in this work obtain a barrier of 33.7 kcal mol<sup>-1</sup>.<sup>26</sup> This suggests that the  $\alpha$ -oxygen site is more likely to produce at extra-framework Fe sites, and then migrates to framework Fe Lewis

acidic site and catalyzes the benzene hydroxylation reaction. As shown in the supporting information (S3), the  $\alpha$ -oxygen species of the Fe Lewis acidity can also be readily obtained by alternative oxidants such as  $\text{O}_3$ .



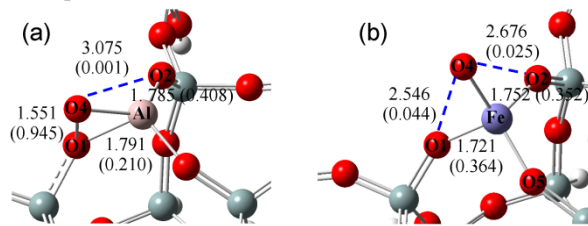
**Fig. 3.** The ONIOM(M06L:B3LYP) energy diagrams of  $\text{N}_2\text{O}$  decomposition and benzene hydroxylation reactions over the framework Lewis acidic sites of [M]-ZSM-5 zeolites ( $M = \text{Fe}, \text{Al}$ ) as well as the local structures of energy minima and transition states for the Fe Lewis acidic site. Selected distances are given in Å.

It has been indicated above that the adsorption of benzene on the  $\alpha$ -oxygen results in the O4-C1 bond formation in a barrierless manner (Step 4), and this greatly facilitates the benzene hydroxylation process in contrast to an appreciable activation energy barrier for extra-framework Fe sites.<sup>8,9,26,27</sup> The superior catalytic effects of framework Fe site are probably due to the less stability of its  $\alpha$ -oxygen species, see more details in the supporting information (S4). The following step (**5**  $\rightarrow$  **6**) is an intra-molecular proton transfer that requires an energy barrier of 21.7 kcal mol<sup>-1</sup> close to that of extra-framework Fe sites.<sup>20</sup> The benzene hydroxylation reaction over the framework Fe Lewis acidic site prefers to that of extra-framework Fe sites, both thermodynamically and kinetically (Fig. 3). Thus, it has been demonstrated that after steaming or high-temperature pretreatment in He, zeolites synthesized with framework Fe sites are more catalytically active than those only with ion exchange.<sup>11,14</sup>

Now we come to discuss the catalytic effects of the framework Al Lewis acidic site ( $\text{Al}_L$ ). It is assumed that  $\text{N}_2\text{O}$  on  $\text{Al}_L$  decomposes in a mechanism resembling that on  $\text{Fe}_L$  shown in Fig. 3. The energy barrier on  $\text{Al}_L$  equals 60.5 kcal mol<sup>-1</sup> and hence  $\text{N}_2\text{O}$  decomposition becomes implausible to occur under normal conditions; furthermore, there are no extra-framework Fe sites in Al-substituted zeolites for assistance. Notwithstanding, the benzene hydroxylation has been considered for  $\text{Al}_L$ , and the adsorption of benzene on the  $\alpha$ -oxygen site does not result in the C1-O4 bond formation, see Fig. S5. Instead, all the C atoms of benzene have long distances from the  $\alpha$ -oxygen site; e.g., C1-O4: 4.543 Å. This differs significantly from the scenario of framework Fe Lewis acidic site. As a result of weak interactions, the adsorbed benzene remains almost intact as in gas phase, and the C-C and C-H bond distances are altered by not more than 0.003 Å. It thus evidences that the presence of Fe sites is indispensable for catalysis of the benzene hydroxylation reaction, consistent with the experimental observations.<sup>28,29</sup>

The distinct catalytic effects of framework Al and Fe Lewis acidic sites may be caused by the structural discrepancy of their  $\alpha$ -oxygen sites, see Fig. 4. The  $\alpha$ -oxygen species (O4) of  $\text{Al}_L$  (**4-Al<sub>L</sub>**) forms direct bond with framework-O1 atom with distance (bond order) of 1.551 Å (0.945) and as indicated in Table 1, O4 and O1 atoms

constitute the peroxide ( $O_2^{2-}$ ) species, which with absence of metal ions seems unable to activate the C-H bonds of hydrocarbons.<sup>30</sup> On the contrary, the  $\alpha$ -oxygen species (O4) in [Fe]-ZSM-5 zeolite (**4-Fe<sub>L</sub>**) does not form chemical bonding with framework-O atoms and features the anion radical ( $O^{\cdot-}$ , Table 1 and Fig. 4).<sup>31</sup> That is, the Fe-O $^{\cdot-}$  species has been created over the framework Fe Lewis acidic site, which has been postulated for extra-framework Fe sites and shows good catalytic performances for benzene hydroxylation<sup>31</sup> and ethylene epoxidation<sup>32</sup> reactions.



**Fig. 4.** The  $\alpha$ -oxygen structures generated by  $N_2O$  decomposition on the framework Al (a) and Fe (b) Lewis acidic sites. Selected distances are given in Å (Bond orders in parentheses).

**Table 1.** Selected distances (r), Mulliken charges (q) and spin densities (s) for the Lewis acidic ( $M_L$ ) and  $\alpha$ -oxygen ( $4-M_L$ ) sites in [M]-ZSM-5 zeolites (M = Al, Fe) as well as  $H_2O_2$ <sup>a</sup>

	4-Al <sub>L</sub>	4-Fe <sub>L</sub>	Al <sub>L</sub>	Fe <sub>L</sub>	H <sub>2</sub> O <sub>2</sub>
r(O1-O4) /Å	1.551	2.546			1.467
q(O1)	-0.387	-0.635	-0.611	-0.720	-0.274
q(O4)	-0.309	-0.303			-0.274
q(M)	1.057	1.230	1.029	1.235	
s(O1)		0.321		0.260	
s(O4)		1.036			
s(M)		3.224		4.182	

<sup>a</sup> Calculated at the ONIOM(M06L:B3LYP)//B3LYP level.

In summary, we have theoretically explored the Lewis acidity of three-coordinated framework Al and Fe sites in zeolites and, for the first time, their catalytic effects for the benzene hydroxylation reaction. The  $\alpha$ -oxygen species is assumed to produce at extra-framework Fe sites and then migrate to framework Fe Lewis acidic sites or by alternative oxidants. The  $\alpha$ -oxygen species corresponding to framework Fe Lewis acidity shows unique catalytic performances for the benzene hydroxylation reaction, thus explaining satisfactorily the experimental results that zeolites synthesized with framework Fe sites have superior catalytic effects to those with only ion exchange. On the contrary, framework Al Lewis sites are not catalytic active for this reaction and the catalytic distinctness with Fe is ascribed to structural divergence of their  $\alpha$ -oxygen sites. The  $\alpha$ -oxygen species of the framework Fe Lewis acidity features the Fe-O $^{\cdot-}$  species that has been proposed to form over extra-framework Fe sites.

The National Natural Science Foundation (No. 20903019) and Fundamental Research Funds for the Central Colleges (SWU113049 and XDJK2014C106) are acknowledged for financial support. E. A. Pidko (Eindhoven University of Technology) is greatly thanked for helpful discussions. Shanghai Supercomputing Center is acknowledged for computing time.

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