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Hybrid density functional/molecular mechanics studies on activated adsorption of oxygen on zeolite supported gold monomer

Subhi Baishya and Ramesh C. Deka[a)]
Department of Chemical Sciences, Tezpur University, Napaam 784028, India

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Density functional theory calculations on oxygen adsorption over gas phase and faujasite supported Au monomer has been studied using hybrid quantum mechanics/molecular mechanics method, surface integrated molecular orbital molecular mechanics implemented in GAMESS package. Three different oxidation states of Au (0, +1, +3) and three different adsorption modes viz., top, bridge, and dissociative adsorption of oxygen have been considered in our calculations. Redshift in the ν_{O-O} value from that in gas phase O_2 indicates activation of O_2 upon adsorption over faujasite supported gold monomer. The activation of O_2 is an important step in the catalytic oxidation of CO. The presence of adsorbed O_2 increases the interaction of the Au monomer with the faujasite support. In faujasite supported cationic Au monomer, O_2 preferably remains bridge bonded to Au rather than being dissociated. © *2011 American Institute of Physics*. [doi:10.1063/1.3667206]

I. INTRODUCTION

Nanosized materials differ considerably from the bulk material and have drawn much attention from the past decade owing to the unique reactive behavior. Studies have been devoted to both supported and unsupported nanosized metal clusters and their catalytic applications. Bulk gold is inert, but effectively catalyzes the low temperature CO oxidation on reducing the dimensions.[1–3] Apart from the CO oxidation reaction, other reactions being catalyzed include water-gas shift (WGS) reaction,[4] chemoselective hydrogenation,[5] and selective oxidation of olefins,[6,7] etc. However, to gain insight into the catalytic mechanism of the CO oxidation reaction, oxygen adsorption behavior on gold clusters is necessary. The reaction of O_2 molecule with metal clusters of various sizes is specifically important as it can help to identify a potential catalyst for oxidation reactions. Pioneering experimental works on the adsorption of oxygen molecule on Au cluster anions by Cox *et al.*[8,9] showed a dramatic even-odd oscillation in the reactivity with only even atom cluster anions (i.e., those with odd number of electrons) exhibiting the adsorption of one O_2 molecule. It has also been found that odd cluster anions exhibit negligible or very little adsorption and that anionic gold clusters cannot bind two O_2 molecules. However, their work indicated no activity of neutral and cationic Au clusters toward O_2 molecule except Au_{10}^+ cluster. Low temperature activity studies of molecular oxygen on gold cluster anions by Salisbury *et al.*[10] showed the adsorbed oxygen to be oxygen molecule instead of O, O_3 adsorption or co-adsorption of two O_2 molecules. Studies by different groups[8–14] generalized that the adsorption strength of O_2 is greatest in anionic gold clusters although adsorption has been observed on neutral and rarely on cationic clusters. An important experimental outcome is that O_2 can interact better with Au clusters having odd number of electrons and that anionic Au clusters with even number of Au atoms adsorb one O_2 easily while those with odd Au atoms showed no or very little adsorption. Density functional theory (DFT) study by Mills *et al.*[15] on O_2 binding to Au clusters and Au(111) surface modified by adsorption of Au clusters on it predicted that binding of O_2 is strong when the number of electrons is odd and hence all anionic gold clusters adsorb O_2 molecule. Ding *et al.*[16] studied the adsorption properties of O_2 molecule on anionic, cationic, and neutral Au_n clusters ($n = 1$–6) using B3LYP functional. Their work predicted the binding energy of O_2 to cationic gold clusters to be very small (<0.5 eV) and in the case of neutral clusters, Au_5 can adsorb one O_2 molecule while Au_3 can weakly adsorb up to two O_2 molecules. In addition to these, a number of theoretical studies[17–24] have been made mostly on the adsorption of O_2 on anionic clusters, but studies on neutral and cationic clusters are really scarce.

Gold dispersed on solid support forms an important class of catalyst due to their unique catalytic property. Zeolites, owing to their ability to disperse gold, because of the internal distribution of the pores and the ability to control particle size, form a very promising type of support for gold nanoparticles. Zeolites also possess adjustable acidic properties and have pores and cavities of molecular dimensions. Au^+ species dispersed inside NaY and ZSM-5 zeolites has been shown to exhibit high activity for CO and NO chemisorption as well as direct NO decomposition reactions.[25–27] The Au^0 and Au^+ sites in Au supported on ZSM-5 and mordenite have been considered responsible for low temperature CO oxidation and the water-gas shift reaction.[28,29] Different experimental works[30–34] have been reported for determining the active sites in gold/zeolite support system for the CO oxidation reaction and Au^+, Au^{3+}, or $Au_n^{\delta+}$ or neutral Au_n have been proposed to be the reactive sites for the reaction depending on reaction condition. Despite many experimental findings, studies related to the mechanistic determination of the CO oxidation reaction remain unattempted. The dissociative mode of O_2 adsorption on single gold crystals has been

a)Author to whom correspondence should be addressed. Electronic mail: ramesh@tezu.ernet.in.

considered energetically unfavorable but various theoretical calculations have proposed the ability of low coordinated gold atoms to adsorb and dissociate O_2.[15,35–37] A recent study has been made by Boronat and Corma[38] on O_2 activation on different gold surfaces and nanoparticles to separate the effect of particle size, morphology, and support and found that O_2 is most activated in the bridge–bridge conformation with lowest barrier for O_2 activation. In the case of gold particles supported on TiO_2, the metal-support interface has been found to be the most stable sites for O_2 adsorption and the most active sites for O_2 dissociation. Their work demonstrated that O_2 dissociation is sensitive to the structure of gold surface. While theoretical studies about gold supported on oxides such as MgO, TiO_2, and Al_2O_3 are found, but studies on gold/zeolite supported system is very limited. One of the key factors to understand the details of CO oxidation reaction on gold/zeolite support system is the adsorption of O_2. Also it is necessary to understand the change in adsorption behavior with change in the charge state of gold. Gold exhibits varying oxidation states when supported on zeolite depending on the Si/Al ratio. Substitution of a framework Si atom with an Al atom creates an excess negative charge which can be compensated by the inclusion of an extra framework Au atom. To the best of our knowledge, no theoretical studies have been reported on the adsorption of O_2 on faujasite supported Au monomer. It will be quite interesting to study the O_2 adsorption on faujasite supported Au in different charge states, 0, +1, +3 and hence compare the results with the gas phase counterparts. We have considered possible three different modes of O_2 adsorption viz., top mode in which one oxygen atom is directly bonded to Au, bridging mode with O_2 chelating Au, and dissociative mode in which O_2 adsorbs in a dissociative manner.

II. COMPUTATIONAL METHOD

Hybrid quantum mechanics/molecular mechanics method SIMOMM (surface integrated molecular orbital molecular mechanics) (Ref. 39) implemented in GAMESS has been used to carry out the calculations. The zeolite model employed in this work comprises of 642 atoms and an extra framework Au atom (Fig. 1). In the SIMOMM method, the entire system is divided into two regions: the chemically active part which is treated quantum mechanically and the outer inactive part, modeled using molecular mechanics. In our system the quantum mechanical part comprises of a six membered ring of the faujasite zeolite and an Au atom supported on it along with the adsorbed O_2 molecule. This quantum mechanical part is treated with the DFT based B3LYP functional and 6–31 G basis set for Si, Al, O, and H while LANL2DZ basis set incorporating relativistic effective core potential for Au atom. On the other hand, the outer region is modeled using the MM3 parameter. The binding energy for the O_2 molecule is calculated using:

$$\text{B.E.}\,(O_2 \text{ on gas phase Au}) = (E_{Au} + E_{O_2}) - E_{Au-O_2}, \quad (1)$$

$$\text{B.E.}(O_2 \text{ on zeolite supported Au}) = (E_{Au/FAU} + E_{O_2}) - E_{Au-O_2/FAU}. \quad (2)$$

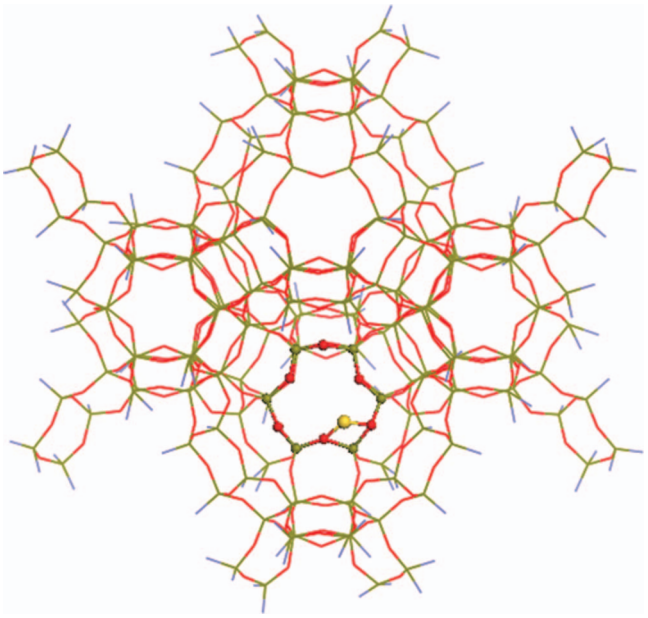

FIG. 1. Faujasite model used in the calculations, the QM part has been shown by ball and stick and the MM part by line. Gray—H, red—O, green—Si, and yellow—Au.

Natural bond orbital (NBO) analysis has been performed using GAUSSIAN09 program package[40] in order to investigate the nature of interaction between the gold atom and oxygen molecule.

III. RESULTS AND DISCUSSION

A. O_2 adsorption over gas phase Au monomer

The triplet oxygen found to be more stable has been considered in our calculations. Considering the top mode of coordination (Fig. 2(a)), when O_2 was adsorbed on gas phase Au atom, the binding energy is found to decrease with increase in oxidation state, i.e., from Au^0 to Au^+. For Au^0, the binding energy is found to be 0.26 eV while for Au^+; the O_2 binding becomes quite unfavorable evident from the negative binding energy value of –0.42eV. However, no adsorption of O_2 on Au^{3+} was found. Electron transfer from Au^0 to O_2 accompanying O_2 adsorption populates the π^* antibonding orbital of O_2, thus decreasing the O–O bond order. O_2 thus reduces to superoxide evident from the elongated O–O bond length of 1.33 Å (1.25 Å in gas phase O_2) indicating O_2 activation upon adsorption on neutral gold atom. However, in the case of O_2 adsorption on cationic gold, i.e., on Au^+, the O–O bond length remains the same as that in O_2 molecule (1.25 Å in Au^+–O_2 as against 1.25 Å in O_2). In other words, the O–O bond is not activated when adsorbed on Au^+ indicating that the interaction here is mostly electrostatic. The variation in O–O bond length is also accompanied by the corresponding change in O–O vibrational frequency with the smallest value for the longest O–O bond length. The ν_{O-O} value is found to be 1067.1 cm^{-1} for the neutral Au which increases to 1441.6 cm^{-1} for Au^+. Referring to Au–O bond, the bond length is 2.21 Å in

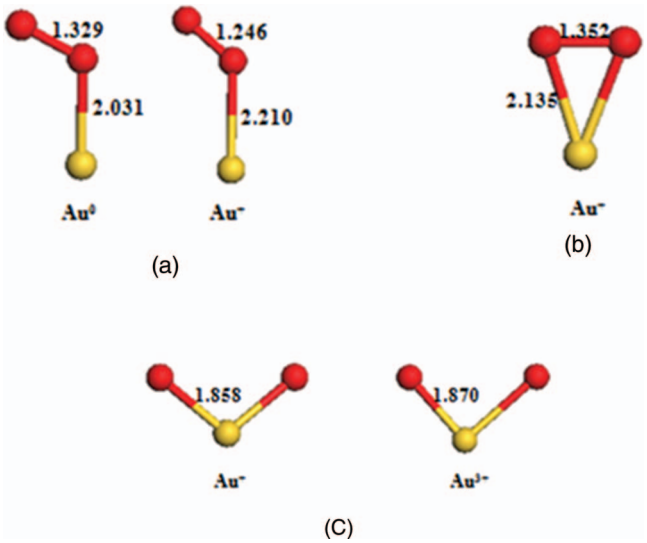

FIG. 2. Optimized structures of O_2 adsorbed on gas phase neutral and charged Au atom. (a) Top coordination, (b) bridged coordination, and (c) dissociative coordination.

Au^+-O_2 as against 2.03 Å in Au^0–O_2 (Table I). This can be inferred based on the fact that the Au–O bond is mostly electrostatic in nature in the former while being covalent (involving electron transfer) in the latter. The adsorbed O_2 molecule is bent in both the cases with the Au–O–O bond angle increasing with increase in oxidation state (119.21° in Au^0 and 130.98° in Au^+) (Table I).

In gas phase Au monomer, O_2 adsorption in the bridge mode has been observed only on Au^+ (Fig. 2(b)), not on Au^0 and Au^{3+}; while in the dissociative mode, adsorption is possible on both Au^+ and Au^{3+} (Fig. 2(c)) but not on Au^0. However, both the bridge and dissociative modes of O_2 adsorption on Au^+ is unfavorable indicated by the negative binding energy, while in Au^{3+} positive binding energy indicates the dissociative adsorption to be favorable. In the bridge mode, the Au–O distance is found to be 2.14 Å while the O–O distance is 1.35 Å in Au^+ (Table I). The Au–O distance in the dissociative mode is ∼1.86–1.87 Å in both Au^+ and Au^{3+}. It can be said that on gas phase Au^{3+}, of all the modes of O_2 adsorption, only the dissociative adsorption is possible, in fact this occurs with a very high binding energy (4.86 eV). On

TABLE I. Computed selected geometrical parameters, binding energy and vibrational frequency of O_2 adsorbed on gas phase neutral and charged gold monomer.

	Bond length (Å)			
	Au–O	O–O	B.E (eV)	ν_{O-O} (cm^{-1})
		Top coordination		
Au^0-O_2	2.03	1.33	0.26	1067.1
Au^+-O_2	2.21	1.25	− 0.42	1441.7
		Bridged coordination		
Au^+-O_2	2.14	1.35	− 0.89	1048.2
		Dissociative coordination		
Au^+-O_2	1.86	2.89	− 3.84	...
Au^{3+}-O_2	1.87	2.85	4.68	...

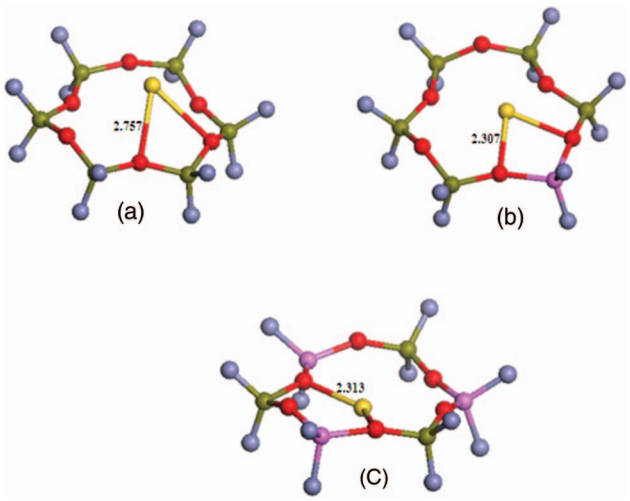

FIG. 3. Optimized structures of faujasite supported Au monomer; (a) Au^0/FAU, (b) Au^+/FAU, and (c) Au^{3+}/FAU, gray—H, red—O, green—Si, magenta—Al, and yellow—Au.

the other hand, bridge and dissociative O_2 adsorption is not possible on Au^0; however, adsorption is favorable in the top coordination. In the case of Au^+, although all the adsorption modes are possible, but these are accompanied by negative binding energy, making it unfavorable.

B. O_2 adsorption over zeolite supported Au monomer

The optimized structures of faujasite supported Au monomer in three different oxidation states 0, +1, +3 are shown in Fig. 3. Selected geometrical parameters are summarized in Table II. The Au–O_z (O_z represents framework zeolite oxygen) distance shows a decreasing trend on going from neutral to cationic clusters having a value of 2.31 Å for Au^{3+}. The Au–Si and Au–Al distances are observed to decrease with an increase in oxidation state. This suggests that the interaction of Au monomer with the faujasite support increases on moving to higher oxidation state. From the NBO charge analysis, it has been observed that anchoring of the Au monomer to the faujasite support causes a withdrawal of charge density from the zeolite to the monomer in both neutral and cationic systems evident from the charge carried by the Au monomer. For instance, the NBO charge for neutral Au has been found to be –0.06 e while for the oxidation state of +1, the NBO charge on Au is 0.64 e.

First, we consider the case of O_2 adsorbed in the top mode of coordination over faujasite supported gold monomer

TABLE II. Computed selected bond lengths (Å) and NBO charge on Au in faujasite supported bare Au monomer in three oxidation states 0, +1, +3.

	Au^0/FAU	Au^+/FAU	Au^{3+}/FAU
		Bond length	
Au–Oz	2.75	2.30	2.31
Au–Si	3.32	2.98	2.97
Au–Al	...	3.08	2.96
		Charge	
Q(Au)	−0.06	0.64	0.59

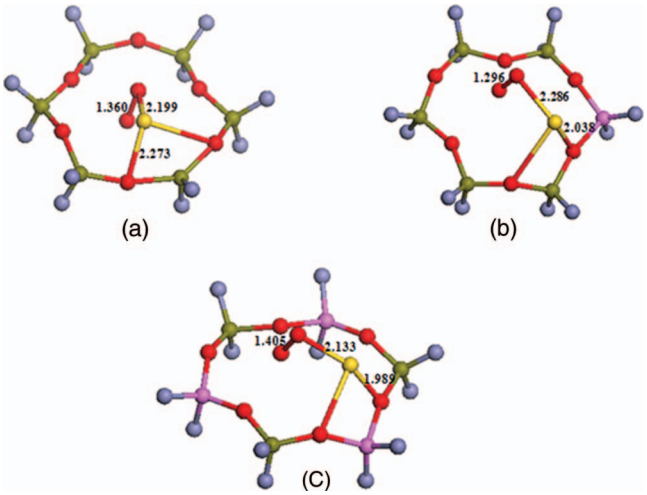

FIG. 4. Optimized structures of O_2 adsorbed (top coordination) on faujasite supported Au monomer; (a) Au^0-O_2/FAU, (b) Au^+-O_2/FAU, and (c) Au^{3+}-O_2/FAU.

(Fig. 4). The Au–O bond distance reveals the interaction of the supported gold monomer with the adsorbed O_2 molecule having the lowest value (2.13 Å) for Au^{3+}-O_2 system indicating stronger interaction between Au monomer and O_2, while the highest bond distance (2.29 Å) has been observed for Au^+-O_2 system that indicates the interaction to be weak. The Au–O distance for the neutral system is found to be intermediate of Au^{3+} and Au^+ (2.19 Å in Au^0-O_2/FAU, Table III). For the O–O bond length the trend is just the opposite of the Au–O bond distance. The O–O bond is longest in faujasite supported Au^{3+}-O_2 being 1.41 Å that approaches the O–O bond length in peroxide ion while in case of faujasite supported Au^0-O_2 it decreases to 1.36 Å similar to the O–O bond distance in superoxide indicating O_2 activation. However, in Au^+-O_2/FAU, the O–O bond length (1.29 Å) is comparable to that in free O_2 (1.25 Å). The NBO charge on O_2 bound to faujasite supported Au monomer is presented in Table IV. The Δq values represent the amount of charge transferred to the O_2 molecule as a result of the interaction with the zeolite supported Au monomer. The highest Δq value of 0.47 e is observed for Au^0-O_2/FAU and the lowest value of 0.13 e for Au^+-O_2/FAU; for Au^{3+}-O_2/FAU Δq has an intermediate value. In Au^+-O_2/FAU the charge transferred is the lowest and consequently the O–O bond length has a value as that in free O_2. The Δq values indicate that charge is transferred to O_2 that goes to the antibonding orbital of O_2 resulting in the lowering of the vibrational frequency of O–O bond. The ν_{O-O} value increases from 916.3 cm^{-1} in Au^{3+}-O_2/FAU to 1237.5 cm^{-1} in Au^+-O_2/FAU; being an intermediate value (1076.3 cm^{-1}) for Au^0-O_2/FAU. (The ν_{O-O} value for free O_2 is found to be 1436.1 cm^{-1}). The NBO charge on Au increases in case of Au^0 and Au^{3+} on adsorption of O_2 compared to that when O_2 is absent also indicating charge transfer while it remains almost same in case of Au^+. The unchanged NBO charge on Au^+ indicates that the interaction of Au^+ and O_2 is merely electrostatic in nature. The Au–O and O–O bond distances are indications of the interaction of faujasite supported Au monomer with the adsorbed O_2 molecule. The shortest Au–O distance and the longest O–O distance in Au^{3+}-O_2/FAU can be attributed to the electron transfer from Au to O_2, when an extra electron goes to the antibonding orbital of O_2 making O–O bond length longer. The interaction in case of Au^+-O_2/FAU is mostly weak electrostatic interaction in contrast to strong electron transfer interaction in Au^{3+}-O_2/FAU. The effect of the support can be evidenced from the fact that the adsorption of O_2 on gas phase Au^{3+} is not possible, however, on zeolite supported Au^{3+}, O_2 gets activated. The shortest Au–O_z (O_z represents the framework zeolite oxygen) has been found to be 2.27 Å in neutral Au monomer which decreases to 1.99 Å in Au^{3+} supported on faujasite zeolite. Decreasing bond length between Au and faujasite oxygen with increasing oxidation state indicates the increased interaction of the Au monomer with the support which favors the activation of O_2 on faujasite supported Au monomer. However, O_2 binding in the top mode to the faujasite supported Au monomer in all the three oxidation states is found to be unfavorable indicated by the negative binding energy value. A change in the zeolite–Au interaction in both the neutral and cationic systems has been observed as a consequence of O_2 adsorption. The Au–O_z distance in Au^0/FAU and Au^{3+}/FAU has a value of 2.75 Å and 2.31 Å, respectively, which decreases to 2.27 Å and 1.99 Å, respectively, when O_2 is adsorbed on the Au monomer.

Unlike in the gas phase, the adsorption of O_2 in the bridge mode is possible in both neutral and charged clusters (Fig. 5). For Au^0 and Au^+, stable aggregates are obtained evident from the positive binding energy values. In fact, O_2 binds to neutral Au in presence of faujasite support with a high binding energy of 1.63 eV while with a much lower value of 0.03 eV in Au^+. The adsorption, however, is accompanied by

TABLE III. Computed selected bond lengths (Å), binding energy (eV), and vibrational frequency of O_2, ν_{O-O} (cm^{-1}) adsorbed on faujasite supported neutral and charged gold monomer. O_2(t)-top coordination, O_2(b)-bridged coordination, O_2(d)-dissociative coordination.

	Au^0-O_2(t)/FAU	Au^0-O_2(b)/FAU	Au^0-O_2(d)/FAU	Au^+-O_2(t)/FAU	Au^+-O_2(b)/FAU	Au^+-O_2(d)/FAU	Au^{3+}-O_2(t)/FAU	Au^{3+}-O_2(b)/FAU	Au^{3+}-O_2(d)/FAU
Au–O	2.19	2.07	1.95	2.29	2.04	2.05	2.13	2.05	2.06
O–O	1.36	1.38	2.09	1.29	1.42	1.42	1.41	1.40	1.41
Au–Si	2.43	3.36	2.85	2.90	3.21	3.26	2.85	2.84	2.88
Au–Al	...	...	...	3.11	2.89	2.96	2.93	3.30	3.42
Au–O_z	2.27	2.71	2.40	2.04	2.14	2.28	1.99	2.26	2.31
ν_{O-O}	1076.3	1062.2	600.3	1237.5	1034.8	1018.7	916.3	1040.5	1029.5
B.E	−1.56	1.63	−0.77	−0.85	0.03	0.34	−0.61	−0.13	0.04

TABLE IV. Computed NBO charges (Q) and charge transferred (Δq) in the different adsorption modes of O_2 on faujasite supported Au monomer.

	Au^0-O_2/FAU			Au^+-O_2/FAU			Au^{3+}-O_2/FAU		
	Top	Bridged	Dissociative	Top	Bridged	Dissociative	Top	Bridged	Dissociative
Q(Au)	0.49	0.42	0.77	0.63	0.98	0.98	0.85	0.95	0.97
Q(O)	−0.24	−0.35	−0.52	−0.17	−0.26	−0.25	−0.27	−0.23	−0.23
Q(O)	−0.23	−0.18	−0.41	0.04	−0.25	−0.23	0.05	−0.21	−0.22
Δq	−0.47	−0.53	−0.93	−0.13	−0.51	−0.48	−0.21	−0.44	−0.45

a negative binding energy in case of Au^{3+}. The Au–O distance has a higher value of 2.07 Å in Au^0 while it remains similar in Au^+ and Au^{3+} (∼2.04 Å). The O–O bond distance has a shorter value of 1.38 Å in Au^0 in accordance with higher Au–O distance whereas a longer value of ∼1.41 Å in the cationic systems as a consequence of shorter Au–O distance. This indicates stronger interaction of O_2 with the cationic Au compared to neutral Au (Table III). The corresponding vibrational frequency, ν_{O-O} is lowered from that in free O_2 with the highest value of 1062.2 cm^{-1} for Au^0 and almost similar lower value for Au^+ and Au^{3+} (∼1040.5 cm^{-1}). The NBO charge on O_2 reveals transfer of charge (Δq value, Table IV) to O_2 in all the three oxidation states. For Au^0 and Au^+, about 0.5 e charge is transferred to O_2 while a slightly lower amount in Au^{3+}. The O–O bond elongation might result from this charge transfer as a consequence of populating the antibonding orbital of O_2. The Au–O_z distance (O_z represents framework zeolite oxygen) is observed to have a higher value for Au^0 (2.71 Å) indicating less interaction with the support while shorter bond lengths in Au^+ (2.14 Å) and Au^{3+} (2.26 Å) indicating increased interaction. However, in all the three oxidation states, the Au–O_z distance in Au^n-O_2(b)/FAU ($n = 0$, $+1$, $+3$) has a slightly lower value compared to that in faujasite supported bare monomer. An increase in the NBO charge on Au from –0.06 e (in faujasite supported bare monomer) to 0.42 e (in O_2 adsorbed faujasite supported monomer) in neutral Au is observed as a result of O_2 coordination in the bridge mode. Likewise, an increase from 0.64 e to 0.98 e and from 0.59 e to 0.95 e is observed in Au^+ and Au^{3+}, respectively.

When the dissociative mode of O_2 adsorption on faujasite supported Au monomer (Fig. 6) is considered the situation is different from the gas phase. Unlike in gas phase Au^0, O_2 adsorption is possible in faujasite supported neutral Au with Au–O bond length of 1.95 Å with the O atoms of O_2 remaining far apart at a distance of 2.09 Å. The adsorption, however, is unfavorable evident from the negative binding energy of –0.77 eV. In faujasite supported Au^+ and Au^{3+}, the adsorption in dissociative mode is favorable, with faujasite supported Au^+ possessing higher binding energy (0.34 eV) compared to Au^{3+}. It has been observed that the O atoms of O_2 are at a distance of ∼1.41 Å in both Au^+ and Au^{3+} approaching that in peroxide ion, or in other words, in faujasite supported cationic monomer, O_2 prefers to remain in the peroxide form rather being dissociated. This can also be evidenced from the corresponding vibrational frequency, ν_{O-O} given in Table III. In Au^0, ν_{O-O} has a much lower value of 600.3 cm^{-1} while the value is almost similar for Au^+ (1018.7 cm^{-1}) and Au^{3+} (1040.5 cm^{-1}). The NBO charge on O_2 correlates with the observed O–O bond length. The amount of charge transferred to O_2 is quite high in Au^0 (0.93 e) compared to Au^+ (0.48 e) and Au^{3+} (0.45 e) resulting in the O atoms of O_2 to remain far apart in the neutral Au.

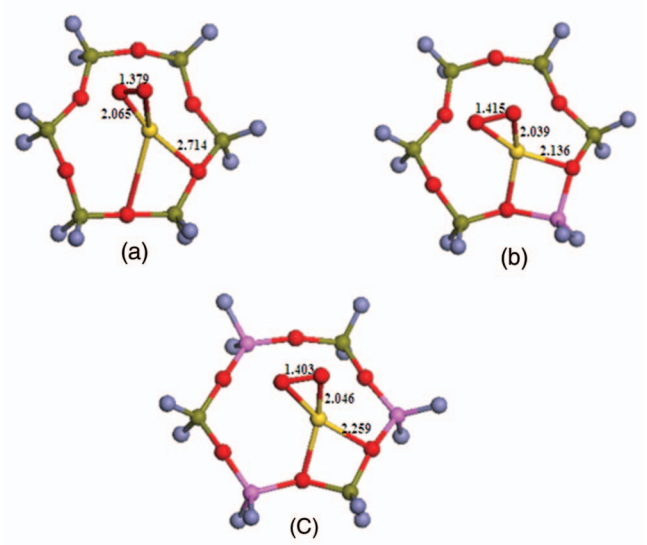

FIG. 5. Optimized structures of O_2 adsorbed (bridge coordination) on faujasite supported Au monomer; (a) Au^0-O_2/FAU, (b) Au^+-O_2/FAU, and (c). Au^{3+}-O_2/FAU.

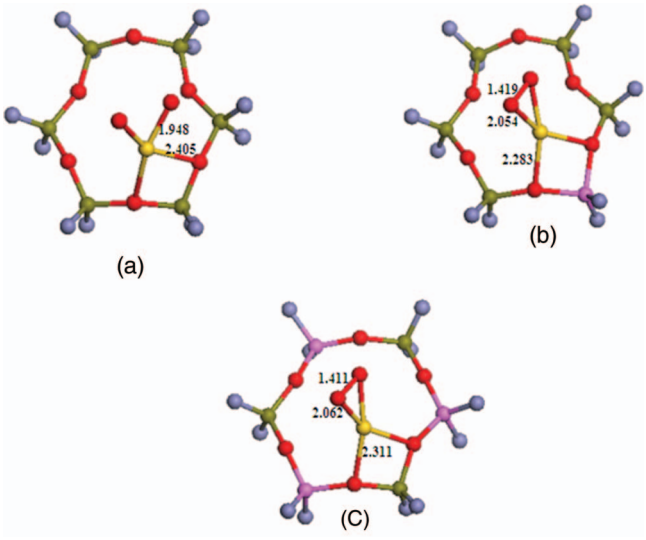

FIG. 6. Optimized structures of O_2 adsorbed (dissociative coordination) on faujasite supported Au monomer; (a) Au^0-O_2/FAU, (b) Au^+-O_2/FAU, and (c) Au^{3+}-O_2/FAU.

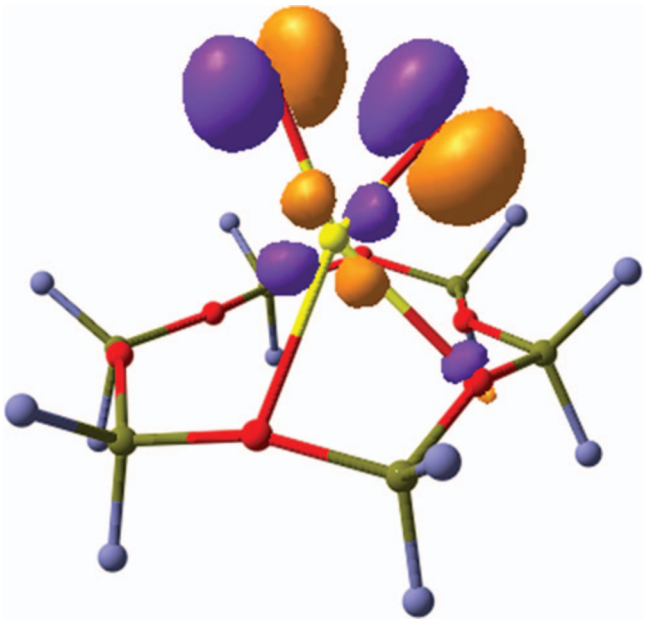

FIG. 7. HOMO-1 orbital of Au^0-O_2/FAU showing the σ^* occupancy of O_2 and thus breaking the O–O bond.

NBO analysis of free gas phase O_2 molecule shows zero occupancy of the σ^* and the π^* orbitals showing O=O double bond (1.25 Å). When O_2 is adsorbed on Au^{3+}/FAU an increase in occupancy of the π^* orbital of O_2 from 0 to 0.68540 is observed which contributes to the elongation of the O–O bond (1.41 Å) in Au^{3+}-O_2/FAU approaching the O–O bond of a peroxide species. NBO analysis on Au^+-O_2/FAU system shows a slight increase in occupancy of σ^* orbital of O_2 from 0 to 0.00329 resulting further elongation of O–O bond (1.42 Å). In the case of Au^0-O_2/FAU no O–O bond is found due to occupancy of the σ^* orbital of O_2. The HOMO-1 orbital showing the occupancy of σ^* orbital and thus breaking the O–O bond which is shown in Fig. 7. When O_2 is coordinated in dissociative mode, the NBO charge on Au increases from –0.06 e in faujasite supported bare Au^0 to 0.77 e in O_2 adsorbed Au^0/FAU. In the case of Au^+ and Au^{3+}, it increases from 0.63 e to 0.98 e and from 0.59 e to 0.97 e, respectively. Comparing the NBO charge on Au when O_2 is adsorbed in the bridge and dissociative mode, we find that the increase in charge from the value in faujasite supported bare monomer is almost similar in both Au^+ and Au^{3+} which might result in the similar elongation of O–O bond length. This is indicated by the O–O bond length (Table III) that approaches the value in peroxide (~1.40–1.42 Å) in both the oxidation states for the two adsorption modes. However, the increase is quite high for the dissociative mode compared to the bridge mode in neutral Au and consequently higher amount of charge is transferred from Au in the former mode. This is evident from the O–O bond distance in both the adsorption modes in Au^0/FAU, being much higher in the dissociative mode. In Au^0/FAU, Au–O distance has a lower value of 1.95 Å while similar values are observed in Au^+/FAU and Au^{3+}/FAU. The Au–O_z distance is almost similar in both the cationic states. However, the Au–O_z distance is found to decrease from 2.76 Å in faujasite supported bare Au^0 to 2.40 Å in O_2 adsorbed faujasite supported Au^0. On the other hand, the decrease is observed to be slightly less in Au^+ (from 2.31 Å to 2.28 Å) and in Au^{3+} the Au–O_z distance remains same.

IV. CONCLUSIONS

Our study on O_2 adsorption on faujasite supported Au monomer in three different oxidation states (0, +1, +3) reveals activation of O_2 indicated by the elongation of O–O bond length and corresponding redshift in the ν_{O-O} from the value in gas phase free O_2. Activation of O_2 is an important step in the catalytic oxidation of CO. It has been observed that the O_2 binding in the top mode is accompanied by negative binding energy value in all the three oxidation states making it unfavorable. In neutral Au, O_2 binding, however, is favorable in the bridge coordination with a high binding energy. On the other hand, in faujasite supported cationic Au, O_2 reverts back to the bridge bonded form rather than being dissociated. However, the presence of O_2 facilitates the interaction of Au monomer with the faujasite support evident from reduced Au–O_z distances.

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