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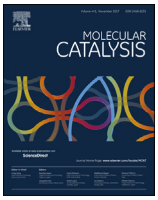

Theoretical study of nitrogen dioxide and nitric oxide co-adsorption and DeNO$_x$ reaction on Cu-SAPO−34 and Cu-SSZ−13 in presence of Brønsted acid sites

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ABSTRACT

The decomposition of co-adsorbed nitric oxide (NO) and nitrogen dioxide (NO_2) on copper-exchanged SAPO−34 and SSZ−13 proceeds with lower activation barriers in all intermediate steps, as compared to the DeNOx reaction of dinitrosyls. Upon co-adsorption on copper cations, NO and NO_2 form an η^1—O adsorption complex with N—N bond and in the presence of Brønsted acid sites, oxygen atoms from the adsorption complex bind to the framework via hydrogen bonds. Direct protonation of the adsorption complex may occur at either the NO_2 end ($ONNO_2H$), or at the NO-end, ($HONNO_2$). Upon $ONNO_2H$ formation, the N—N bond is weakened, while NO protonation ($HONNO_2$) strengthens the N—N bond and a nearly cyclic structure with the transition metal cation is formed. Two of the reaction steps have high energy barriers: the release of N_2O on SSZ−13 after protonation transfer to $ONNO_2$, and the decomposition of N_2O on a ZeolCuO site. The first reaction step is the release of N_2O and protonation of the adsorption complex plays a detrimental role. The activation barrier obtained by intrinsic reaction coordinate calculations is higher for SSZ−13 (116 kJ mol^{-1}), but much smaller for SAPO−34 (65 kJ mol^{-1}). After desorption of molecular oxygen, the N_2O molecule is re-adsorbed and its dissociation with release of molecular nitrogen is assisted by hydrogen bond formation, which stabilizes the transition states and lowers the energy barriers. After the release of molecular nitrogen, surface copper oxide, ZeolCuO site is left and it is more reactive than copper hydroxyl, ZeolCu(OH)$^+$.

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1. Introduction

Nitrogen dioxide and nitric oxide are released in combustion processes and remain as major air pollutants in industrial and urban areas. The research on nitrogen oxides abatement in the last decades led to industrial implementation of transition metal oxides and zeolite catalysts, which are much cheaper than the noble metals used in automotive catalytic converters [1–7]. Among the zeolite catalysts, those with chabazite structure, namely SSZ−13 and the silicoaluminophosphate analog SAPO−34, exhibited high conversion of NO$_x$ and selectivity towards N_2 while retaining hydrothermal stability [8]. As a result of numerous computational, spectroscopic, and catalytic studies, significant advances in the understanding of the DeNOx reaction mechanism have been reached and the adsorption complexes of NO, N_2O and NO_2 with alkaline, alkaline-earth, and transition metal extraframework cations were elucidated [9–17]. Nitric oxide gained a prevailing number of studies, because it has high dissociation energy (632.6 kJ mol^{-1}) whereas NO_2 is more reactive and the dissociation energy for the first oxygen atom is much lower, 306.2 kJ mol^{-1}; [18] in either case, however, a catalyst is needed to overcome the reaction barriers. While NO does not form aggregates in the gas phase, the co-adsorption of two moleculas on extraframework cations in zeolites via the oxygen atoms (η^2-O,O complex) yields a cyclic complex with N—N bond [19,20]. NO_2 forms a gas-phase dimer, N_2O_4, which was also detected in the supercage of Mn^{2+} exchanged FAU zeolite by XRD studies [17]. The disproportionation of N_2O_4 to nitrosyl-nitrato species can be triggered upon certain conditions [21,22]. In alkali cation exchanged FAU zeolite disproportionation of N_2O_4 to NO$^+$ and $NO_3{}^-$ occurred, which was examined by density-functional methods with cluster models and by applying periodic boundary conditions (PBC) [23]. The necessity to have alkali cations at sites SIII in FAU for adsorption and stabilization of the disproportionation species was emphasized. [23,24] Nitrate species were detected experimentally in studies of NO_2, NO, and H_2O competitive adsorption on H-type mordenite [25]. The NO$_x$ decomposition to molecular nitrogen and oxygen inevitably

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includes co-adsorption and a bimolecular reaction step, because two nitrogen containing molecules need to be in proximity to form the N≡N bond. In theoretical studies, coupled cation adsorption sites, consisting of closely positioned cations $Cu^+\cdots Cu^+$, as well as oxygen-bridged copper cations Cu—O—Cu or Cu-(O_2)-Cu, have been considered for MFI zeolites, and they were found equally or comparably active in the DeNOx reaction [26–35]. Single cation active centers were preferred as models for FER, CHA and FAU zeolite frameworks [29–33], and there is no general conclusion whether two closely spaced cations are indispensable for the reaction to proceed. The excellent performance of SSZ-13 prompted tests of other reactions, such as NO oxidation to NO_2, and this process was proposed as a test for copper cation dimer formation [36]. In the search of new catalysts, or for improving the catalytic performance of known frameworks, various promoters were considered and the role of protons was revealed by computational studies [27]. Protonation did not affect all reaction steps in positive way. While the first reaction step of N_2O formation was favorably affected by protonation of the adsorption complex, in the step of N_2O decomposition the energy barrier was increased by 25–30 kJ mol^{-1}. In CuSSZ−13 and CuSAPO−34 the protonation of Cu-η^2-OO dinitrosyl complexes facilitated N—O bond breaking and N_2O formation, [33] but the high stability of the remaining $CuOH^+$ group was found to be the key factor for the higher activation energy of the N_2O dissociation step. It is worth noting, that though the binding energy of the N—O bond in the free N_2O molecule is 167.4 kJ mol^{-1}, the activation barrier in presence of protons is higher, 195–250 kJ mol^{-1}, [27,33] and this is due to the formation of stable hydroxyl species of the copper cations, $CuOH^+$ or Cu—OH^+—Cu. Without proton transfer, the calculated energy barrier of N_2O dissociation on CuSSZ−13 was smaller, 144 kJ mol^{-1}, but it was found to be higher in copper-exchanged ferrierite, 186 kJ mol^{-1} [29,30,33]. The computational studies on co-adsorption of nitric oxide (NO) with other nitrogen oxide species are scarce. Many studies have revealed that nitrous oxide (N_2O) forms as a stable intermediate in nitric oxide dissociation and that the N_2O decomposition is the rate determining step of the process [27,29,30,32,33]. The presence of NO in the catalytic dissociation of N_2O had a versatile effect, depending on the catalyst topology: NO generally played inhibiting role [37,38], except for Fe-ZSM-5, where the reaction was strongly promoted in presence of NO [39–41]. The reaction of N_2O dissociation in the presence of nitric oxide (NO) was examined by density functional theory and the active center in the zeolite for N_2O decomposition was found to be Zeol-$[FeOH]^+$, which is formed in the presence of water vapors and NO [32]. Again, the rate-determining process was N_2O dissociation. Detailed studies on NO_2 and NO co-adsorption are not available, though various intermediate species, including nitro-, nitrite isomers and nitrates were considered on FeZSM5 [32]. In the present study the co-adsorption of NO and NO_2 at extraframework copper cations in SAPO−34 and SSZ−13 in presence of Brønsted acid sites is examined. The hydrogen bond formation and proton transfer to the adsorption complexes $ONNO_2$ has strong influence on the type of binding to metal cations and on the energy barriers of the elementary reaction steps.

2. Structure and methods

2.1. Structural models

The chabazite (CHA) structure consists of double six-membered rings of oxygen-bridged tetrahedral atoms (Si, Al, P-in silicoaluminophosphate analogs), which are interconnected by tilted four-member rings. In SAPO Si substitutes P at tetrahedral sites and similarly to the substitution of Si for Al in zeolites the resulting negative framework charge is compensated by either a proton or an extraframework cation. The strict alternation of Al and P at tetrahedral sites in SAPO−34 limits the range of possible Si → P substitutions and the maximum level of Si content per unit cell as determined by magic angle spinning NMR and element analysis [42–47] is 1.32, which indicates that most unit cells would have a single Si atom at T-site and also there will be cells with double Si – P substitution. SSZ-13 has a chabazite structure with the Si/Al > 5 ratio and in this aluminosilicate the Si/Al may vary in a broader range, compared to the silicoaluminophosphate SAPO-34 [48–51]. The oxidation state of transition metal cations and their local coordination to the zeolite framework are very sensitive to the preparation conditions, the Si/Al ratio and the cation exchange level [7]. The preferred cation location in both SSZ-13 and SAPO-34 is the six-membered-ring (6MR), which provides best cation coordination [48,49]. The large 8MR windows host dimeric forms, hydrates and hydroxyl complexes of the cations [36,48,49]. Divalent state of individual copper cations has been determined experimentally in chabazite structures, but at high Si/Al (respectively P/Si) ratios the distances between the negative framework charges become large, so significant part of the copper cations would be in a monovalent form and compensating a single framework charge. TPR studies of Cu-SSZ-13 have shown that upon increasing the Si/Al ratio, the formation of Cu^+ via autoreduction increases [48]. The models employed in the present study include either double or single Al → Si (resp. Si → P) substitution, and Cu^{2+}, Cu^+ and protons as charge compensating cations. The study of proton assisted reaction requires proximity of a proton from a Brønsted acid site and a copper cation and the models in this case consist of double framework substitution, compensated by monovalent copper cations and a proton.

2.2. Periodic calculations

The periodic calculations were performed using the PBE density functional [52,53] as implemented in Gaussian 09; [54] Brillouin-zone sampling was restricted to the Γ point. The models for periodic calculations included eight unit cells and an all-electron basis set was applied. The divalent copper cations at site A in Cu-SAPO-34 are charge compensated by a Si—O(3)—Al—O(2)-Si linkage in a six-membered ring; at site B the linkage is Si—O(4)—Al—O(3)—Si. The atom numbering and cation site positions in the chabazite cage are illustrated on Fig. 1 with four unit cells. The monovalent copper cations are charge-compensating a single, closely positioned Si → P substitution. The models for SSZ-13 are constructed in a similar way, but the framework T-site substitution which creates a negative charge is Al → Si. Thus, the linkages containing the negative framework charge are Al—O(3)—Si—O(2)—Al, and Al—O(4)—Si—O(3)—Al. For the models involving a Brønsted acid site and a monovalent cation, the proton is placed at an O(2) site which has higher acidity than the O(3) site, and it is more favorably positioned to deliver a proton to the adsorption site [42,43,55].

2.3. ONIOM calculations

The ONIOM models were designed so as to include the two stronger Brønsted acid sites, O(4) and O(2), as marked in Fig. 2. The high-layer ONIOM [56–64] models with the linking hydrogen atoms were used in transition state optimizations by the synchronous transit-guided quasi-Newton (STQN) method [65,66] and in classical trajectory simulations, using BOMD (Born-Oppenheimer Molecular Dynamics) [67]. The reaction path calculations are performed with cations at site A and Brønsted acid sites at O(2) atoms from the double six-membered rings in SAPO-34 and SSZ-13, see Fig. 1. The activation energies for each reaction step were determined by Intrinsic reaction coordinate calculations (IRC) on models of single unit cell [68,69].

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