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Theoretical Study on the Reaction Mechanism of Nickel Atoms with Carbon Dioxide

Alexander M. Mebel*,† **and Der-Yan Hwang***,‡

Institute of Atomic and Molecular Sciences, Academia Sinica, P.O. Box 23-166, Taipei 10764, Taiwan, and Department of Chemistry, Tamkang University, Tamsui 25137, Taiwan

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Ab initio and density functional calculations of the potential energy surfaces for the Ni + CO_2 → NiO + CO reaction in the lowest triplet and singlet electronic states have been carried out at the B3LYP/6-31G*, B3LYP/6-311G*, B3LYP/6-311+G(3df), CCSD(T)/6-311G*, and CCSD(T)/6-311+G(3df) theoretical levels. The reaction is calculated to preferentially occur in the triplet state and to proceed by the formation of a cyclic four-member ring C_{2v}-symmetric NiOCO intermediate (t-cyc) that lies ∼19 kcal/mol above the reactants. The barrier for the initial reaction step is about 23 kcal/mol. From t-cyc the reaction continues via transition state t-TS2 toward the linear t-CONiO complex. The latter is stabilized by ∼10 kcal/mol with respect to the products, NiO ($^3\Sigma^-$) + CO, and can dissociate producing them without exit barrier. The highest barrier at the reaction pathway, about 53 kcal/mol, occurs at t-TS2. The reverse NiO ($^3\Sigma^-$) + CO reaction yielding Ni atoms and CO_2 with exothermicity of 36 kcal/mol is shown to have a barrier of 15 kcal/mol relative to the reactants occurring at the second reaction step. On this basis, nickel oxide is expected to be less efficient for oxidizing CO to CO_2 than the oxides of alkaline earth metals. Reduction of CO_2 to CO can be significantly enhanced in the presence of Ni atoms due to much lower endothermicity (36−37 kcal/mol) and activation barrier (∼53 kca/mol) for the t-Ni + CO_2 → NiO ($^3\Sigma^-$) + CO reaction as compared to those for the unimolecular decomposition of carbon dioxide. The accuracies of different theoretical methods for calculations of the reaction energies have been compared.

Introduction

Transition metals and their compounds can catalyze many important chemical reactions, either homogeneously or heterogeneously. Their reaction mechanisms therefore represent a research topic of great interest. The coordination of the carbon dioxide to the metal center has been considered a key step to reduce this molecule to useful organic substances.[1−4] The interaction between metal atoms and CO_2 has become an attractive subject of experimental and theoretical studies.[5−17] Reactions of metal atoms with carbon dioxide give M−CO_2 species which can exhibit different types of geometries including C_{2v}- and C_s-symmetric cyclic structures as well as trans and nonplanar configurations.[7−12,18−20] On the other hand, carbon monoxide exhibits a rich chemistry with metal oxides. For example, adsorption of CO onto thermally activated CaO or MgO leads to the formation of various anionic $(CO)_x$ species.[21] The MO + CO reactions are therefore related to the catalytic properties of metal oxides and to oxidizing CO on surfaces and in solution. Theoretical calculations of the MCO_2 potential energy surfaces (PES) are able to provide information for the reactions in both forward and reverse directions.

Our previous studies[22−25] revealed that the reforming of carbon dioxide to carbon monoxide can be significantly enhanced in the presence of Ca, Mg, and Be atoms. For instance, the overall endothermicity of the Mg + CO_2 → MgO + CO reaction was calculated to be about 66 kcal/mol,[23] about a half the energy needed for spin-forbidden unimolecular decomposition of CO_2 to CO + O (^{3}P).[22] The endothermicities of the reactions Be + CO_2 → BeO + CO and Ca + CO_2 → CaO + CO were found to be significantly lower, ∼26 and ∼35 kcal/mol, respectively.[24,25] Our previous studies on catalytic reforming of CO_2 with metal atoms concerned the alkaline earth metals.[23−25] In the present paper, we report ab initio calculations of the reaction pathway for carbon dioxide reforming catalyzed with transition metal nickel atom. To our knowledge, no experimental data regarding the reaction mechanism and its possible intermediates are available so far. We will evaluate the expected accuracy of our calculations on the basis of the comparison with the experimental structure and heat of formation for NiO. The Ni + CO_2 reaction will be compared with Be + CO_2, Mg + CO_2, and Ca + CO_2, and unimolecular decomposition of CO_2. Their differences in energy barriers and the heat of reaction will be discussed.

Computational Details

Since the energy difference between the lowest triplet (^{3}F, $3d^84s^2$) and singlet (^{1}D, $3d^94s^1$) electronic states of nickel atom[26] is only 3410 cm^{-1} and the singlet−triplet energy splitting for NiO is not known from experiment, both singlet and triplet reaction pathways may be important. Therefore, we consider the lowest singlet and triplet state PESs for the Ni + CO_2 → NiO + CO reaction. On these surfaces, full geometry optimizations were run to locate all the stationary points at the B3LYP/6-31G(d) level.[27] Harmonic vibrational frequencies were obtained at the same level in order to characterize the stationary points as minima or first-order saddle points, to obtain zero-point vibration energy corrections (ZPE), and to generate force constant data needed in the IRC calculation. To predict more reliable ZPE, the raw calculated ZPE values were scaled by 0.9806 at the B3LYP/6-31G(d) level to account for their average

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* Authors to whom correspondence should be addressed.

† Institute of Atomic and Molecular Sciences, Academia Sinica.

‡ Department of Chemistry, Tamkang University.

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TABLE 1: Total Energies (hartree) and ZPE Corrected Relative Energies (kcal/mol) Calculated at the B3LYP/6-31G(d), B3LYP/6-311G(d), CCSD(T)/6-311G(d), and B3LYP/6-311+G(3df) Levels of Theory of Various Compounds in the Reaction of CO_2 with Ni

	B3LYP/6-31G*		B3LYP/6-311G*		CCSD(T)/6-311G*		B3LYP/6-311+G(3df)		
species	total energy	ZPE	total energy	rel. energy	total energy	rel. energy	total energy	rel. energy	corrected rel. energy[a]
s-CO_2	−188.58094	7.3	−188.64083		−188.21413		−188.65985		
s-Ni	−1508.02232	0.0	−1508.17496		−1506.91470		−1508.24607		
s-CO_2 + s-Ni	−1696.60326	7.3	−1696.81579	18.4	−1695.12883	25.8	−1696.90592	3.0	10.4 (1.5)
s-$NiCO_2$	−1696.62975	7.4	−1696.82359	13.6	−1695.15874	7.2	−1696.90545	3.4	−3.0
s-TS1	−1696.53922	5.6	−1696.73517	67.3	−1695.09537	45.1	−1696.82664	51.1	28.9
s-cyc1	−1696.57687	6.3	−1696.75754	54.0	−1695.08900	49.9	−1696.82905	50.3	46.2
s-TS2	−1696.54237	5.4	−1696.70624	85.3	−1695.04958	73.7	−1696.78738	75.5	63.9
s-cyc2	−1696.56524	5.8	−1696.72909	71.3	−1695.08823	49.8	−1696.79942	68.4	46.9
s-TS3	−1696.53851	5.1	−1696.70045	88.6	−1695.05806	68.1	−1696.79147	72.7	52.2
s-CONiO	−1696.54658	5.7	−1696.71014	83.1	−1695.06894	61.8	−1696.79724	69.6	48.3
s-NiO	−1583.19606	1.4	−1583.34611		−1581.97022		−1583.42346		
s-CO	−113.30945	3.2	−113.34596		−113.09299		−113.35636		
s-NiO + s-CO	−1696.50551	4.6	−1696.69207	93.4	−1695.06321	64.4	−1696.77982	79.5	50.5 (52.7)
t-Ni	−1508.05339	0.0	−1508.20424		−1506.95581		−1508.25084		
s-CO_2 + t-Ni	−1696.63433	7.3	−1696.84507	0.0	−1695.16994	0.0	−1696.91069	0.0	0.0
t-Ni−CO_2	−1696.61978	7.3	−1696.84062	2.8	−1695.16057	5.9	−1696.90815	1.6	4.7
t-TS1	−1696.60891	6.2	−1696.78583	36.1	−1695.10138	42.0	−1696.88133	17.4	23.2
t-cyc	−1696.61107	6.4	−1696.78727	35.4	−1695.11025	36.6	−1696.88084	17.9	19.1
t-TS2	−1696.56551	4.7	−1696.73763	64.9	−1695.06703	62.0	−1696.81815	55.5	52.7
t-CONiO	−1696.58052	5.4	−1696.76922	45.8	−1695.10860	36.7	−1696.84988	36.4	27.3
t-NiO	−1583.24652	1.4	−1583.40314		−1581.99408		−1583.47731		
t-NiO + s-CO	−1696.55597	4.5	−1696.74910	57.5	−1695.08707	49.4	−1696.83367	45.6	37.4 (36.0)

[a] The relative energies calculated as $E_{cor} = E[CCSD(T)/6\text{-}311G^*] + E[B3LYP/6\text{-}311{+}G(3df)] - E[B3LYP)/6\text{-}311G^*]$. The numbers in parentheses show the CCSD(T)/6-311+G(3df) relative energies with ZPE[B3LYP/6-31G(d)] for the reactants and products.

overestimation.[28] The intrinsic reaction coordinate (IRC) method[29] was used to track minimum energy paths from transition structures to the corresponding minimum. A step size of 0.1 amu$^{+1/2}$ bohr or larger was used in the IRC procedures.

The relative energies of various species were then recalculated using three levels of theory, B3LYP with larger 6-311G* and 6-311+G(3df) basis sets and the coupled cluster CCSD(T)/6-311G*.[30] For the reactants and products, we also carried out CCSD(T)/6-311+G(3df) calculations. The 6-311G* basis set for Ni available in the GAUSSIAN 98 program[31] includes valence triple-ζ s, p, and d basis functions and a polarization f function. The Ni 6-311+G(3df) basis set can actually be more correctly designated as 6-311+G(3fg) because it includes three polarization f functions and a g function in addition to the valence and diffuse s, p, and d basis functions. The large CCSD(T)/6-311+G(3df) calculations for the reaction intermediates and transition states are not feasible with our present computing facilities. Therefore, we tried to approximate the CCSD(T)/6-311+G(3df) energies using those calculated by the B3LYP/6-311G*, B3LYP/6-311+G(3df), and CCSD(T)/6-311G* methods. The correction scheme is similar to the G2 and G2M approaches,[32,33] i.e., the energies are evaluated as

$$E_{cor} = E[CCSD(T)/6\text{-}311G^*] + E[B3LYP/6\text{-}311{+}G(3df)] - E[B3LYP/6\text{-}311G^*]$$

In G2 and G2M, the MP2 method is used to obtain the corrections for larger basis sets. However, this method is not reliable for calculations of the first-row transition metals. Therefore, we tried to replace MP2 with B3LYP, although no systematic investigations have been performed so far to study the basis set dependence of the B3LYP energies. As will be seen below, the above correction scheme performs fairly well but not for all cases considered.

Most of the ab initio calculations described here were carried out employing the Gaussian 98 program[31] and for some of them the MOLPRO 98 package[34] was used.

TABLE 2: Vibrational Frequencies (cm^{-1}) of Various Compounds in the Ni + CO_2 → NiO + CO Reaction through the Singlet and Triplet Pathways Calculated at the B3LYP/6-31G(d) Level

species	frequencies
s-$NiCO_2$	335, 459, 620, 761, 1077,1950
s-TS1	602i, 163, 232, 446, 1132, 1916
s-cyc1	319, 573, 575, 826, 964, 1161
s-TS2	282i, 224, 421, 531, 917, 1683
s-cyc2	140, 203, 452, 495, 971, 1786
s-TS3	290i, 52, 140, 447, 970, 1978
s-CONiO	88, 214, 219, 445, 979, 2036
s-NiO	1013
t-Ni−CO_2	56, 67, 574, 623, 1366, 2421
t-TS1	68i, 303, 381, 584, 1215, 1858
t-cyc	334, 386, 395, 725, 1226, 1432
t-TS2	498i, 78, 141, 391, 713, 1946
t-CONiO	82, 82, 187, 187, 263, 902, 2103
t-NiO	926

Results and Discussion

The total and ZPE corrected relative energies of various compounds in the Ni + CO_2 reaction calculated at the B3LYP/6-31G*, B3LYP/6-311G*, B3LYP/6-311+G(3df), and CCSD(T)/6-311G* levels of theory as well as the evaluated E_{cor} energies are listed in Table 1. Table 2 presents vibration frequencies calculated at the B3LYP/6-31G(d) level. The energy diagram along the singlet and triplet reaction pathways using E_{cor} is shown in Figure 1. The optimized geometries of various compounds on the lowest triplet and singlet PESs of the Ni + CO_2 reaction are depicted in Figures2 and 3, respectively.

A. Reaction Energetics. According to experimental measurements, the bond strength in the nickel oxide which has the $^3\Sigma^-$ ground electronic state[35,36] is 90.4 kcal/mol.[37] Based on the experimental heats of formation for the Ni atom (102.8 kcal/mol) and oxygen (59.6 kcal/mol),[38] ΔH_f for NiO is 72.0 kcal/mol. Using this value and experimental ΔH_f for Ni, CO_2 (−94.1 kcal/mol), and CO (−26.4 kcal/mol),[38] one can see that the Ni + CO_2 → NiO + CO reaction is endothermic by 36.9 kcal/

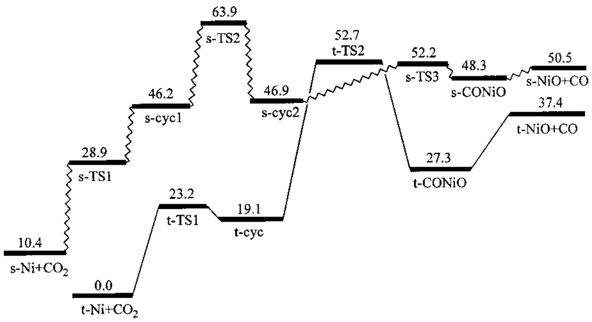

Figure 1. Potential energy diagram for the Ni + CO$_2$ → NiO + CO reaction in the lowest singlet and triplet electronic states calculated using the correction scheme, $E_{\mathrm{cor}} = E$[CCSD(T)/6-311G*] + E[B3LYP/6-311+G(3df)] − E[B3LYP/6-311G*] with ZPE obtained at the B3LYP/6-31G* level and scaled by 0.9806. All relative energies are given in kcal/mol with respect to t-Ni + CO$_2$.

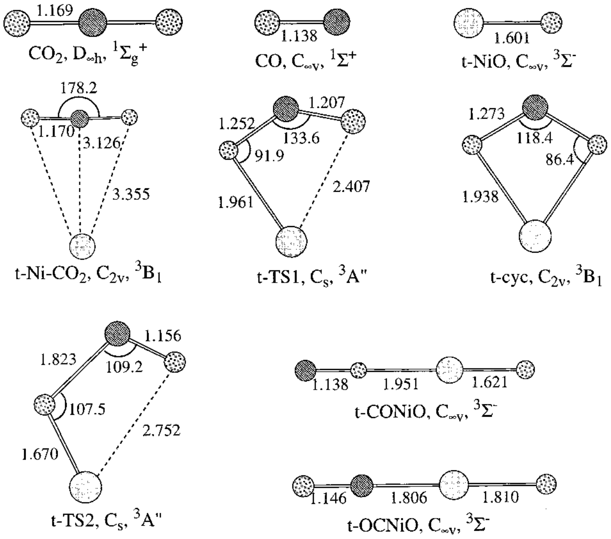

Figure 2. Geometries of the reactants, products, intermediates, and transition states for the triplet pathway of the Ni + CO$_2$ → NiO + CO reaction, optimized at the B3LYP/6-31G* level of theory. (Bond lengths are in Å and bond angles are in degrees).

mol. The B3LYP/6-311G*, B3LYP/6-311+G(3df), and CCSD(T)/6-311G* methods overestimate this value by 20.6, 8.7, and 12.5 kcal/mol, respectively. However, the correction scheme gives the reaction heat as 37.4 kcal/mol, very close to the experimental value. The CCSD(T)/6-311+G(3df) calculation results in $\Delta H_{\mathrm{rxn}} = 36.0$ kcal/mol which agrees well both with the evaluated E_{cor} and experiment.

Nickel oxide ($^3\Sigma^-$) has been extensively studied both experimentally[35−37] and theoretically.[36,39−41] The present calculations give the bond length in this molecule as 1.601 Å, slightly shorter than that in experiment, 1.627 Å.[35] The most sophisticated so far MR-ACPF calculations by Bauschlicher and Maitze[40] also resulted in 1.601 Å, density functional BP86 calculations by Citra et al.[36] gave a slightly longer bond length of 1.644 Å, while BLYP calculations by Doll et al.[41] provided the best agreement with experiment (1.626 Å). The B3LYP method somewhat overestimates the vibrational frequency of NiO, 926 cm^{-1} vs experimental 842.6 cm^{-1}.[36] For the frequency, the best results were obtained by Bauschlicher and Maitze[40] (850 cm^{-1}) and by Citra et al.[36] (823 cm^{-1}), and the BLYP frequency[41] (897 cm^{-1}) is quite close to our B3LYP value. The deviation of the frequency, though significant for spectroscopy, does not affect the energetics of NiO much; the difference in ZPE is small.

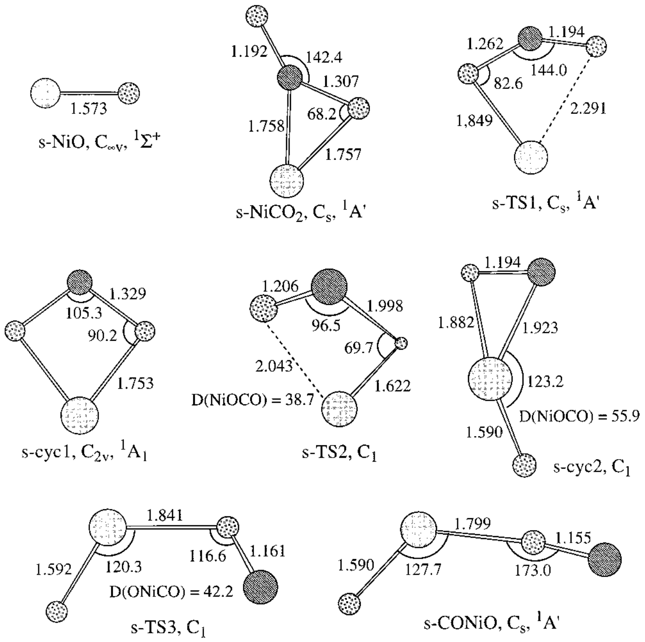

Figure 3. Geometries of the reactants, products, intermediates, and transition states for the singlet pathway of the Ni + CO$_2$ → NiO + CO reaction, optimized at the B3LYP/6-31G* level of theory. (Bond lengths are in Å and bond angles are in degrees).

The bond strength in NiO ($^3\Sigma^-$) calculated at the CCSD(T)/6-311+G(3df) level with ZPE correction based on the experimental vibrational frequency is 87.2 kcal/mol, close to the MR-ACPF result by Bauschlicher and Maitze[40] (87.6 kcal/mol) and in reasonable agreement with experiment. Unfortunately, the correction scheme does not perform as well for the NiO bond strength giving only 78.1 kcal/mol (70.0, 64.2, and 83.9 kcal/mol at the B3LYP/6-311G*, CCSD(T)/6-311G*, and B3LYP/6-311+G(3df) levels, respectively). For the energy of the CO$_2$ → CO + O(^{3}P) reaction, the three aforementioned methods result in 127.4, 113.4, and 129.4 kcal/mol, respectively. This gives the corrected reaction energy as 115.4 kcal/mol, significantly underestimating the experimental value of 125.7 kcal/mol[38] and the CCSD(T)/6-311+G(3df) result (123.1 kcal/mol). Obviously, the scheme using B3LYP/6-311+G(3df) and B3LYP/6-311G* calculations to correct the CCSD(T)/6-311G* energies is deficient for the atomization energies but may be applied to the reactions where the number of chemical bonds is maintained, as in Ni + CO$_2$ → NiO + CO. For the latter, the correction scheme provides a much better result than either of the B3LYP/6-311G*, CCSD(T)/6-311G*, and B3LYP/6-311+G(3df) theory levels. The CCSD(T)/6-311+G(3df) method appears to be the most reliable choice, but it is extremely demanding computationally even for four-atomic molecules containing a Ni atom.

The singlet−triplet energy gap for the Ni atom is difficult to reproduce by single-reference-based ab initio methods. Even at the CCSD(T)/6-311+G(3df) level this energy is computed as 1.5 kcal/mol, B3LYP/6-311+G(3df) gives 3.0 kcal/mol, while the CCSD(T) and B3LYP calculations with the smaller 6-311G* basis greatly overestimate the experimental value. The correction scheme fortuitously gives 10.4 kcal/mol, close to experiment, but this is a result of cancellation of errors. We carried out a full-valence active space MRCI/6-311+G(3df) calculation[42] for the Ni atom and obtained the singlet−triplet energy gap as 6.4 kcal/mol. Better agreement with experiment can be achieved taking into account spin−orbit interaction, but this lies beyond the scope of the present study.

The lowest singlet state of nickel oxide $^1\Sigma^+$ lies 16.7 kcal/mol above $^3\Sigma^-$ at the CCSD(T)/6-311+G(3df) level of theory. The correction scheme reproduces this result fairly well, 13.1 kcal/mol, but worsens the CCSD(T)/6-311G* value of 15.0 kcal/mol. The B3LYP method is clearly deficient for the singlet−triplet energy gap in NiO, overestimating the CCSD(T) values by 17−21 kcal/mol. To our knowledge, no reliable experimental data are available for comparison with our theoretical value on the $^1\Sigma^+-^3\Sigma^-$ energy difference in NiO.

B. Reaction Mechanism. As seen in Figure 1 and Table 1, the triplet state (t) pathway corresponds to the lower energy reaction channel. At the initial reaction step the triplet t-Ni atom attaches to the singlet CO_2 with formation of a planar cyclic intermediate t-cyc via transition state t-TS1. t-cyc has $^3B_1$ electronic state and C_{2v} geometry where Ni forms two bonds with the oxygens of CO_2 with the bond lengths of 1.94 Å. The CO_2 fragment in t-cyc is significantly distorted as compared to the free CO_2 molecule, the CO bonds are stretched to 1.27 Å and the OCO angle changes from 180° to 118.2°. The geometry distortion is stronger than in isolated CO_2^- anion; the CO bonds are slightly longer and the OCO angle is significantly smaller than those in CO_2^-, 1.23 Å and 137.9°, respectively.[43] The geometry of t-TS1 is planar and it has the $^3A''$ electronic state. With the 6-311G* basis set, the B3LYP and CCSD(T) energies of t-cyc are 35.4 and 36.6 kcal/mol, respectively, relative to t-Ni + CO_2, however, at the B3LYP/6-311+G(3df) level the relative energy decreases to 17.9 kcal/mol. Thus, the corrected energy of the cyclic intermediate is 19.1 kcal/mol. t-cyc is separated from the reactants by a low barrier at t-TS1, 0.7 and 5.4 kcal/mol at B3LYP/6-311G* and CCSD(T)/6-311G*, respectively. At the B3LYP/6-311+G(3df) level, the barrier disappears because the energy of t-TS1 is lower than that of t-cyc. The correction scheme gives for the barrier 23.2 and 4.1 kcal/mol in the forward and reverse directions, respectively. The IRC calculations at the B3LYP/6-31G(d) level of theory confirmed that t-TS1 connects t-Ni + CO_2 and the t-cyc intermediate.

It is worth mentioning that our calculations gave another local minimum on the triplet PES, a t-Ni−CO_2 complex of C_{2v} symmetry. The energy of the complex is higher than that of t-Ni + CO_2, by 5.9 kcal/mol at the CCSD(T)/6-311G* level. This indicates that the complex is separated from the reactants by a barrier. Since t-Ni−CO_2 is not expected to play a significant role in the reaction, we did not search for the corresponding transition state.

From the cyclic t-cyc the reaction proceeds to produce a linear t-CONiO complex ($^3\Sigma^-$) via transition state t-TS2 ($^3A''$). t-TS2 seems to correspond to the fragmentation of t-cyc to NiO and CO but before it can be completed a new Ni−C bond is formed yielding t-CONiO. The B3LYP/6-31G(d) IRC calculation confirmed that the first-order saddle point t-TS2 does connect the cyclic t-cyc and the linear t-CONiO. The relative energy of t-TS2 with respect to the reactants is high, from 55.5 to 64.9 kcal/mol at various levels of theory. The correction scheme gives the t-TS2 energy as 52.7 kcal/mol. At this level of theory, the t-CONiO complex lies 27.3 kcal/mol above the reactants and 10.1 kcal/mol below the t-NiO + CO products. The t-CONiO complex dissociates to t-NiO + CO without exit barrier. Thus, the reverse t-NiO + CO reaction can rapidly produce the linear t-CO−NiO intermediate bound by ~10 kcal/mol without entrance barrier. The complex binding energy is similar at all theoretical levels employed in this study. Another t-OCNiO linear structure is not a local minimum on the triplet PES and has two imaginary frequencies at the B3LYP/6-31G* level.

The singlet reaction pathway is less important but more complex than the triplet pathway. At the initial reaction step the singlet s-Ni atom attaches to the CO_2 molecule with formation of a planar cyclic C_{2v}-symmetric intermediate s-cyc1 via transition state s-TS1. The barrier separating s-cyc1 from the reactants exists only at the B3LYP level; CCSD(T)/6-311G* calculations give the s-TS1 energy 4.8 kcal/mol lower than that of s-cyc1. This indicates that s-cyc1 is not likely to be a local minimum on the singlet PES. From the four-member cycle s-cyc1 the reaction proceeds to produce a three-member ring intermediate s-cyc2 via transition state s-TS2. This reaction step involves a cleavage of one C−O and one Ni−O bond, the strengthening of the second Ni−O bond and the formation of a new Ni−C bond. At the CCSD(T)/6-311G* level s-TS2 and s-cyc2 lie 47.9 and 24.0 kcal/mol above s-Ni + CO_2, respectively, and the correction scheme places them 53.5 and 36.5 kcal/mol higher than the reactants in the singlet electronic state.

From s-cyc2 the reaction continues by formation of a C_s-symmetric s-CONiO complex via a nonplanar transition state s-TS3. The latter is 42.3 kcal/mol higher in energy than s-Ni + CO_2 at the CCSD(T)/6-311G* level and this energy does not significantly change (41.8 kcal/mol) if the correction scheme is applied. The s-CONiO complex is stabilized with respect to the singlet s-NiO + CO products by only 2.2−2.6 kcal/mol and decomposes to them without exit barrier. The s-Ni + CO_2 → s-NiO + CO reaction is found to be endothermic by 38.6 kcal/mol at CCSD(T)/6-311G* and by 40.1 kcal/mol with the basis set correction. The reactants, products, intermediates, and most of the transition states on the singlet PES have higher energies than those on the triplet PES. Therefore, the singlet surface is not expected to play a significant role in the reaction of Ni atoms with carbon dioxide. Although the energies of t-TS2 and s-TS3 are relatively close (62.0 and 68.1 kcal/mol, respectively, at the CCSD(T)/6-311G* level), their geometries are different and the singlet−triplet intersystem crossing should not be important for the reaction mechanism.

We have also found another complex between Ni and CO_2 in the singlet electronic state, s-NiCO_2, which does not lie on the s-Ni + CO_2 → s-NiO + CO reaction pathway. In this complex the Ni atom forms two bonds with the C and O atoms of CO_2. The corresponding CO bond is stretched to 1.31 Å and the CO_2 fragment is bent (142.4°) in the outside direction with respect to Ni. The s-NiCO_2 complex is calculated to be bound relative to the separated Ni and carbon dioxide in singlet state by 18.6 kcal/mol at the CCSD(T)/6-311G* level and by 13.4 kcal/mol taking into account the basis set correction. The B3LYP calculations predict much lower binding energy, from 4.8 kcal/mol with the 6-311G* basis set to −0.4 kcal/mol (unbound) with 6-311+G(3df).

C. Comparison of Reaction Mechanisms of CO_2 with Ni and Alkaline Earth Metals (Be, Mg, and Ca). According to the calculated PES of the Ni + CO_2 reaction, in the lowest triplet electronic state the barrier for the initial reaction step, about 23 kcal/mol, is similar to those for the reactions of Be[24] and Mg[23] but higher than that for the reaction of Ca, about 13 kcal/mol.[25] The formation of the cyclic t-cyc complex is endothermic by 19.1 kcal/mol, which is higher than the endothermicity for the formation of cyclic MgOCO (14.3 kcal/mol).[23] On the other hand, the formation of cyclic BeOCO is 6.9 kcal/mol exothermic,[24] and the production of cyclic CaOCO in the Ca + CO_2 reaction is nearly thermoneutral.[25] The cyclic NiOCO complex (t-cyc) is expected to be metastable with respect to the reactants, since it is separated from them by a small barrier. In this sense, cyclic NiOCO is akin to cyclic MgOCO which can dissociate back to Mg + CO_2 with a relatively low barrier of ~6 kcal/mol.[23] Cyclic BeOCO[24] and CaOCO[25] are much more stable kinetically; the barriers for their dissociation to the metal atom and carbon dioxide were calculated to be 29.7 and 14.9 kcal/mol, respectively. The lower energies of cyclic CaOCO and BeOCO are due to the stronger bonding between the Ca and Be atoms in the singlet state and CO_2.

The overall endothermicity of the t-Ni + CO_2 → t-NiO + s-CO reaction is similar to that for s-Ca + CO_2 → s-CaO + CO,[25] about 10 kcal/mol higher than for s-Be + CO_2 → s-BeO + CO[24] but ~30 kcal/mol lower than for s-Mg + CO_2 → s-MgO + CO.[23] The differences can be attributed to the variations in the metal−oxygen bond strengths, about 90 kcal/mol in NiO,[37] 61 kcal/mol in MgO,[23] 101 kcal/mol in BeO,[38] and 92 kcal/mol for CaO.[38] On this basis, the Be atom is expected to be the most efficient in the reforming of CO_2 into CO among the metals we have considered so far, followed by Ca, Ni, and Mg atoms. A peculiarity of the $NiCO_2$ and $BeCO_2$ PESs is the existence of linear complexes between the metal oxides and carbon monoxide. The binding energy of the t-CONiO complex with respect to the separated oxides is about 10 kcal/mol. BeO can form much stronger bound linear complexes with CO, OBeOC (21.6 kcal/mol) and OBeCO (36.9 kcal/mol).[18,24,44] Similar complexes for $CaCO_2$ were not found.[25] For $MgCO_2$, Ortiz and co-workers[45] reported a OMgCO linear complex that is bound with respect to separated MgO and CO by only 3.6 kcal/mol at the MP2/6-31+G*//HF/6-31G* level. A OMgOC linear complex, although a local minimum at the HF level, is unbound by 1.3 kcal/mol at MP2/6-31+G*.[45]

In contrast to the reactions of BeO, MgO, and CaO with CO which can produce metal atoms and carbon dioxide with high exothermicity and effectively without barrier, the reverse t-NiO + CO → t-Ni + CO_2 reaction exhibits a significant barrier. This barrier occurs after the initial barrier-less formation of t-CONiO and varies between 10 and 15 kcal/mol relative to t-NiO + CO at different levels of theory. This means that t-NiO cannot remove CO transforming it into CO_2 as efficiently as the oxides of the alkaline earth metals, except BeO. For the latter, the reaction mechanism is expected to be quite different; due to the strong Lewis acid character of BeO, it forms stable OBeOC and OBeCO complexes.[18,24,44] OBeCO is 10.7 kcal/mol more thermodynamically stable than Be + CO_2. Therefore, one can expect that the BeO + CO reaction would produce OBeCO rather than Be + CO_2.[24] Nickel oxide can also form the CONiO complex but the latter would rather dissociate back to NiO + CO requiring about 10 kcal/mol than to produce Ni + CO_2 via the barrier of ~25 kcal/mol.

Conclusions

The reaction between Ni atom and carbon dioxide producing NiO and CO is shown to preferentially occur in the triplet electronic state. The reaction is calculated to proceed by the formation of a cyclic four-member ring NiOCO intermediate (t-cyc) of C_{2v} symmetry that lies ~19 kcal/mol above the reactants. The barrier for the initial reaction step is about 23 kcal/mol. From t-cyc the reaction continues via transition state t-TS2 toward the linear t-CONiO complex. The latter is stabilized by ~10 kcal/mol with respect to the products, NiO ($^3\Sigma^-$) + CO, and can dissociate producing them without exit barrier. The highest barrier at the reaction pathway, about 53 kcal/mol, occurs at t-TS2. The reverse NiO ($^3\Sigma^-$) + CO reaction yielding Ni atoms and carbon dioxide with exothermicity of 36 kcal/mol is shown to have a barrier (~15 kcal/mol relative to the reactants) occurring at the second reaction step. Therefore, nickel oxide is expected to be less efficient for oxidizing CO to CO_2 than the oxides of alkaline earth metals. Reduction of CO_2 to CO can be significantly enhanced in the presence of Ni atoms because the t-Ni + CO_2 → NiO ($^3\Sigma^-$) + CO reaction is spin-allowed and exhibits much lower endothermicity (36−37 kcal/mol) and the activation barrier (~53 kca/mol) than those for unimolecular decomposition of carbon dioxide (126 and 131 kcal/mol, respectively).

On the methodological point of view, we have suggested a scheme to introduce a basis set correction for the CCSD(T)/6-311G* energies of the first-row transition metal compounds using the B3LYP/6-311G* and B3LYP/6-311+G(3df) calculations. The approach is demonstrated to perform satisfactorily for the energy of the Ni + CO_2 → NiO ($^3\Sigma^-$) + CO reaction and for the singlet−triplet energy gap in NiO but is not as accurate for the atomization energy of NiO. Further testing of the correction scheme is required for first-row transition metal species but from the present results this approach seems to provide better accuracy than the B3LYP/6-311G* and CCSD(T)/6-311G* methods and, in most cases, than B3LYP/6-311+G(3df). Note that it has become customary to compute the energetics of large transition metal molecules using the B3LYP approach with moderate basis sets. However, our calculations show that such methods are unable provide a satisfactory accuracy for small Ni-containing molecules.

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Supporting Information Available: Supporting Information Available: Reaction path summaries. This information is available free of charge via the Internet at http://pubs.acs.org.

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