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INTEGRATED EXPERIMENTAL AND DFT STUDY OF PALLADIUM AND NICKEL METALS SUPPORTED ON REDUCIBLE METALLIC OXIDES FOR SELECTIVE HYDROGENATION OF ALKYNES AND DIENES BONDS.
by
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Abstract

This thesis investigates series of studies geared towards underpinning the capacity of ceria to serve as a stand-alone reactive catalyst, and to act as catalyst support for different catalyst configurations. Experimental and density functional theory (DFT) approach were used to critically predict and to design ceria-containing catalysts. Ceria owes the catalytic propensity to the ability to undergo switch in the oxidation state from the +4 to +3 states. To realize this trait involves the formation of oxygen vacancies on the ceria surface either through the intrinsic (reduction in H_2 stream, use of electric field or heating at a high temperature) or extrinsic (addition of dopants) effects. Employing DFT, the latter approach is beneficial in providing prior knowledge of the suitability of dopant(s) that can initiate oxygen vacancies on ceria surface.

In the first approximation, the decomposition of a typical environmental pollutant on defect ceria surface was studied. Methanethiol (CH_3SH) is a volatile organic compound that poses a high health risk and causes corrosion to equipment in petroleum refineries. The removal of the sulfur content in methanethiol using potent catalysts assume a fundamental importance from industrial and environmental perspectives. Motivated by experimental studies involving stand-alone cerium oxide (CeO_2) catalysts, defects CeO_2 surface with an oxygen vacancy ($CeO_2(111)\_V_o$) was used to explore the decomposition chemistry of methanethiol based on first principle density functional theory (DFT) calculations. The study presents potential formation pathways for the major experimentally reported compounds, namely, CH_4, H_2S, CO, CO_2, CH_3SCH_3, and COS. Initial uptake of CH_3SH takes place via either C-S or S-H bond fissions through modest activation barriers. In initial decomposition pathways, V_o spots represent strong acidic sites, and thus facilitating rupture of C-S and S-H fissions. Formation of CO takes place through a series of H transfer reactions that commence from the CH_2^* adduct. Adjacent HS^* and HO^* sites undergo a hydrogen diffusion reaction to ultimately produce H_2S rather than water. Several investigated reactions lead to the filling of the vacant oxygen sites with S atoms leading to the generation of $CeO_{2-x}S_y$ phases. The latter exhibit a neat-metallic character. Through the occurrence of both of an Eley-Rideal and Langmuir-Hinshelwood-type mechanisms, $CeO_{2-x}S_y$ phases maintained their catalytic activity. The findings provide a detailed atomistic understanding of the desulfurization capacity of stand-alone ceria surfaces.

The outcome of this study necessitated the actual formation of vacancies on ceria surface via the inclusion of dopants into the ceria lattice. The accurate actualization of this task was verified with the density functional theory.

Experimental and computational studies have pinpointed the reduction chemistry of Ce atom through the creation of oxygen vacancies, the analogous process when ceria surface is decorated with cations remain poorly understood. Where such results are available, a synergy between experimental and first principle calculation is scarce. Niobium materials are evolving and their use in catalysis is being widely investigated due to their high surface acidity, thermal, and chemical stability. Thus, this dissertation reported the structural and electronic properties of various configurations of mixed Ce-Nb oxides. This was aimed at elaborating on the factors that strengthens the potential catalytic improvements. Evaluations of the samples through XRD, FTIR, N_2-adsorption-desorption, SEM, EDS and TGA analysis were discussed. First principles DFT calculations provide structural features of the Ce-Nb solutions at the low concentration of Nb via computing atomic charge distribution. Contraction in the lattice parameter after Nb doping was confirmed with both XRD and DFT results. SEM analysis reveals particle growth at the loading of 50 wt%, which is detrimental to the catalysts performance. FTIR results established the Ce-Nb-O bond at 1100 cm^{-1} and the TGA analysis confirms the thermal stability of Nb doped ceria. Tetrahedral O atoms demonstrate an increase in electronegativity and this in turn facilitates catalytic propensity of the material because the O atoms will exhibit higher affinity for adsorbed reactants. CeO_2 after Nb doping displays a noticeable band gap narrowing, confirming the improvement in the catalytic behavior. The 4d states of the Nb_2O_5 is found to fill up the 4f states of CeO_2 around the Fermi energy level promoting electrons excitations of the CeO_2. Reported electronic, structural, and thermal characteristics indicate promising catalytic applications of niobium promoted ceria.

Further investigations were undertaken in order to ascertain the promising catalytic properties of the designed Nb-CeO_2 catalysts. Pertinent industrial reactions that involves the selective hydrogenation of alkynes and dienes bonds were tested on either CeO_2 or Nb_2O_5-CeO_2 supports.

The presence of phenylacetylene (PA) in the styrene (ST) stream poisons the catalyst during polymerization reaction, increasing the operational cost. Preparation of low cost, and active hydrogenation catalysts that are stable and highly selective to ST is expedient. Different loadings of nickel and niobium metals supported on cerium (IV) oxide were prepared via the incipient wet impregnation (IWI) approach. Potential reaction pathways were modelled using density functional theory (DFT) calculations. The catalysts were characterized to examine their physical and chemical properties. The results show substantial influence of Nb on the NiCe catalysts. H_2-TPR reveals that Nb offers high interaction with the CeO_2 support that promoted O vacancies necessary to induce facile switch in the Ce oxidation states from +4 to +3. XPS analysis confirms that the surface of the Nb doped sample encompasses abundantly adsorbed O initiated by the vacant sites on the surface. The Ni doped catalysts are active towards PA hydrogenation if the Ni content on the catalysts determined by ICP-OES is fixated at 5%. Ni loading above this value depletes the BET surface area and increases the particle crystallite size, leading to poor activity performance. Gas phase PA Hydrogenation shows steady increase in the conversion with rise in temperature (150°C-300°C). Observed products are limited to styrene and ethylbenzene, indicating the absence of oligomer species. The Nb catalysts display highest conversion at the optimum value of 5% Nb content. The catalysts selectivity towards ST was highest on the Nb catalysts reaching 96% and 91% on the Ni-5%NbCe and Ni-10%NbCe catalysts, respectively. The high performance of Nb catalysts stem from the hydrogen spill over mechanism that affords the dissociated activated hydrogen on Ni active sites to spill to the neighboring Nb sites, thus, limiting the ensemble effect of Ni-Ni interaction. Analysis of the reaction pathway reveals that the transfer of hydrogen to PA is exothermic by 124.6 kJ/mol. Desorption of ST from the catalyst surface requires a mere energy value of 15 kJ/mol. The easy desorption of ST formed from the catalysts surface enhances the selectivity due to the electron transfer effect of Nb atoms to CeO_2 support. Reported results compare favorably in terms of performance with commonly

employed selective catalysts for PA hydrogenation.

Regulating the catalysts activity and selectivity by means of reducible support for the industrially relevant hydrogenation of 1,3-butadiene to more valuable butenes products was investigated. Supported palladium and nickel-palladium catalysts on ceria were prepared and characterized with TGA, XRD, H_2-TPR, H_2-TPD, XPS, FTIR, N_2 adsorption-desorption, SEM, EDS and EDS mapping to examine their chemical and physical properties. The reaction pathways guiding the reaction were determined with the density functional theory (DFT). H_2 pretreatment of the samples confer slight increase in the lattice constants and the crystallite sizes, which is associated with the formation of oxygen vacancies, initiated by both the change in the ceria oxidation states from +4 to +3 and the elongation of Ce-O bond. H_2-TPR confirms that the palladium oxide is reduced and nickel oxide species strongly interact with CeO_2 support. The Ce^{3+} concentration determined by XPS shows that the palladium catalysts is more decorated with the reduced Ce state than the palladium-nickel catalysts owing to the PdO and NiO species that demands reduction. The catalysts show similar BET surface area with the 4Pd-Ce presenting the lowest value due to the particles aggregation, which is confirmed from the EDS mapping analysis. Butadiene conversion shows steady rise with temperature (40 °C-120 °C) until the full conversion was reached on all the catalysts. The products distribution reveals that 4% Pd content directs the products toward butane when 40 °C is exceeded. Lowering the Pd content and the simultaneous inclusion of Ni into the catalysts preserve the activity. Constructed mechanisms by DFT calculations feature low reaction barriers for involved surface hydrogenation steps; and thus, accounts for the observed low temperature of the surface hydrogenation activity. Selective formation of 1-butene partially stems from its relatively weaker binding to Ni sites in reference to Pd sites. The mapped out mechanisms entail higher reaction barrier for the formation of 2-butene; in an agreement with experimental observation pertinent to its formation at higher temperatures when compared with that of 1-butene. Reported results proves the function of Ni in a PdNi catalysts system for butadiene hydrogenation.

Finally, the selective hydrogenation of 1,3-butadiene was tested on Ni catalysts supported on Nb_2O_5-CeO_2, prepared with the incipient wet impregnation approach. Different characterization techniques that span TGA, XRD, H_2-TPR, TPO, H_2-TPD, XPS, FTIR, N_2 adsorption-desorption, SEM, EDS and EDS mapping were employed to analyze the chemical and physical properties of the catalysts. The density functional theory (DFT) was used to map out the reaction pathways controlling the hydrogenation reaction. XRD results reveal the formations of nickel oxide and nickel metals for the calcined and reduced sample, respectively. H_2-TPR shows that the inclusion of niobium oxide in the catalysts confer stronger metal support interaction that promotes the surface and bulk reduction temperature of cerium oxide and leads to the improvement in the formation of Ce^{3+} on the surface of the catalysts as confirmed from the XPS analysis. 1,3-butadiene conversion was tested between 50 °C-300 °C and all the catalysts exhibit total conversion even at lower Ni loading, suggesting the high activity of the catalysts as confirmed from the measurement of the turn over frequency (TOF). The selectivity potential of the catalysts assume a rather different configuration not previously reported for pure butadiene stream. The catalysts show selectivity to the expected butenes but rather than forming butane, propene and propane were formed at higher reaction temperature. We proposed the probable reaction mechanism that involves the decomposition of 2-butene to propene and surface carbene and validated the mechanism with the Thermogravimetric analysis of the spent catalysts. Niobium oxide containing catalysts depicts the highest coke resistivity tendency. This will serve as a promising outcome to be applied in the designing of nickel catalysts for reactions that are prone to high deactivations from carbon deposits.