Forschungszentren

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**Titel des Beitrags:**
Oxidation of Magnesia-Supported Pd30 Nanoclusters and Catalyzed CO Combustion: Size-Selected Experiments and First-Principles Theory

**Abstract:**
Exptl. and theor. investigations of the oxidn. reaction of CO to form carbon dioxide, catalyzed by size-selected Pd30 clusters soft-landed on MgO(100), are described. The consequences of pretreatment of the deposited clusters with mol. oxygen, 16O2, at a temp. of ~370 K followed by annealing at around 450 K are explored. Subsequent to the above pretreatment stage, the system was cooled to 120 K, and after exposure to 18O2 and 13C16O the temp. was ramped and a temp.-programmed reaction (TPR) spectrum recorded. The onset of catalyzed combustion of CO starts at a temp. of 180 K, and the TPR spectrum shows oxidn. to occur over a broad temp. range, up to 550 K. Using first-principles d.-functional theory, the optimal adsorption geometry of the Pd30 cluster on the MgO(100) surface is found to be a square-base pyramidal structure, with an excess electronic charge of 1.25e, originating from the underlying magnesia support, found to be localized near the interfacial region of the cluster with the supporting surface. Structural and energetic properties of a variety of oxygen adsorption sites on the supported palladium cluster and effects due to multiple adsorbed O2 mols. were explored. It is found that the barriers for dissocn. of the adsorbed mols. depend strongly on the locations of the adsorption sites, with very small (<0.1 eV) dissocn. energy barriers found for adsorption sites on the
Pd30 cluster that are closer to its interface with the Mg(100) surface. This correlates with our finding that adsorption at these interfacial sites is accompanied by excess charge accumulation on the adsorbed mol. through excess partial (0.25e) occupation of the mol. antibonding 2p* orbital, resulting in activation of the mol. to a peroxo-like state. This activation mechanism depletes the excess charge on the cluster, resulting in a self-limiting partial oxidn. of the cluster. The information obtained through isotope labeling in the TPR expts. is explored through first-principles quantum simulations of various reaction pathways, with a focus on the multiple coadsorption system Pd30O10(CO)13/MgO. These theor. calcns. allow us to correlate the measured isotope and temp.-dependent TPR features, with operative Langmuire-Hinshelwood, LH, and Mars-van Krevelen-type (MvK) reaction mechanisms, catalyzed by the partially oxidized cluster. The LH mechanism was found to contribute to the reaction at lower temps., while the MvK dominates for higher temps. [on SciFinder(R)]

**Stichworte:**  
Adsorption (coadsorption oxidn. of magnesia-supported Pd30 nanoclusters and catalyzed CO combustion and size-selected expts. and first-principles theory) Dissociation Energy (dissocn energy oxidn. of magnesia-supported Pd30 nanoclusters and catalyzed CO combustion and size-selected expts. and first-principles theory) Clusters (metal, nanoclusters oxidn. of magnesia-supported Pd30 nanoclusters and catalyzed CO combustion and size-selected expts. and first-principles theory) Clusters Nanoparticles (nanoclusters, nanoclusters oxidn. of magnesia-supported Pd30 nanoclusters and catalyzed CO combustion and size-selected expts. and first-principles theory) Adsorbed substances Adsorption Annealing Bond angle Bond length Combustion catalysts Crystal orientation Density functional theory Electric charge Interface Molecular orbital Molecular structure determination methods Oxidation Oxidation Oxidation catalysts Quantum chemistry Simulation and Modeling Surface structure (oxidn. of magnesia-supported Pd30 nanoclusters and catalyzed CO combustion and size-selected expts. and first-principles theory) Oxidation Reaction mechanism (surface oxidn. of magnesia-supported Pd30 nanoclusters and catalyzed CO combustion and size-selected expts. and first-principles theory) oxidn magnesia supported palladium nanocluster catalyzed carbon monoxide combustion size selected expt first principle theory

**Kongressstitel:**  
CAN 156:571938 Catalysis, Reaction Kinetics, and Inorganic Reaction Mechanisms 266317-62-8 Role: CAT (Catalyst use), PEP (Physical, engineering or chemical process), PRP (Properties), RCT (Reactant), PROC (Process), USES (Uses), RACT (Reactant or reagent) (nanoclusters; oxidn. of magnesia-supported Pd30 nanoclusters and catalyzed CO combustion and size-selected expts. and first-principles theory); 1309-48-4 (Magnesia) Role: CAT (Catalyst use), PEP (Physical, engineering or chemical process), PRP (Properties), RCT (Reactant), PROC (Process), USES (Uses), RACT (Reactant or reagent) (oxidn. of magnesia-supported Pd30 nanoclusters and catalyzed CO combustion and size-selected expts. and first-principles theory); 266317-62-8D Role: FMU (Formation, unclassified), PEP (Physical, engineering or chemical process), PRP (Properties), FORM (Formation, nonpreparative), PROC (Process) (oxidn. of magnesia-supported Pd30 nanoclusters and catalyzed CO combustion and size-selected expts. and first-principles theory); 630-08-0 (Carbon monoxide) Role: PEP (Physical, engineering or chemical process), POL (Pollutant), PRP (Properties), RCT (Reactant), REM (Removal or disposal), OCCU (Occurrence), PROC (Process), RACT (Reactant or reagent) (oxidn. of magnesia-supported Pd30 nanoclusters and catalyzed CO combustion and size-selected expts. and first-principles theory); 7782-44-7 (Oxygen); 14797-71-8 (Oxygen-18) Role: PEP (Physical, engineering or chemical process), PRP (Properties), RCT (Reactant), PROC (Process), RACT (Reactant or reagent) (oxidn. of magnesia-supported Pd30 nanoclusters and catalyzed CO combustion and size-selected expts. and first-principles theory)

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