

**PROPERTIES OF LANTHANIDE OXIDES AS SUPPORTS  
FOR TRANSITION METAL CATALYSTS**

Final Technical Report

by

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## OBJECTIVES

The overall objective of this research program has been to develop an improved understanding of not only the catalytic and surface properties of the pure lanthanide oxides, but of the behaviors that they induce when used as oxidic supports for dispersed transition metal catalysts. Suitable experimental methods were developed to enable preparation of several of the lanthanide oxides having substantially higher surface areas than those of commercially available materials. In order to fully characterize the surface and bulk properties of the prepared oxides, we have employed a wide variety of physical and instrumental techniques, including thermal gravimetric analysis, differential thermal analysis, temperature-programmed dehydration/decomposition, selective chemisorption, x-ray diffraction, infrared spectroscopy, scanning and transmission electron microscopy, and x-ray photoelectron spectroscopy. Catalytic behaviors of the pure oxides were probed using several diagnostic-type reactions, such as isomerization/hydrogenation of alkenes and dehydration/dehydrogenation of alcohols, while the catalytic properties of transition metals supported on the oxides were investigated for CO hydrogenation and for the hydrogenolysis and dehydrocyclization of alkanes.

## SUMMARY OF RESULTS

During the 11 years that this program was supported by the Department of Energy, several distinct but interrelated areas of investigation developed. The following sections summarize the most significant results obtained in each of these areas of emphasis.

### Alkene Isomerization/Hydrogenation on Lanthanum Oxide

The catalytic behavior of lanthanum sesquioxide for double-bond isomerization of the *n*-butenes was studied in the temperature range 0-50°C. Initial activity for individual conversions of all three *n*-butene reactants increases with increasing pretreatment temperature, due to removal

of surface hydroxyls, attains a maximum following evacuation at  $-650^{\circ}\text{C}$ , and then declines with further increase in pretreatment temperature, due to increases in surface anion disorder. Initial reaction rates of each isomer at  $0^{\circ}\text{C}$  are described by a Langmuirian rate equation of the form  $\text{Rate} = kbp/(1 + bP)$ , which reduces to a zero-order expression in the case of 1-butene reactant. Double bond migration in the *n*-butenes occurs very rapidly over  $\text{La}_2\text{O}_3$ , but the rates of direct *cis* = *trans* interconversion are, by contrast, negligibly slow throughout the temperature range investigated, due to the comparably low activity or density of surface sites that permit the necessary anti- $\pi$ -allyl = syn- $\pi$ -allyl rotation. As a result, although conversion of 1-butene involves characteristically high initial *cis/trans* product ratios, the sole primary product observed for both 2-butene reactants is 1-butene. Tracer studies employing the three perdeuterated *n*-butenes indicate that proton abstraction is the rate-determining step for each interconversion, and that the hydrogen transfer process involved in double-bond migration occurs via the intramolecular mechanism that is typically observed for most base-catalyzed isomerizations. Both directions of the one = *cis* interconversion are accompanied by a much larger initial H-D isotope effect (9 to 10) than those observed for the one = *trans* reaction (1 to 3), suggesting that the two reversible processes may proceed by dissimilar mechanisms or occur on different types of surface sites.

The activity exhibited at  $0^{\circ}\text{C}$  by  $\text{La}_2\text{O}_3$  pretreated at  $600-650^{\circ}\text{C}$  for hydrogenation of ethylene is comparable to that shown for 1-butene isomerization. By contrast, the hydrogenation rates for both propylene and the *n*-butenes under the same conditions are 3 to 4 orders of magnitude lower than that for ethylene. This behavior is probably due to the formation of energetically favorable  $\pi$ -allylic species from propylene and the *n*-butenes, which then occupy surface sites that could otherwise be utilized for the hydrogenation reaction. Isomerization/hydrogenation co-reaction studies and selective poisoning measurements have demonstrated that

ethylene hydrogenation can occur on the same sites that catalyze *n*-butene isomerization, but that hydrogenations of propylene and the *n*-butenes occur on a different array of surface sites.

Infrared Study of Lanthanide Oxide Surface/Catalytic Properties

The natures of adsorption sites on  $\text{La}_2\text{O}_3$ ,  $\text{Nd}_2\text{O}_3$ , and selected praseodymium oxides were investigated by examining surface reactions of probe molecules using infrared spectroscopy. Additionally, the dehydration/rehydration behaviors and crystallographic phase transitions of these oxides were examined by varying the oxide pretreatment temperature and spectroscopically monitoring rehydration of the sesquioxides. Following rehydration of  $\text{Ln}_2\text{O}_3$  to  $\text{Ln}(\text{OH})_3$  ( $\text{Ln} = \text{La}, \text{Nd}$ ), the effect of increasing vacuum pretreatment temperature in the range 350 to 1000°C is to gradually remove both surface hydroxyl species (up to 650°C) and surface carbonate entities (up to 900°C) and to increase the extent of conversion of the C-type (cubic) polymorph to the A-type (hexagonal). Increasing crystallinity causes a concomitant decrease in surface oxide basicity. The removal of hydroxyl and carbonate species, as well as increases in surface basicity, correlate closely with increases in catalytic activity for several reactions, including the isomerizations/hydrogenations of alkenes described above and the dehydration/dehydrogenation of alcohols that will be discussed below.

On  $\text{Ln}_2\text{O}_3$  pretreated at ~650°C, ammonia weakly coordinates to  $\text{Ln}^{3+}$  sites at ambient temperature. Carbon dioxide, on the other hand, strongly chemisorbs onto surface  $\text{O}^{2-}$  sites to generate unidentate  $\text{CO}_3^{2-}$  species, which transform into bidentate structures at 350°C. Exposure of  $\text{Ln}_2\text{O}_3$  to a  $\text{CO}_2/\text{NH}_3$  mixture at 50°C results in the formation of carbamate species, which dehydrate at ~250°C to produce cyanate entities that are coordinated through their oxygen atoms to  $\text{Ln}^{3+}$  sites. The cyanate bonding rearranges to produce bidentate-coordinated species at 500°C. The latter remain strongly adsorbed and polymerize at ~800°C.

Formic acid adsorption onto  $\text{Ln}_2\text{O}_3$  at  $50^\circ\text{C}$  produces formate ions and, above  $300^\circ\text{C}$ , unidentate carbonate species. Similarly, acetic acid adsorption results in acetate and carbonate ions, but carboxylate species are also observed at  $250^\circ\text{C}$ . Acetaldehyde adsorption at  $50^\circ\text{C}$  occurs by associative coordination to  $\text{Ln}^{3+}$  sites; the adsorbed species transform into bidentate acetate ions following vacuum heating at  $100^\circ\text{C}$ . Exposure of  $\text{Ln}_2\text{O}_3$  to ethanol at  $50^\circ\text{C}$  generates surface ethoxides bound to  $\text{Ln}^{3+}$  sites. At  $150^\circ\text{C}$ , these are dehydrated to unidentate acetate ions, which desorb above  $300^\circ\text{C}$ . Exposure to ethanol at  $350^\circ\text{C}$ , by contrast, produces more strongly adsorbed ethoxide and both uni- and bidentate acetate entities. The latter results from decomposition of acetaldehyde that is produced by ethanol dehydrogenation via a surface ethoxide intermediate.

#### Dehydration/Dehydrogenation of Alcohols on Lanthanide Oxides

The multi-pathway (dehydration/dehydrogenation) conversion of ethanol was used to investigate the nature and behavior of catalytically active sites on  $\text{La}_2\text{O}_3$  and  $\text{Nd}_2\text{O}_3$ . Catalytic reaction data, coupled with infrared spectroscopic characterizations of adsorbed species, indicate that at least two different types of catalytically active sites are generated on activated  $\text{La}_2\text{O}_3$  and  $\text{Nd}_2\text{O}_3$  surfaces that are prepared by thermal dehydration of the corresponding trihydroxides. One kind of site (designated Type I) is much less numerous than the other (Type II), but is more strongly basic and has a much higher initial activity for alcohol dehydration at  $300\text{--}400^\circ\text{C}$ , via a probable ethoxide intermediate. The parallel alcohol dehydrogenation pathway, on the other hand, occurs only on Type II sites, which also have moderate dehydration activity. The acetaldehyde resulting from dehydrogenation readsorbs exclusively on the more strongly basic Type I sites, where it undergoes a series of secondary condensation reactions that cause a decrease in the overall rate of alcohol dehydration. The comparative behavioral features of the two kinds of sites may be due to differing surface environments, with Type I sites being in more structurally defective and/or

more energetic surface locations than are Type II sites. Increases in pretreatment temperature of the oxides cause thermally induced transformations of Type I sites into Type II sites by a surface annealing or restructuring process, with corresponding modifications in the observed catalytic behaviors for the two alcohol conversion pathways.

#### Influence of Support and Precursor on Behaviors of Dispersed Cobalt Catalysts

Temperature-programmed reduction, x-ray photoelectron spectroscopy, and x-ray diffraction techniques were used to characterize the effects caused by variations in support and metal precursor on the catalytic and reduction behaviors of dispersed cobalt catalysts used for CO hydrogenation.  $\text{SiO}_2$ ,  $\text{CeO}_2$ , and  $\text{La}_2\text{O}_3$  were used as supports, while cobalt nitrate, chloride, and acetate salts were used as metal precursors. The effect of precalcination on subsequent reduction and catalytic behaviors of the metal was also studied. At 1 atm total pressure, and using an  $\text{H}_2/\text{CO}$  ratio of 2/1 at a reaction temperature of 250°C, the nitrate-derived catalysts had, in general, the highest activities for CO hydrogenation. The chloride-derived catalysts had inferior activities, unless a precalcination step was employed prior to reduction. The support material played a dominant role in determining reaction selectivity, with the average chain length of hydrocarbon products decreasing in the order  $\text{Co}/\text{La}_2\text{O}_3 > \text{Co}/\text{CeO}_2 > \text{Co}/\text{SiO}_2$ . The metal precursor employed did not have a significant effect on reaction selectivity, but it strongly influenced overall catalytic activity.

It has also been shown that both the support and the precursor affect the precalcination process. Complete conversion of the precursor to  $\text{Co}_3\text{O}_4$  during calcination occurs only for the  $\text{CeO}_2$ -supported catalyst;  $\text{Co}_3\text{O}_4$  was not detected for silica-supported cobalt acetate. Precalcination of the  $\text{La}_2\text{O}_3$ -supported catalysts resulted in formation of the perovskite  $\text{LaCoO}_3$ . These materials had different reduction behaviors than did the uncalcined catalysts, as shown by changes in CO hydrogenation activity, temperature-programmed reduction profiles, and x-ray photoelectron spectra.

### Alkane Conversions over Supported Nickel Catalysts

A pulse-flow reaction system was used to study the conversions of  $C_2$ - $C_7$  alkanes over  $SiO_2$ -,  $La_2O_3$ -, and charcoal-supported nickel catalysts. The effects of nickel loading level, reaction temperature, and reactant structure were examined in order to obtain a better understanding of the processes involved in the conversions of a variety of alkanes over these catalysts. The observed catalytic activity appear to be related to the size of the nickel particles present on the catalyst after reduction.

At  $400^\circ C$  and in the absence of added  $H_2$ , small nickel particles ( $<1$  nm), such as those on charcoal-supported catalysts with loading levels of  $\leq 2$  wt% Ni, catalyzed the unimolecular dehydrocyclizations of alkanes possessing linear units of six or more carbon atoms, but displayed virtually no activity for the conversion of alkanes having continuous chains of fewer than six carbon atoms. Homologation reactions did not occur over these small particles, and the formation of surface carbonaceous layers typically accounted for  $<10\%$  of converted reactant.

Over nickel particles predominantly in the size range 1-3 nm, such as were present at loading levels of 0.5-5 wt% on  $SiO_2$ -supported catalysts and on 5 wt% Ni/charcoal, the formation of gas phase products by hydrogenolysis and dehydrocyclization reactions at  $400^\circ C$  occurs by multimolecular pathways that involve the fragmentation of reactant molecules, followed by reassembly of the fragments. The formation of gaseous products over these catalysts was accompanied by the deposition of surface carbonaceous materials in quantities comparable to or greater than the sum of the gas phase products. These catalysts were also active for homologation reactions that yield product molecules having longer carbon chains than the original reactant.

Lanthanum oxide-supported catalysts with loading levels of 0.5-5 wt% Ni contained predominantly large metal particles ( $>3$  nm) and rapidly deactivated at  $400^\circ C$  due to the formation of surface carbonaceous deposits. The only gas phase product observed in the initial stages of the reaction was methane.

## PUBLICATIONS

The following publications have resulted from the financial support of the Department of Energy during the course of this project:

Rosynek, M.P., Fox, J.S., and Jensen, J.L., *J. Catal.* 71, 64 (1981).

Bukur, D.B., Lang, X., Rossin, J.A., Zimmerman, W.H., Rosynek, M.P., Yeh, E.B., and Li, C., *Ind. Eng. Chem. Research* 28, 1130 (1989).

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Bukur, D.B., Lang, X., Mukesh, D., Rosynek, M.P., and Li, C., *Ind. Eng. Chem. Research*, accepted for publication.

## STUDENTS

The following graduate students were financially supported by the Department of Energy and earned degrees as a result of this project:

Gregory N. DelliSante, Ph.D., 1983.

Sheau-Sheng Chen, Ph.D., 1984.

Robert J. Koprowski, Ph.D., 1985.

Kyte H. Terhune, M.S., 1985.

Amina A. Khalifa, M.S., 1986.

Christine A. Polansky, Ph.D., 1988.

Dale R. Palke, Ph.D., 1989.

William P. Addiego, Ph.D., 1989.