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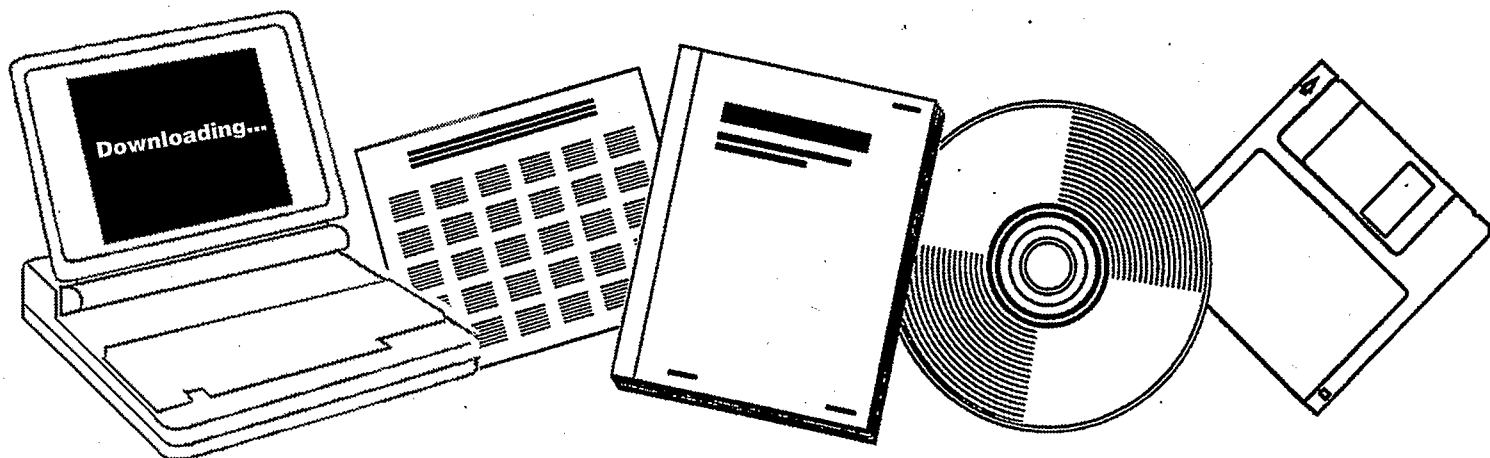
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**PROPERTIES OF LANTHANIDE OXIDES AS
SUPPORTS FOR TRANSITION METAL CATALYSTS:
PROGRESS REPORT FOR THE PERIOD MAY 1, 1986
TO APRIL 30, 1987**

TEXAS A AND M UNIV., COLLEGE STATION.
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Progress Report for the Period
May 1, 1986 to April 30, 1987

by

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Objective

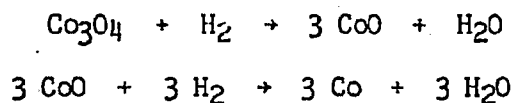
The overall objective of this project is to provide an understanding of the manner in which variations in oxidic support materials, particularly lanthanide oxides, and metal precursors influence the reduction, surface, and catalytic properties of dispersed non-noble Group VIII transition metals. During the past year, we have performed detailed temperature-programmed reduction (TPR) studies of two series of silica-supported cobalt catalysts, in an effort to elucidate the role played by various metal precursor compounds in determining the surface state of dispersed cobalt. As a result of these investigations, we have gained a general understanding of the potential complexity of the metal reduction process and, in particular, of the marked effect exerted by adsorbed water and surface hydroxyls.

Experimental

All experiments were performed with the TPR/Mass Spectrometry system described in our previous Progress Report, using a 12 cm³/min stream of 5 mole% H₂/N₂ reductant, a 20°C/min temperature ramp, and 20 to 50 mg samples of catalysts having metal loading levels of 3 to 6 wt%. Consumption of H₂ was monitored by a thermal conductivity detector (TCD); evolution of gaseous reduction/decomposition products was detected simultaneously by continuous diversion of a small fraction of the TCD effluent directly into an ultra-high vacuum system containing a quadrupole mass spectrometer. Metal precursors investigated included chloride, nitrate, and acetate salts. Each was deposited, using an incipient wetness impregnation technique, onto two types of silica support, viz., a porous gel (Davison Chemical Co., grade 57) having a surface area of 275 m²/g and a non-porous, SiCl₄-derived fumed silica (Cabot Corp., grade M-5), having a surface area of 200 m²/g.

Summary of Results

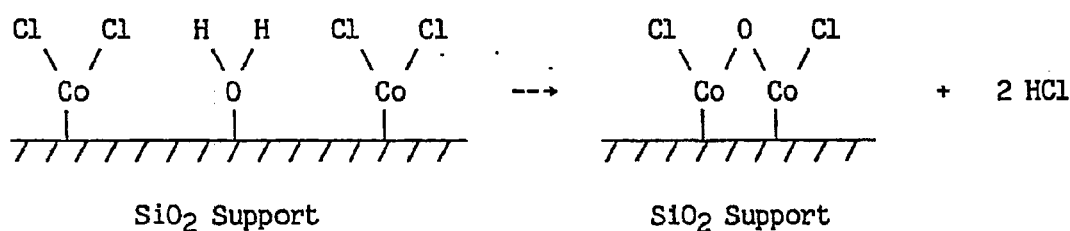
Pre-calcination, in 1 atm of either air or pure oxygen, at 500°C prior to reduction produces virtually identical results for all three of the cobalt precursors on both silica supports. The Co_3O_4 formed in all cases by this treatment reduces quantitatively to metallic cobalt, as evidenced by a characteristic TPR peak having a maximum at $400 \pm 20^\circ\text{C}$, corresponding to the two-step reduction process:



Successive re-oxidation/-reduction cycles result in the same TPR behavior. The Co_3O_4 generated by pre-calcination is quite uniform in all cases, as indicated by the relatively narrow (PWHM = 50°C) and symmetric TPR peak produced.

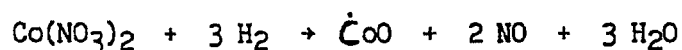
By contrast, direct reduction in H_2 , without pre-calcination, produces distinctly different behaviors for each of the three precursors investigated, and depends, furthermore, on the extent of surface dehydration/-dehydroxylation that has occurred prior to reduction commencement. Reduction of silica gel-supported CoCl_2 that has been pre-dried in a vacuum oven at 70°C produces two distinct TPR peaks, at 500° and 580°C, having approximately equal areas. Exposure to atmospheric water vapor at 110°C prior to TPR causes a decrease in the area of the low-temperature peak and a corresponding increase in the high-temperature peak. With the non-porous fumed silica support, on the other hand, only the low-temperature peak is observed, regardless of the extent of sample dehydration. We postulate that, during the TPR temperature increase, surface-bound CoCl_2 may interact at 100-400°C with water retained in the silica gel pores to form a bridge-bonded

oxychloride that is more difficult to reduce than CoCl_2 and results in the TPR peak at 580°C . This process is retarded by either prior removal of excess surface water, as effected by vacuum drying, or the absence of a micropore structure in the support, as is the case with fumed silica. The process may be represented schematically as follows:



Treatment in O_2 of the cobalt produced by reduction of $\text{CoCl}_2/\text{SiO}_2$ produces a uniform dispersion of Co_3O_4 , similar to that formed by pre-calcination, as shown by a characteristic peak at $\approx 400^\circ\text{C}$ when the resulting re-oxidized material is subjected to subsequent TPR.

In the case of $\text{Co}(\text{NO}_3)_2/\text{SiO}_2$, unlike that for CoCl_2 -derived catalysts, the NO_3^- anion is itself reducible in H_2 and produces a distinctively sharp TPR peak at $\approx 275^\circ\text{C}$ on both silica supports, corresponding to the process:



Evolution of NO was confirmed by mass spectral analysis of the TPR effluent. The nature of the CoO generated by nitrate reduction differs markedly from that formed via pre-calcination and subsequent Co_3O_4 reduction, since it does not give rise to the expected TPR peak at $\approx 400^\circ\text{C}$. The ease of reduction of the nitrate-derived CoO depends critically on the extent of sample dehydration prior to TPR commencement. With vacuum-dried samples, a subsequent TPR peak at $650\text{--}700^\circ\text{C}$ is observed, corresponding to virtually complete reduction of CoO to metallic cobalt. However, for samples exposed

to atmospheric water vapor prior to TPR treatment, two weak and very broad peaks occur, at 700°C and 850°C, and less than 20% reduction of cobalt occurs below 1000°C, the maximum temperature employed in the TPR experiments. Clearly, the presence of excess surface water during nitrate reduction results in an evidently highly dispersed form of cobalt oxide that is extremely difficult to reduce in H₂. Subsequent TPR of the material produced by re-oxidation in O₂ at 500°C of the Co(NO₃)₂/SiO₂ TPR end product gives the characteristic Co₃O₄ peak at ~ 400°C, but it is much broader than that for either the pre-calcined catalyst or the CoCl₂-derived catalyst. The role played by surface water in influencing the nature of nitrate-derived cobalt oxide is not yet fully understood and is the subject of current investigation.

Cobalt acetate differs from both of the other two cobalt compounds employed, since the precursor anion is decomposable, but not reducible. During TPR, acetate thermally decomposes into methane, carbon dioxide, and a form of cobalt oxide. The latter produces a weak form of the characteristic CoO/Co₃O₄ TPR peak at ~ 400°C, followed by a strong, broad peak at ~ 800°C that corresponds to complete cobalt reduction. Re-oxidation in O₂ at 500°C generates a highly dispersed CoO_x, as indicated by a weak TPR peak at 400°C, followed by a uniform, slow consumption of H₂ up to 900°C. As for Co(NO₃)₂/SiO₂, the nature of the cobalt oxide formed by reduction/-decomposition of Co(CH₃COO)₂/SiO₂ in the presence of excess surface water is not yet completely elucidated and remains the subject of continuing study.

Publications

A manuscript entitled "The Influence of Support on the Reduction Behavior of Dispersed Cobalt Catalysts," based on results obtained in this investigation, has recently been submitted for publication in the Journal of Catalysis. A copy of this manuscript is enclosed for reference purposes. Two additional papers, describing the effect of support variations on the catalytic behavior of dispersed cobalt for CO hydrogenation, are currently nearing completion.

Personnel

The following graduate students, all doctoral candidates, are currently being supported by funding from this project:

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