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Single-Source Precursors of Structured Catalysts for the Hydrogenation of 1,3-Butadiene

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The clusters of clusters $M_4O[(CO)_9Co_3CCO_2)]_6$, M = Zn (**I**), Co (**II**), are single-source precursors for porous, high surface area materials, referred to as ZnCo and CoCo, respectively. These two cobalt metal based materials were investigated as catalysts for the hydrogenation of 1,3-butadiene under a variety of reaction conditions. Both ZnCo and CoCo are active catalysts in the 50–300 °C temperature range, however, different activities and selectivities for the formation of products are exhibited. At reaction temperatures below 150 °C these catalysts show no loss of activity at up to 4 days on stream. Comparison of the catalytic properties of CoCo with a cobalt-supported alumina catalyst at similar metal loading shows that the cluster-derived catalyst exhibits both higher activity and different selectivity than the conventional supported cobalt catalyst. The observed hydrogenation activity and selectivity of these new materials relative to conventional catalysts or catalysts prepared from simpler precursors suggest that both the composition and microstructure derived from the complex precursor architecture contribute to the catalytic behavior. At reaction temperatures around 300 °C the activity of ZnCo and CoCo catalysts decrease due to the formation of carbon on the surface of the cluster materials and the partial collapse of the porous structure.

Introduction

The chemical synthesis of molecular precursors of materials provides new ways to old materials as well as the development of new materials.[1,2] In the case of materials that possess significant catalytic properties,[3-5] the precursor route offers access to active atoms in new microstructures. We have described a potentially general approach to the synthesis of large molecular architectures based on the idea of a metal cluster as a ligand substituent. Thus, by using the cobalt cluster substituted carboxylate ligand, $[(CO)_9Co_3CCO_2]^-$, we have synthesized several soluble species containing a large number of metal atoms, i.e., $Zn_4O[(CO)_9Co_3CCO_2]_6$ (**I**),[6-8] $Co_4O[(CO)_9Co_3CCO_2]_6$ (**II**)[8,9] (Figure 1), $Mo_2[(CO)_9Co_3CCO_2]_4$,[10] and $(CO)_3CoCd_3[(CO)_9Co_3CCO_2]_3(THF)_3$.[11] These compounds are related to the so-called dendritic molecules[12,13] but our building blocks have thus far been restricted to monofunctional ligands.

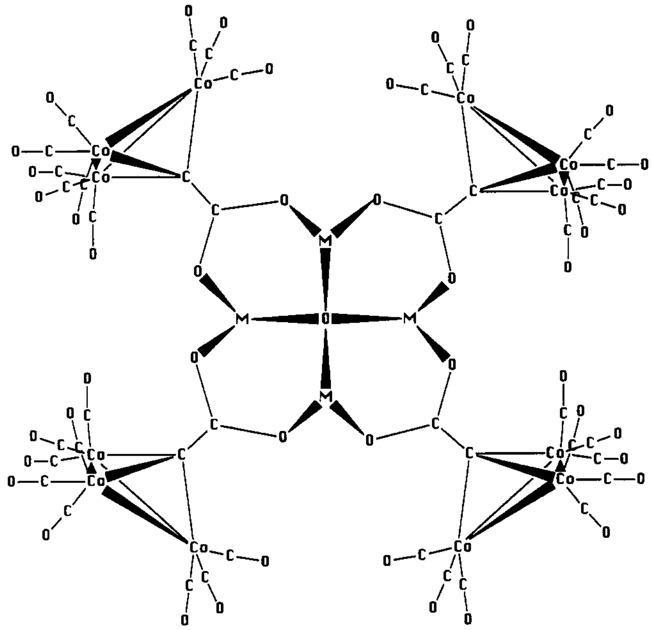

Figure 1. Schematic drawing of the molecular structures of $M_4O[(CO)_9CoCCO_2]_6$, M = Zn (**I**), Co (**II**) viewed down an S_4 symmetry axis of the M_4 tetrahedron. The $[(CO)_9CoCCO_2]^-$ ligands lying above and below the plane of the paper are not shown for clarity.

The thermal conversion of **I** by loss of 54CO and $6CO_2$ molecules according to eq 1 results in a highly porous solid

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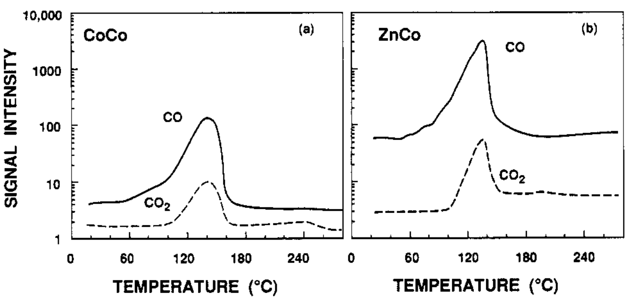

Figure 2. Results of the TPD experiments conducted on CoCo and ZnCo precursors in the 25–300 °C temperature range. Flow of helium 100 cm^3/min, mass of the precursor 10 mg, temperature ramp 6 °C/min.

product which we designate as ZnCo.[14] Heating in the

$$Zn_4O[(CO)_9Co_3CCO_2]_6 \rightarrow 54CO + 6CO_2 + Co_{18}Zn_4C_6O \quad (1)$$

temperature range 180–250 °C in vacuo or in a flow of He or N_2 produces a narrow distribution of pore sizes (≈50 Å), exposed cobalt metal, and overall surface areas of ≈100 m^2/g. Extreme air sensitivity suggests high overall activity and we have now explored the catalytic activity of ZnCo and CoCo (prepared in similar fashion from the pyrolysis of **II**) for the hydrogenation of 1,3-butadiene. It is well-known that this reaction can be conducted at low reaction temperatures and that it constitutes a relatively fast and simple test of catalytic properties.[15-17]

Hence, even though we are not primarily interested in developing a new hydrogenation catalyst, we chose it as a convenient characterization reaction. That is, the principal objective of this study was to determine if the microstructure of the materials produced from the pyrolysis of **I** and **II** (ZnCo and CoCo) would result in differences in catalytic activity and selectivity toward hydrogenation relative to conventional catalysts or catalysts prepared from precursors possessing a simpler structure. Further, we wished to determine whether activity and selectivity would vary as a function of the different core metals Zn and Co.

Experimental Section

Catalysis Precursors. Catalytic materials used for the hydrogenation of 1,3-butadiene were prepared by the chemical methodology described in detail elsewhere.[6-8] Infrared spectroscopy was used to monitor purity of the crystalline samples of **I** and **II** used in these studies. Consistent with the earlier thermal gravimetric analysis (tga) of **I**,[6] the tga of **II** exhibited a single weight loss of 58.6% (calculated for loss of 54CO and $6CO_2$, 57.4%) at a slightly lower temperature than that for **I**. Results of thermal programmed desorption (TPD) experiments conducted on **I** and **II** in the 25–300 °C temperature range over 45 min are presented in Figure 2. CO and CO_2, with the former being more abundant, were produced as expected. Under these conditions, the temperature at which maximum concentrations of CO and CO_2 are observed is the same for both catalysts.

The 8 wt % Co/Al_2O_3 catalyst, which was used for comparison of the activities of CoCo and Co supported on alumina, was prepared by the incipient wetness impregnation from the water suspension of cobalt nitrate and high surface area alumina supplied by Harshaw Corp. After evaporation of water from the mixture, the resulting thick paste was dried at 150 °C in the oven overnight and then calcined at 500 °C. Prior to each experiment CoO/Al_2O_3 was reduced in a hydrogen flow at 650 °C for 4 h. In most cases, data were collected after 5 h time on stream, in order to provide sufficient time for the stabilization of the reaction conditions.

Catalytic Measurements. Steady-state measurements were performed using two single-pass flow reactors made of quartz silica with an i.d. of 9.5 and 4 mm. The reactors were heated by an electric furnace over a length of 15 cm. The temperature inside the reactor was monitored by a K-type thermocouple and was controlled by a programmable temperature controller (OMEGA 2012). The lower i.d. reactor allowed for the better distribution of the catalyst material throughout its cross-sectional area at low catalyst loadings. Experimental conditions were selected in order to minimize the effect of the exothermicity exhibited by the hydrogenation reaction. Helium was used as a carrier gas, and a typical set of operating conditions during activity measurements was as follows: temperature 150 °C, helium and hydrogen flow rates 50 cm^3/min each, and C_4H_6 flow rate 1.6 cm^3/min. Catalyst loadings were varied, however, the majority of the activity measurements was conducted in the 9.5-mm-i.d. reactors using 25-mg loadings of **I** or **II**, whereas during experiments performed in the other type of reactor (4-mm i.d.) loadings were fixed at 6 mg, unless otherwise specified. When the catalyst loadings were changed, the reactor size was also changed to maintain approximately the same ratio of reactor volume to catalyst volume. This is akin to maintaining the same space velocity if in both reactors the height of the catalyst bed is about the same. Prior to each catalytic experiment the ZnCo and CoCo precursors, **I** and **II**, were pretreated in a flow of helium at 200 °C for 2 h (unless stated otherwise) in order to form well-defined, porous material of the composition $M_4O[Co_3C]_6$, M = Zn, Co, which served as the putative catalyst. In situ catalysis preparation was required as any exposure of the catalysts to air results in violent oxidation and destruction of the catalytic properties.

Reaction products were analyzed by a 5890 Hewlett-Packard gas chromatograph equipped with a FID detector. Effluent gases (i.e., 1-butene, *n*-butane, *cis*-2-butene, *trans*-butene, and 1,3-butadiene) were separated on a picric acid column (6 ft × $^1/_8$ in.) supplied by Alltech. Carbon balances, which were calculated for all experiments, were closed within 5%. Conversion is defined as one minus the ratio of the amount of carbon detected in the products and the amount of carbon in the feed, while selectivity is defined as the amount of carbon converted to a given product divided by the total amount of carbon converted.

X-ray Photoelectron Spectroscopy. XPS measurements of CoCo and ZnCo catalysts were conducted with a KRATOS XSAM 800 spectrometer using a magnesium anode. Samples in the form of thin films were prepared by evaporating a concentrated solution of **I** and **II** in THF on the surface of the gold-plated holders. The holders were mounted on the heatable, direct insertion probe and were placed in the sample transfer chamber. Pretreatment was for 2 h at 200 °C under a 10^{-8}-Torr vacuum. The reaction gas mixture was bled into the vacuum chamber such that the steady state pressure was 0.3 Torr while the sample was heated for 2 h at 100, 200, and 300 °C. Between the pretreatment and each of reactions the transfer chamber was evacuated down to 10^{-8} Torr and the sample cooled down before introducing it into the analysis chamber. The Co(2p), C(1s), O(1s) and Zn(2p) ionization regions were analyzed for **I** and **II** and for ZnCo and CoCo after pretreatment at 200 °C and after reaction at 100, 200, and 300 °C without removing the sample from the system or exposing it to the laboratory atmosphere. The reported binding energies were referenced to adventitious carbon at 285 eV.

Other Physical Measurements. The BET total surface area measurements were conducted using a Quantachrome unit with nitrogen as the adsorbing gas at 77 K and helium as the carrier. During TPD measurements, gases were analyzed by a UTI 100C quadrupole mass spectrometer equipped with a fast-response continuous inlet system. Mass to charge ratios of 28 and 44 were used for the analysis of CO, and CO_2 respectively, after appro-

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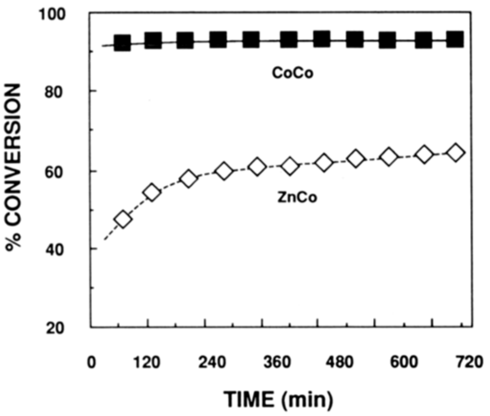

Figure 3. Conversion of butadiene vs time-on-stream for C_4H_6 hydrogenation on CoCo and ZnCo catalysts. Total gas flow rate 100 cm^3/min, mass of the catalyst during reaction 10 mg, loading of the precursor 25 mg, temperature 150 °C.

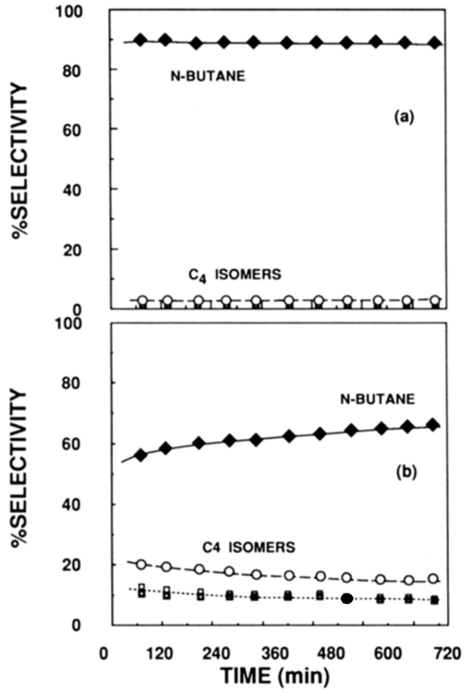

Figure 4. Selectivities of products vs time-on-stream during hydrogenation of butadiene on (a) CoCo and (b) ZnCo catalysts. Total gas flow rate 100 cm^3/min, mass of the catalyst during reaction 10 mg, loading of the precursor 25 mg, temperature 150 °C.

priate calibration. The 4-mm-i.d. reactor was used for the TPD studies as gas residence times were lower compared to the reactor with the higher i.d.

Results and Discussion

The catalyst activity versus time-on-stream during 1,3-butadiene hydrogenation was measured for CoCo and ZnCo catalysts at 150 °C and the results are presented in Figure 3. After 12 h of experiment, both catalysts exhibit steady-state activity; however, for the CoCo catalyst conversion of butadiene approaches 100%, whereas for the ZnCo catalyst butadiene conversion does not exceed a value of 65%. Figure 4 indicates that the selectivities differ as well. For the CoCo catalyst the main reaction product is *n*-butane (Figure 4a, selectivity ~90%). In the case of the ZnCo catalyst (Figure 4b), *n*-butane is still the major reaction product but the proportion of butene isomers (1-butene, *cis*-2-butene, and *trans*-butene) are significantly larger. Clearly the presence of zinc in the ZnCo catalyst leads to a different distribution of the reaction products compared to the CoCo catalyst.

Table I. BET Total Surface Areas[a] of Precursors and Catalysts

material	before pretr	after pretr
CoCo	8.4	88.0
ZnCo	7.7	116
Al_2O_3	204	204
8% Co/Al_2O_3	205	205

[a] In m^2/g using a pretreatment temperature of 200 °C.

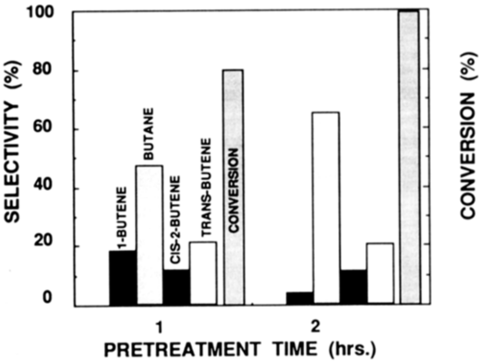

Figure 5. Effect of the pretreatment time at 200 °C on the activity and selectivities of CoCo catalyst. Mass of the precursor 12 mg, total gas flow rate 100 cm^3/min, reaction temperature 70 °C.

It is important to note that when the hydrogenation reaction was conducted in the presence of **I** and **II** at temperatures below 100 °C (i.e., prior to thermal decomposition), without any catalyst pretreatment, no measurable conversion of butadiene was observed. Thus, the precursors of ZnCo and CoCo are inactive for the hydrogenation reaction and loss of the CO and CO_2 ligand moieties is required for activity. Furthermore, the material produced from the thermal decomposition of $(CO)_9Co_3CCOOH$ alone has similar activity for the hydrogenation reaction to that for CoCo but the product selectivities are different.

To determine if the difference in activities of ZnCo and CoCo could be attributed to surface area differences, a series of BET surface area measurements was conducted on four different catalyst samples. The results of these measurements are presented in Table I and indicate that the total surface area of ZnCo and CoCo catalysts before and after 200 °C nitrogen pretreatment are comparable. After pretreatment they both are in the range of ~90 m^2/g with ZnCo surface area exceeding that of CoCo. Thus, if the reaction rates were similar for both catalysts, the activity of ZnCo for the hydrogenation of butadiene should be higher. Since this is not the case, the different activities of the two materials cannot be simply due to differences in surface areas.

The effect of the pretreatment time at 200 °C on the activity and selectivity of CoCo is presented in Figure 5. To enhance the effect of pretreatment temperature, the hydrogenation reaction was conducted at 70 °C such that butadiene conversions were below 100%. The activity–selectivity results for CoCo show that butane is still the major reaction product and changes in pretreatment time do not produce any qualitative changes in behavior. Increasing pretreatment time over 2 h has no effect on catalyst activity or selectivity. The same experiments showed no significant differences in the activity of Zn

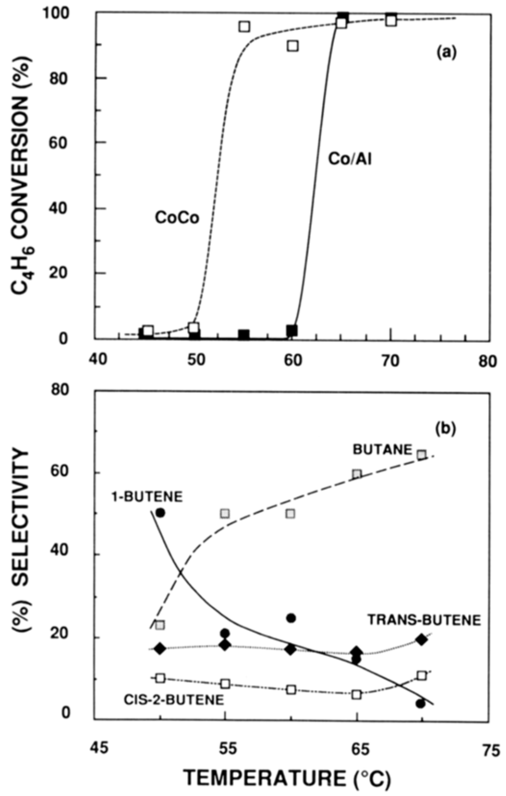

Figure 6. (a) Results of the low temperature activity measurements conducted on CoCo and Co promoted alumina catalysts. (b) Selectivities of products during C_4H_6 hydrogenation on CoCo catalyst. Total flow rate 100 cm^3/min, loading of the precursor 6 mg, loading of Co/Al_2O_3 35 mg.

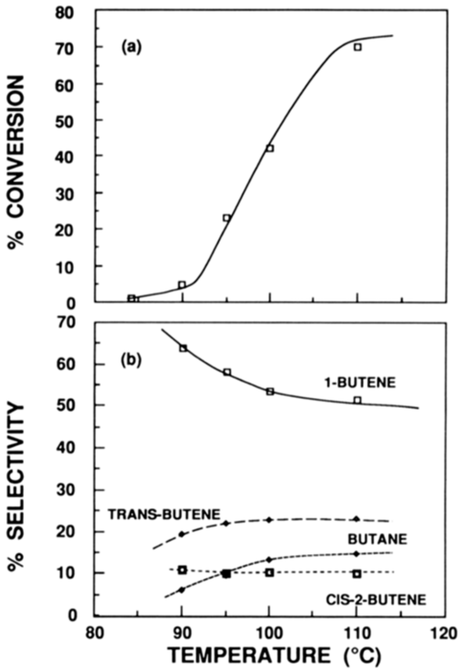

Figure 7. (a) Results of the low temperature activity measurements conducted on ZnCo catalyst. (b) Selectivities of products during C_4H_6 hydrogenation on ZnCo catalyst. Total flow rate 100 cm^3/min, precursor loading 6 mg.

clusters with different pretreatment times. Thus, it appears that the pretreatment time is related to the extent of transformation of the precursor cluster into the active CoCo structure. Once complete, no significant changes in the activity occur. Presumably at 200 °C the steady state structure of the ZnCo precursor is achieved more rapidly than that of CoCo.

Once a steady activity is achieved the catalysts remain fully active. (The maximum period monitored was four days.) Note that when a similar reaction is conducted over metal-supported catalyst such as Pt or Ni, a significant deactivation occurs.[18]

To explore the origin of the differences of CoCo and ZnCo catalysts further, the effect of the reaction temperature on the activity and selectivity was examined. Figure 6 presents conversion and selectivity results obtained during hydrogenation of butadiene on CoCo catalyst as a function of temperature. Figure 6a includes activity results of the hydrogenation experiment conducted on Co/Al_2O_3 which will be discussed in detail below. Similar results obtained for the ZnCo catalyst are presented in Figure 7. The shape of both graphs in Figures 6a and 7a indicate that the temperature dependence of butadiene conversion exhibits ignition type of behavior due to the exothermicity of the hydrogenation reaction. For the CoCo catalyst a rapid increase in the C_4H_6 conversion starts at 50 °C, while the increase in the conversion with temperature for ZnCo catalyst starts around 90 °C confirming lower activity of this material. In the case of ZnCo catalysts there is a small discrepancy in the conversion-temperature results between Figures 3 and 7. This is partially due to the fact that these were two different batches of catalysts, and it is difficult to reproduce exactly all conditions. This is understandable considering the small amount of catalysts used. Selectivity results indicate that the major reaction product for CoCo is butane (except at the lowest temperature where conversion is low), whereas for ZnCo it is 1-butene. A specific rate for the conversion of butadiene estimated for the CoCo catalyst at 3% conversion at 373 K is in the order of 1.4×10^{-7} mol/(s m^2) where as for ZnCo it is 9.3×10^{-8} mol/(s m^2). These rates are of the same order of magnitude as those reported for the hydrogenation of 1,3-butadiene on palladium catalysts.[19] In the region of the lower butadiene conversion, i.e., below 5%, the major reaction product is 1-butene for both catalysts.

Formation of 1-butene as a primary product is consistent with the reaction mechanism proposed by Pradier and Berthier.[17] These authors suggest that in order to be catalytically activated butadiene has to be adsorbed on the surface as the di- or tetra-σ bonded species proposed by Avery and Sheppard.[20] The other form of adsorbed butadiene, the so-called "butylidyne", is catalytically inactive and involves only one carbon atom bonded to the surface.[21] The results of temperature variation on activity and selectivity suggest that the initial reaction step during hydrogenation of C_4H_6 on CoCo involves surface adsorption of butadiene followed by reaction with adsorbed hydrogen to yield butene. Since butane is formed by surface hydrogenation of butenes, the higher selectivities toward the latter products exhibited by ZnCo catalyst suggest that the presence of Zn atoms activates desorption of butenes from the surface. If the CoCo catalyst functions via the same reaction mechanism,[17] the observed high

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butane selectivity indicates promotion of this product by the readsorption of butenes at higher temperatures, when the surface of the catalyst is partially free of butadiene.

The hydrogenation reaction conducted on CoCo and ZnCo catalysts at temperatures approaching 300 °C produces a large change in behavior. Under these conditions, conversion of butadiene decreased dramatically from ~95 to around 15% and from 70 to ~20% for CoCo and ZnCo, respectively. A change in selectivity results is reflected by a shift in the major reaction products. In both cases 1-butene was a major product at low conversion levels. A likely factor responsible for this type of behavior is the formation of surface carbon covering the active sites on both materials (see below). Exposing the catalysts to an overnight treatment in a flow of helium at 300 °C restored the activity of both materials to ~60% of their initial levels at 150 °C. Full activity is not expected as we have shown previously that the pores begin to collapse at 300 °C resulting in a significant loss in surface area.[14] On the basis of these results, it was concluded that the high-temperature He treatment caused desorption of most of the weakly adsorbed carbon residues from the surface of both materials.

To determine if CoCo catalyst exhibits different activity compared to cobalt promoted alumina, additional experiments were conducted in order to compare CoCo and 8% Co promoted Al_2O_3. Activity experiments were conducted at similar loadings of cobalt. The BET surface area measurements reported in Table I show that there is no change in the surface area of alumina after promotion with cobalt. A simple calculation of the Al_2O_3 surface coverage by cobalt, assuming monolayer distribution of the Co promoter, indicates that only ~10% of the alumina is covered by cobalt atoms. This corresponds to an active area of 20 m^2/g. To distinguish between activities and selectivities of both materials the ignition temperature was measured for both catalysts. Figure 6a, indicates that the ignition temperature for the reaction conducted in the presence of CoCo is around 53 °C, while the similar temperature for the Co/Al_2O_3 catalyst is ~10 °C higher. In the case of cobalt alumina catalyst, the only reaction product detected by FID gas chromatography was *n*-butane whereas the CoCo catalyst produces significant amounts of isomeric butenes as well. This behavior suggests that the hydrogenation of the second double bond of butadiene is faster on the dispersed catalyst. We conclude that it is the unique, well-defined, high surface area structure of the CoCo catalyst which results in a higher activity and different selectivity than those exhibited by the Co/Al_2O_3 catalyst prepared by the traditional wet impregnation technique. Note that a disadvantage of the latter method is the fact that it does not allow for a controlled distribution of the promoter on the surface of the catalyst support, i.e., although assumed to be monodispersed, it may not be.

To analyze structural and compositional changes responsible for the high-temperature deactivation of CoCo and ZnCo catalysts and also to get a better understanding of the state of the surface during reaction, a series of XPS experiments was conducted. A sample transfer chamber connected to the spectrometer allowed for treatment of samples in vacuum, inert or reaction atmospheres without exposure to oxygen, thus preventing oxidation of the sample surface. Figure 8 presents Co(2p) and C(1s) binding energy regions for CoCo in three different states: as precursor (**II**), as virgin catalyst after pretreatment at 200 °C which showed no change after reaction at 200 °C, and after reaction at 300 °C. Similar results are shown in Figure 9 for Co(2p), C(1s), and Zn(2p) regions of the ZnCo catalyst. Data from the XPS measurements are summarized in Table II.

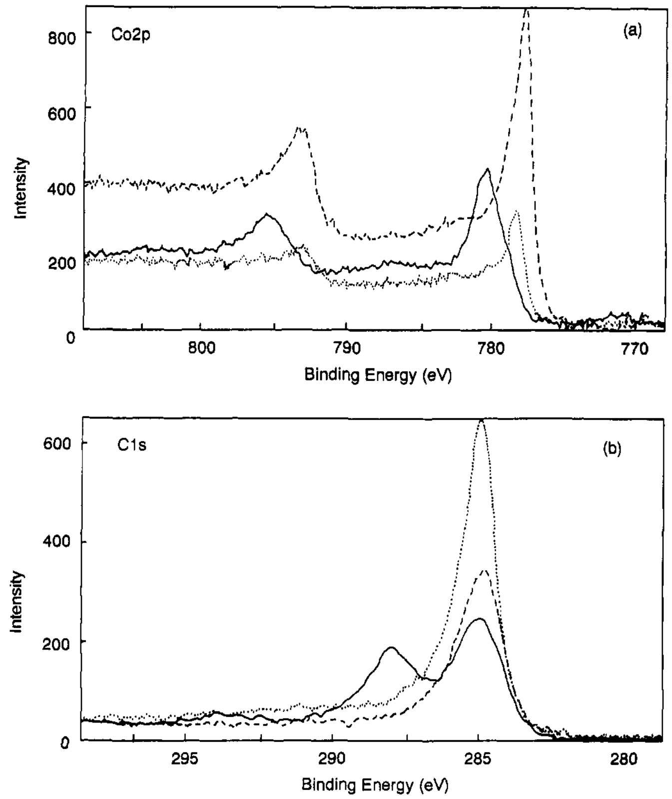

Figure 8. Results of the XPS measurements conducted on the CoCo precursor and the CoCo catalyst. (a) Signal intensity ($\times 10^{-3}$) vs Co2p binding energies. (b) Signal intensity ($\times 10^{-3}$) vs C1s binding energies. The solid line corresponds to the CoCo precursor, dashed line corresponds to the CoCo sample after 200 °C pretreatment (no change after 200 °C reaction), dotted line corresponds to the CoCo sample after 300 °C reaction.

Table II. XPS Binding Energies and Relative Intensities for the Two Precursors and Catalysts

binding energies/ intensity × 10^{-3}	before pretr	pretr 200 °C	reaction 100 °C	reaction 300 °C
		CoCo		
Co2p	780.2/77	778.1/163	778.2/158	778.1/62
O1s	532.3/96	532.8/63	532.9/64	533.3/69
C1s	287.8, 285.0/47[a]	285.0/66	285.0/70	285.0/128
		ZnCo		
Co2p	780.0/50	778.0/49	778.0/44	778.1/12
Zn2p	1021.4/63	1021.6/141	1021.5/130	1021.6/11
O1s	532.8/60	531.0/33	531.4/32	532.8/13
C1s	287.7, 285.0/19[a]	285.0/43	285.0/46	285.0/87

[a] For the ionization at 285 eV.

On the basis of these results, it is evident that in both ZnCo and CoCo the 200 °C pretreatment causes a significant shift (≈2 eV) of the cobalt peaks toward the binding energy characteristic of metallic cobalt.[14,22] At the same time, there is a significant change in the carbon region. Before pretreatment of both samples there is a characteristic double carbon peak with maxima at 287.8 eV, due to carbon in the CO and CO_2 moieties of **I** and **II** and at 285.0 eV due to adventitious carbon and the carbon

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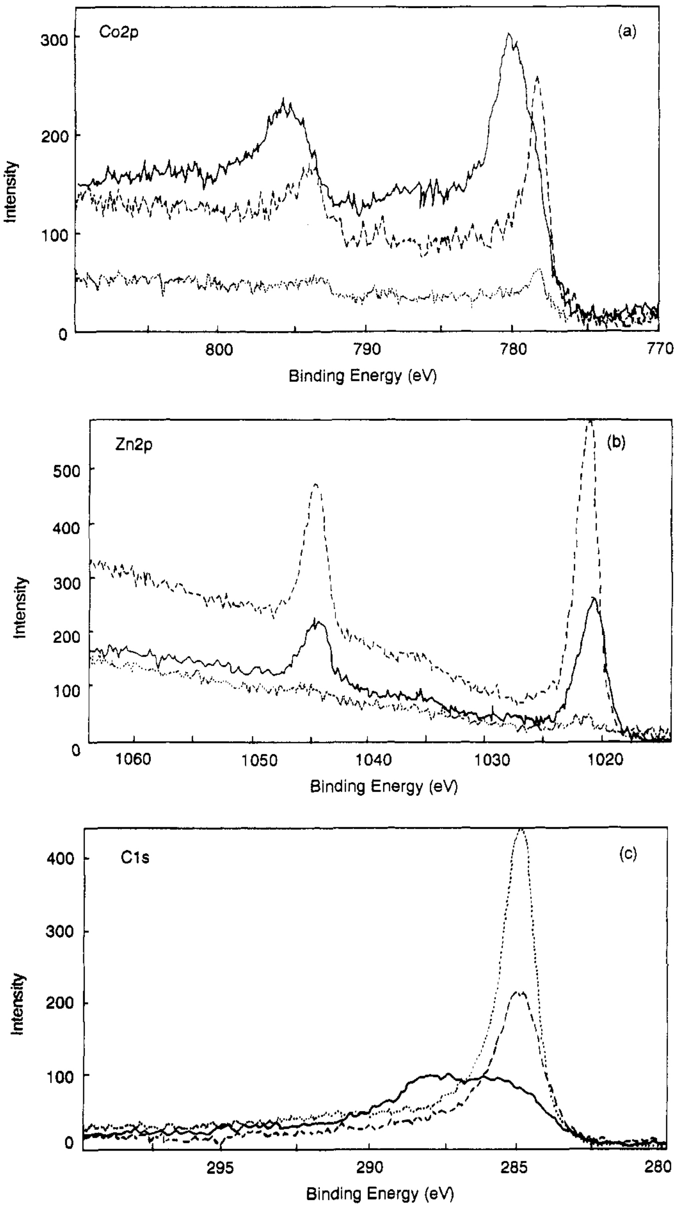

Figure 9. Results of the XPS measurements conducted on the ZnCo precursor and the ZnCo catalyst. (a) Signal intensity ($\times 10^{-3}$) vs Co2p binding energies. (b) Signal intensity ($\times 10^{-3}$) vs Zn2p binding energies. (c) Signal intensity ($\times 10^{-3}$) vs C1s binding energies. The solid line corresponds to the ZnCo precursor, dashed line corresponds to the ZnCo sample after 200 °C pretreatment (no change after 200 °C reaction), dotted line corresponds to the ZnCo sample after 300 °C reaction.

bound to the metal atoms. After the 200 °C pretreatment, the carbon peak has just a single maximum at 285.0 eV. The peak related to CO and CO_2 disappears in agreement with the tga and TPD results (Figure 2). Within experimental error, there is no change in the position of the Zn(2p) ionization during pretreatment. However, the Zn binding energy is not very sensitive to chemical environment.[22]

When the pretreated catalyst sample was exposed to the reaction mixture, which included helium, hydrogen, and butadiene (49, 49, 2 vol %) at 100 and 200 °C, no significant changes in the Co(2p), Zn(2p), and C(1s) binding energies were observed. However, in the case of the ZnCo catalyst, there was a change in the relative intensities of the ionizations. After pretreatment at 200 °C, the ratio of Zn/Co increases compared to **I**. This suggests that during heating zinc diffuses from the bulk of the catalyst to the surface. This increase in the surface concentration of Zn is likely to be the factor responsible for different product selectivities observed during hydrogenation of butadiene on ZnCo catalyst.

When the reaction temperature was raised to 300 °C a large increase in the C(1s) line is observed, while the Co(2p) and Zn(2p) intensities decrease. This suggests that at temperatures approaching 300 °C an overlayer of carbon is formed on the surface of both catalysts. These XPS results agree with the activity data showing that at 300 °C the activity and selectivity of CoCo and ZnCo decrease significantly. For the ZnCo catalyst at 300 °C, the surface concentration of Zn with respect to Co decreases. This result can be explained by the fact that at temperatures around 300 °C vaporization of surface zinc can take place.[14]

Both the activity and XPS studies presented here show that in the 100–200 °C temperature range the reactants produce no detectable change of the surface structures of ZnCo and CoCo catalysts. This negative result is strengthened by the observation of significant changes in the surface compositions of both catalysts at 300 °C. The changes which result in the decrease of catalytic activity can be related to carbon deposition and, in the case of ZnCo, to the evaporation of zinc from its surface. Evaporation of Zn would decrease the surface area of the ZnCo structure and thus decrease the activity.

Summary

In summary, the results reported in this study indicate that the material derived from cobalt-based clusters of clusters exhibit unique properties during catalytic hydrogenation of butadiene. These properties can be attributed to a precursor derived microstructure. Differences in precursor composition are expressed in the differences in activities and selectivities observed for the CoCo and ZnCo catalysts. Since related clusters of clusters can be synthesized with both different structures and metal contents, this single source precursor approach to the preparation of catalytic materials can be extended to other systems.

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