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Novel cluster-derived catalysts for the selective hydrogenation of crotonaldehyde

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The controlled pyrolysis of transition metal cluster substituted metal carboxylates, e.g., $M_4O[(CO)_9Co_3CCO_2]_6$, where M = Co and Zn, and $M'_2\{(CO)_9Co_3CCOO\}_4$, where M′ = Co, Mo, and Cu, results in the formation of high surface area, amorphous solids that are active and selective catalysts for the hydrogenation of crotonaldehyde. In contrast to conventional metal catalysts that are selective for the double bond hydrogenation, these new solids exhibit high regioselectivities for the conversion of crotonaldehyde (2-butenal) to crotyl alcohol (2-butenol). Further, the observed selectivities depend on the metal cluster carboxylate structure.

Keywords: organometallic clusters; crotonaldehyde hydrogenation; selective hydrogenation; novel catalysts for

1. Introduction

Recently, we have described a new approach to the development of heterogeneous hydrogenation catalysts with unique properties using clusters of clusters [1,2]. The use of organometallic precursors to prepare small catalyst particles is a well known approach in catalysis [3,4]. Unfortunately, these materials often lose their structure upon activation, reaction, or interaction with the support [5,6]. Coordination compounds with complex cluster substituents ("clusters of clusters") have been found to be suitable precursors for high surface area self-supported metal catalysts [1]. By the simple expedient of replacing alkyl groups in metal carboxylate coordination compounds by the cluster fragment, $(CO)_9Co_3C$–, we have been able to synthesize high molecular weight, tractable molecules in high yield [7,8]. These clusters have structures that are preserved upon controlled pyrolysis, leaving behind solids with high surface areas that exhibit a distinct activity and selectivity

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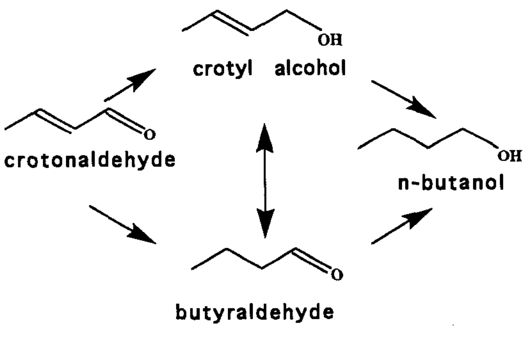
depending on the stage of decomposition of the clusters. Our previous work has focused on studies of the hydrogenation of 1,3-butadiene [9,10] on catalysts made from precursors containing Co, Zn, Cu or Mo metal cores coordinated to the complex Co–carbonyl cluster ligands.

This paper reports results obtained using clusters of clusters as precursors for catalysts for the selective hydrogenation of α–β unsaturated aldehydes to unsaturated alcohols. Although stoichiometric reagents and homogeneous catalysts (including two-phase systems) have been reported for the regioselective reduction of crotonaldehyde (2-butenal) to crotyl alcohol (2-butenol) [11,12], a stable heterogeneous catalyst for this intramolecular hydrogenation has not been reported (see scheme 1). Typical hydrogenation catalysts (i.e., Pt supported on SiO_2) convert crotonaldehyde, to the thermodynamically favored products (butyraldehyde (1-butanal), and *n*-butanol) rather than to the desired kinetic product crotyl alcohol (2-butenol) [13]. When butanol is observed, catalyst deactivation is often a problem. To the best of our knowledge, the highest stable selectivity reported for the gas phase reactions is 37% (yield 5%) for a TiO_2-supported Pt catalyst [13]. Liquid phase reactions have much higher selectivities (as high as 90% selectivity with 90% yield [14]), however in most of the cases, the catalyst recovery, the separation of the products from the solvents, reactants and catalyst deactivation are important considerations [15]. To improve selectivity of crotyl alcohol, the catalysts have been modified by alloying [16], by adding promoters [17], by incorporating strong interaction support [13] or by controlled poisoning [18]. In the following, a new method for the preparation of catalysts using clusters of clusters leading to materials exhibiting greatly improved regioselectivity for the gas phase hydrogenation of crotonaldehyde to crotyl alcohol is reported.

2. Experimental

2.1. CATALYSTS PREPARATION

The preparative methods for the molecular precursors $M_4O[(CO)_9Co_3CCO_2]_6$,



Scheme 1.

where M = Co and Zn have been described elsewhere [1,2,7,8]. The synthesis of the $M_2\{(CO)_9Co_3CCOO\}_4$ precursor and its characterization have also been described elsewhere [10]. The general strategy for the synthesis consists of replacing acetate in metal acetates by the cluster carboxylate, $(CO)_9Co_3CCO_2^-$. Detailed characterization of the resulting precursors is conducted by transmission IR, single crystal X-ray diffraction and chemical analysis [7]. Catalysts are formed in situ by the controlled pyrolysis of the molecular precursors in helium or hydrogen.

2.2. CATALYST CHARACTERIZATION

In all the experiments care was taken not to expose the precursors to air. The weight loss taking place during thermal decomposition was measured with a Cahn RG Electrobalance. The sample was heated linearly in flowing helium or hydrogen (100 ml/min, NPT). The electronics of the electrobalance was purged with flowing argon. All the gases used were ultra high purity and were further passed over traps to remove water. The species evolving from the molecular precursors during the activation, were identified using a quadrupole mass spectrometer (UTI-100-C) equipped with a fast response continuous inlet system [9].

Other characterization methods used were in situ diffuse reflectance IR (DRIFTS) studies conducted during pyrolysis of the molecular precursors, XPS measurements, and BET surface area measurements. XPS measurements of the fresh molecular precursors were performed after evacuating the samples in a pretreatment chamber, then the precursors were converted into the catalytic material, and the spectra of the resulting solids were measured. The BET surface areas were measured with a Quantachrome unit at 77 K with nitrogen as the adsorbate and helium as the carrier gas. Materials were prepared in situ from the appropriate precursors to avoid changes due to oxidation in air.

2.3. CATALYTIC ACTIVITY

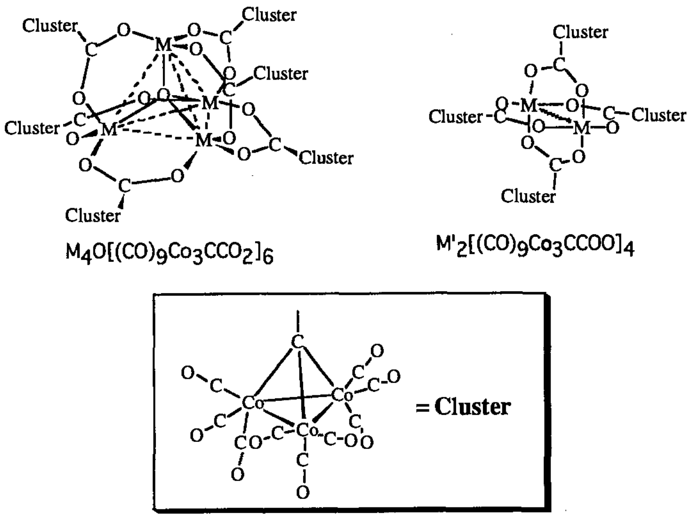
The hydrogenation of crotonaldehyde was studied in a quartz flow microreactor (4 mm i.d.) system described elsewhere [9] at atmospheric pressure in the temperature range 353–453 K. The molecular precursors (~ 15 mg) were activated in situ in hydrogen at 373 K for 2 h to yield low temperature catalysts (LT catalysts) or at 473 K for 2 h to yield high temperature catalysts (HT catalysts). Hydrogen and helium flows metered by electronic flow controllers were bubbled over crotonaldehyde kept at a temperature of 273 K and the feed lines were kept at 323 K such that condensation was not a problem.

The reactor effluent was analyzed by gas chromatography on a Varian 3700 GC provided with a FID detector. A 10% carbowax 20M on chromosorb 80/100 mesh packed column (Alltech) was used to separate the effluents which were crotonaldehyde, crotyl alcohol, butanol, butyraldehyde and butane.

3. Results and discussion

The cluster substituted carboxylates used in the preparation of catalysts have characteristic shapes, i.e., $M_4^{II}O\{(CO)_9Co_3CCOO\}_6$ is a ~ 25 Å diameter sphere and $M_2^{II}\{(CO)_9Co_3CCOO\}_4$ is a ~ 20 Å diameter, ~ 10 Å high pill box, where M^{II} is a metal cation, e.g., Co^{2+} (scheme 2).

The clusters were pyrolyzed in the TGA by heating linearly from room temperature to 673 K in flowing hydrogen for 190 min [9]. The weight loss versus temperature shows the occurrence of two plateaus in the temperature ranges of 373–393 K and at 473–493 K. After determining the temperature range in which the plateaus appeared, the pyrolysis procedure was modified to allow the solids to reach equilibrium by heating from room temperature to 393 K remaining at that temperature for 2 h and then increasing the temperature to 493 K for 2 h. Fig. 1 shows the weight loss for the $M_4^{II}O\{(CO)_9Co_3CCOO\}_6$ and $M_2^{II}\{(CO)_9Co_3CCOO\}_4$ precursors showing the first plateau which corresponds to the loss of external carbonyl ligands. Subsequent heating to 493 K, results in the second plateau corresponding to the break-up of the carboxylate core. Thus, two distinct amorphous materials, which are designated LT (low temperature) and HT (high temperature), respectively, are formed. In the case of the LT materials, X-ray photoelectron spectroscopy, mass spectrometry–temperature programmed decomposition and infrared spectroscopic studies indicate that the carboxylate core remains intact yielding spherical or pill-like particles, respectively, with cobalt metal surfaces [9]. The detailed structures of the HT materials are not known but that both of these solids are air sensitive, amorphous, porous, and high surface area (up to 200 m^2/g) solids [9]. It is important to note that active, high surface area materials are not formed if the cluster core decomposes before the external clusters [19].



$M_4O[(CO)_9Co_3CCO_2]_6$

$M'_2[(CO)_9Co_3CCOO]_4$

Scheme 2.

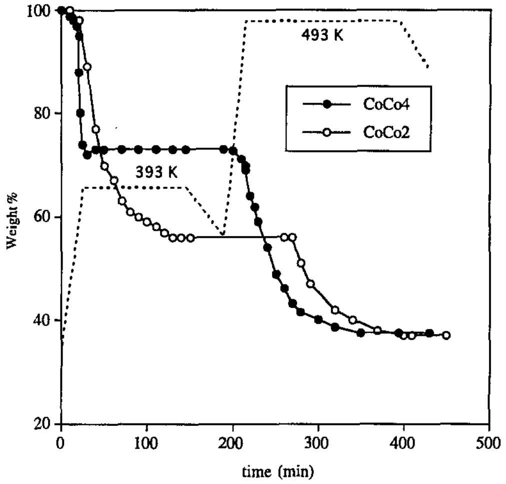


Fig. 1. Thermogravimetric analysis plot of activation of the cluster of clusters performed before reaction: (a) activation of CoCo2, (b) activation of CoCo4.

To evaluate their catalytic activity, the cluster carboxylate precursors were pyrolyzed in situ in hydrogen flow for 2 h, at either 393 K for the preparation of the LT material, or at 493 K for the HT material. Fig. 2 shows the conversion and selectivity for the catalysts derived from the $M_4^{II}O\{(CO)_9Co_3CCOO\}_6$ clusters with M = Co and Zn (denoted as MCo4), and at different temperatures. As expected, the selectivity decreases as the temperature increases. The best yield of crotyl alcohol to date, obtained on the catalysts prepared from $Co_4^{II}O\{(CO)_9Co_3CCOO\}_6$, is 25% (84% conversion, 30% selectivity). The corresponding TOF = 8×10^{-3} s^{-1} at 423 K. The TOF value is based on hydrogen chemisorption measurements and BET data. The catalyst prepared from $Zn_4^{II}O\{(CO)_9Co_3CCOO\}_6$ (ZnCo4, same shape, less stable core than CoCo4) has

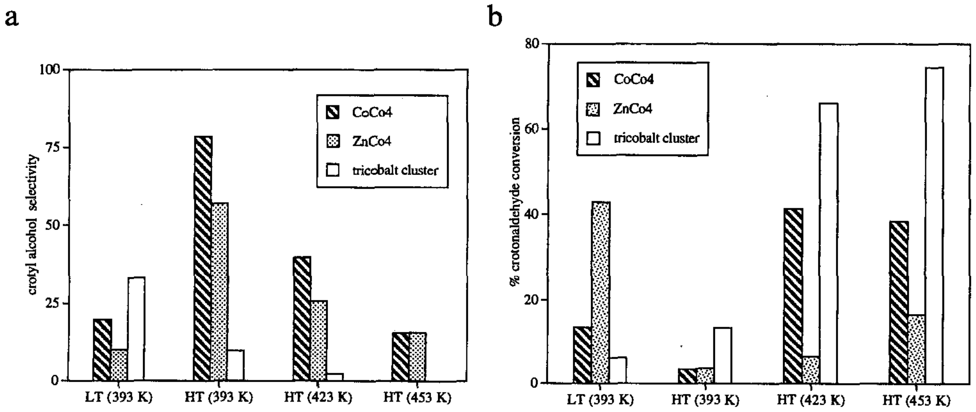


Fig. 2. Crotonaldehyde hydrogenation using LT and HT CoCo4, ZnCo4 and tricobalt cluster catalysts: (a) crotyl alcohol selectivity, (b) crotonaldehyde conversion.

slightly lower selectivity than CoCo4 but, except for the LT catalysts, they have lower activity giving a maximum yield of the desired product of about 5%. CoCo4 retains its activity and selectivity during 40 h of operation.

Two control experiments were performed. First, the activities and selectivities of a solid prepared by the pyrolysis of $(\mathrm{CO})_9\mathrm{Co}_3\mathrm{CCOOH}$ (the carboxylate ligand alone or tricobalt cluster) and, second, a conventionally prepared 5% Co/γ-alumina catalyst were examined in like fashion. Fig. 2 shows that the tricobalt cluster is active but does not exhibit selectivity for crotyl alcohol yielding mainly butyraldehyde. Furthermore the cluster deactivates rapidly and exhibits low surface area. The supported $\mathrm{Co}/\gamma\text{-}\mathrm{Al}_2\mathrm{O}_3$ catalysts exhibit similar characteristics, i.e. low selectivity and rapid deactivation (yield <5%) showing that the high selectivities observed for the cluster carboxylate derived materials originate in the unique structures of the precursors.

Catalysts prepared from $\mathrm{M}_2^{\mathrm{II}}\{(\mathrm{CO})_9\mathrm{Co}_3\mathrm{CCOO}\}_4$ with M = Co, and Cu, referred as MCo2, give the selectivities and conversions shown in fig. 3. CoCo2 exhibits the best selectivity to crotyl alcohol of 100% (fig. 3) at 373 K but gives low conversion (4% yield). As conversion increases the crotyl alcohol selectivity decreases. The selectivities and conversions of the MoCo2 and CuCo2, also shown in fig. 3, show that high selectivities for the MCo2 catalysts are only observed at low conversions. In general, the yields observed in the MCo2 structures are lower than in MCo4 structures. In the case of M = Co, the only difference between the two precursors CoCo2 and CoCo4 lies in the core structures which determine the disposition of the cluster ligands in space. Therefore, even though we do not know the detailed geometric structure of the catalytic materials under reaction conditions, the differences in catalytic selectivities and activities are clearly linked to the precursor structures.

The BET surface areas of the various catalysts after in situ decomposition at

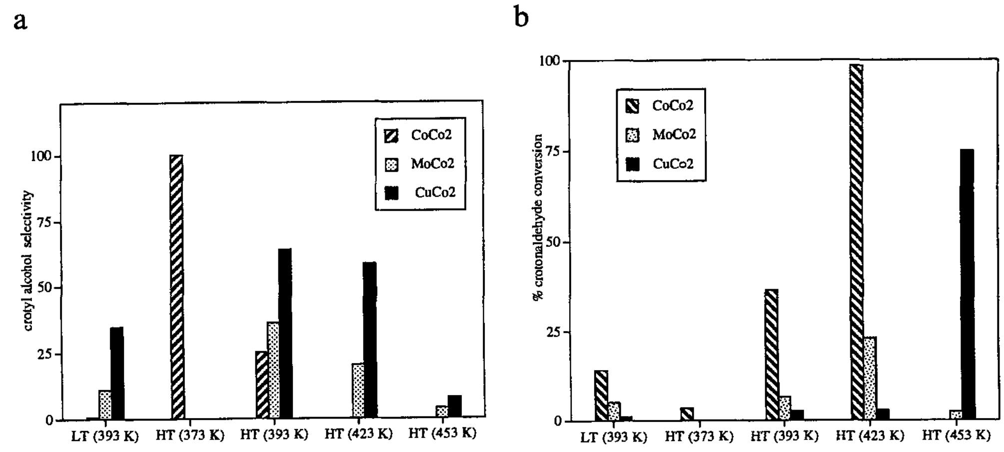


Fig. 3. Crotonaldehyde hydrogenation using LT and HT CoCo2, MoCo2 and CuCo2 catalysts: (a) crotyl alcohol selectivity, (b) crotonaldehyde conversion.

Table 1
BET surface areas (m^2/g)

Catalyst type	Treatment	
	373 K/2 h (LT)	473 K/2 h (HT)
CoCo4	160	52
ZnCo4	280	200
CoCo2	53	65
MoCo2	60	7
CuCo2	125	22
tricobalt cluster	8	29

373 K and 473 K are listed in table 1. It can be seen that the LT MCo4 catalysts have relatively high surface area which decreases upon formation of the HT catalysts. The surface area of the LT MCo2 is lower than the area of the MCo4 catalysts but the HT CoCo2 and CoCo4 areas are comparable, hence its different activities cannot be related to differences in surface areas.

The phenomenological origin of the high regioselectivity observed for intramolecular hydrogenation in these new materials appears to reside in the relatively high activation energies observed for hydrogenation. The activation energies are related to their structures which can be tailored by choice of the precursors. In contrast to typical supported metal hydrogenation catalysts where the activation energy for double bond hydrogenation is 3–10 kcal/mol, here it is 15–20 kcal/mol. That is, increased selectivity is associated with an increased barrier height for the reactions leading to formation of thermodynamically more stable products (butyraldehyde) relative to reaction forming crotyl alcohol. The overall specific activities (i.e. rate per unit area) for these catalysts are comparable to those of supported catalysts and the observed, high activity despite a higher activation energy implies the participation of a large fraction of active sites. Consequently, these catalysts must possess sites of narrow activity distribution, i.e. energetically more uniform. These results suggest that the utilization of a single precursor for the preparation of a self-supported metal catalyst under mild conditions provides similar sites of uniform activity and, hence, more control over selectivity. Further work is underway to determine more specifically the origin of the observed selectivity and the consequences of this new approach to the preparation of heterogeneous catalysts.

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