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Catalysts of Supported Iron Derived from Molecular Complexes Containing One, Two, and Three Iron Atoms

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The syntheses and characterization of catalysts derived from $Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$ supported on γ-Al_2O_3 are described. The temperature-programmed decomposition (TPDE) spectra of the $Fe(CO)_5$ and $Fe_3(CO)_{12}$ catalysts are different, suggesting that the nuclearity of the precursor complex can influence the chemistry of supported complexes. $Fe_2(CO)_9$ dry mixed with Al_2O_3 probably undergoes some decomposition to $Fe(CO)_5$ and $Fe_3(CO)_{12}$ prior to bonding to the support. Activation at low temperatures ($\lesssim$150 °C) leads primarily to the formation of zerovalent subcarbonyl species, some of which are reversibly formed. Activation at high temperatures ($\gtrsim$300 °C) leads to extensive oxidation of the Fe by reaction with the surface hydroxyl groups of the Al_2O_3 and loss of reversibility. Compared to the TPDE of the bulk unsupported carbonyls, Al_2O_3 stabilizes subcarbonyl species over a broad range of temperatures and inhibits their migration, preventing the formation of an Fe mirror. Chemisorption of CO indicates that catalyts derived from the iron carbonyls can be more than an order of magnitude more dispersed than catalysts synthesized by the traditional technique of impregnation with salts of Fe^{3+}.

Introduction

Catalysts of supported iron have been extensively studied due to their use in a variety of reactions such as hydrogenation, dehydrogenation, ammonia synthesis and decomposition, and Fischer–Tropsch synthesis. These catalysts are often made by impregnating alumina with an aqueous solution of $Fe(NO_3)_3$ followed by calcination and reduction at high temperatures (these will be termed "traditional catalysts"). Compared to the other group 8B metals, supported iron has some rather anomalous chemistry: At loadings $\lesssim$1% it is very difficult to reduce Fe^{3+} below Fe^{2+},[1] and the metal dispersion is about an order of magnitude lower than usual (~1% is typical for Fe).[2,3] This chemistry of traditional Fe catalysts suggests the use of zerovalent complexes of Fe as catalyst precursors. Such complexes should be capable of providing a direct route to highly dispersed, low-valent, supported Fe.

In this paper the techniques of temperature-programmed decomposition (TPDE) and chemisorption are used to synthesize and characterize catalysts of the zerovalent complexes $Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$ supported on alumina. This "homologous" sequence of complexes of varying nuclearity is also used to provide information on the influence of the nuclearity of the precursor complex on the nature of the catalysts.

Experimental Section

The catalysts were usually prepared by in situ impregnation at 23 °C from pentane solution onto 0.500 g of γ-Al_2O_3 (Conoco Catapal SB, 60–80 mesh, $a_s = 250\ m^2/g$, average pore diameter = 7 nm) which had been previously calcined at 500 °C in flowing O_2 and cooled in He. The solutions were made just prior to impregnation to minimize decomposition which was observed if solutions of $Fe(CO)_5$ were allowed to stand (in the absence of light and air) for more than a few hours. In some experiments powdered carbonyl was dry mixed (in situ) with the calcined alumina to avoid any complications from solvent. For these runs the mixture was pretreated by mechanically agitating the closed reactor for about 10 min near 60 °C to encourage the carbonyl to sublime evenly onto the support. The catalyst was then cooled to 0 °C and swept with He to determine the amount of CO evolved during this pretreatment. The catalysts were characterized by TPDE in flowing He. This technique gives a continuous plot of the evolutions of CO and H_2 during catalyst activation as well as the total evolutions of CO, H_2, CH_4, CO_2, and C_2 and C_3 hydrocarbons. Carbonyl which sublimed from the reactor during catalyst activation was condensed in a cold trap downstream from the reactor and analyzed by UV spectroscopy to allow the calculation of the true catalyst loading. Details of the method of catalyst synthesis,[4] the high-purity vacuum system,[4] and the TPDE technique have been published.[5,6]

The average oxidation number (ON) of the catalysts was determined after TPDE to 600 °C by titration with small pulses of O_2 at 500 °C to form Fe^{3+}. Determination of the amount of O_2 consumed allows a trivial calculation of what the average ON of the Fe had been. Correction was made for a small quantity of CO_2 formed during the titration.

Metal dispersion was measured by using H_2 and CO chemisorption at 0 °C for the carbonyl-derived catalysts and 23 °C for traditional Fe/Al_2O_3. Pressures were monitored with a Sundstrand electronic pressure sensor coupled to a precision digital voltmeter. The amount of chemisorbed gas was determined in the usual manner by first determining the total (physical + chemical) adsorption followed by evacuating and repeating the adsorption isotherm. The system is accurate to 0.001 cm^3 of gas adsorbed. The evacuation time was 5 min for H_2 and 15 min for CO. At sufficiently high pressure the difference between the two curves becomes nearly constant and is taken to be the amount of chemisorbed gas. Correction was made for a small amount of irreversible adsorption on the Al_2O_3 as found in blank experiments in which the support was treated identically as in a normal run except for the carbonyl being omitted.

Results

After impregnation $Fe_3(CO)_{12}$(ads) is dark green and $Fe(CO)_5$(ads) is light tan. During pretreatment dry mixes of $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ are observed to take on a uniform color (tan and brownish green, respectively) with the complete disappearance of bulk particles. Subsequent sweeps with He at 0 °C showed that 0.3 CO/complex was evolved during the pretreatments. Activation of $Fe_3(CO)_{12}$(ads) (wet mix) for 30 min at 75 °C turns the catalyst tan and causes the loss of roughly 2 CO/complex. Figures 1–3 show the TPDE spectra at a heating rate (β) of 5 °C/min of the iron carbonyls supported on Al_2O_3. Separate runs were also done at lower loadings and with β = 30 °C/min. The response of the hydrogen detection system is nonlinear at very low concentrations of H_2,[6] so runs at both low loadings and low β are less accurate ($[H_2] \propto \beta$). Due to the insolubility of $Fe_2(CO)_9$ in hydrocarbon solvents, impregnation was attempted in CH_2Cl_2 and $CHCl_3$. However, in both cases IR spectra of the fresh solutions indicated reaction with the solvent. In addition, blank runs with CH_2Cl_2 and $CHCl_3$ indicated that these solvents react with the support to evolve considerable amounts of CO and H_2 (much more than occurs in a normal run) as well as moderate amounts of CH_4, CO_2, and C_2H_4. Consequently, only dry-mix runs of $Fe_2(CO)_9$ are reported. The stoichiometries of the various runs are shown in Table I. Very small quantities of C_2H_4 and C_2H_6 were observed in both solvent and dry-mix runs, being ~0.007 molecule/complex. No C_3 hydrocarbons were observed. The average ON values after TPDE based on gas evolutions (see Discussion) or direct titration with O_2 are also shown in Table I.

Table II contains the results of a brief investigation for the existence of reversibly formed subcarbonyl species. Only $Fe(CO)_5$ was recovered in these experiments, but no $Fe(CO)_5$ was detected during the TPDE (in He) of $Fe_3(CO)_{12}$(ads).

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Table I. Gas Evolutions during TPDE to 600 °C

carbonyl	β, °C/min	final loading % Fe	sublimn during activn, %	gas evolution per complex CO	H_2	CH_4	CO_2	ON by gas evolution	ON by O_2 titration
$Fe(CO)_5$	5	0.274	58	4.6	0.88	0.027	0.092	2.0	2.0
$Fe(CO)_5$	30	0.081	32	4.7	0.94	0.027	0.22	2.0	
$Fe_2(CO)_9$[a]	5	0.297	7[b]	6.4	1.65	0.069	0.18	1.9	
$Fe_2(CO)_9$[a]	30	0.090	~7[b]	6.8	1.7	0.029	0.13	1.8	1.7
$Fe_3(CO)_{12}$	5	0.098	11	9.1	3.4	0.057	0.76	2.4	
$Fe_3(CO)_{12}$[a]	5	0.323	0.1	9.8	1.98	0.089	0.34	1.6	1.7
$Fe_3(CO)_{12}$	30	0.073	6	9.7	2.9	0.090	0.67	2.2	

[a] Dry mix. [b] Recovered as $Fe(CO)_5$; based on mol % Fe.

Table II. Reversibly Formed Subcarbonyl Species

catalyst	loading, % Fe	temp of activn, °C	temp of CO flow, °C	% recovery[a]
$Fe(CO)_5$	0.101	120	100	9.6
			150	8.5
				tot 18.1
$Fe_3(CO)_{12}$	0.114	90	90[b]	0.0
			90	14.0
			150	11.5
			200	2.0
				tot 27.5

[a] Based on mol % Fe; only $Fe(CO)_5$ was recovered. [b] A flow of He was used.

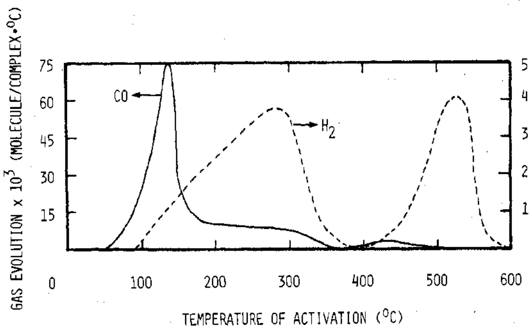

Figure 1. TPDE of $Fe(CO)_5/Al_2O_3$ (0.274% Fe).

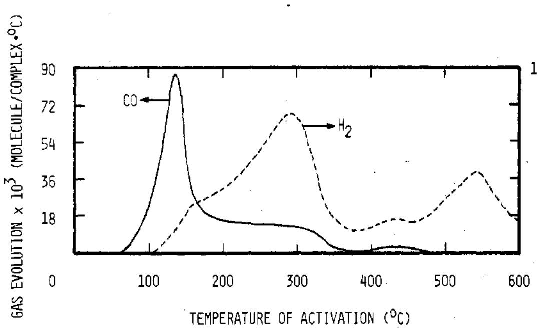

Figure 2. TPDE of $Fe_2(CO)_9/Al_2O_3$ (dry mix, 0.297% Fe).

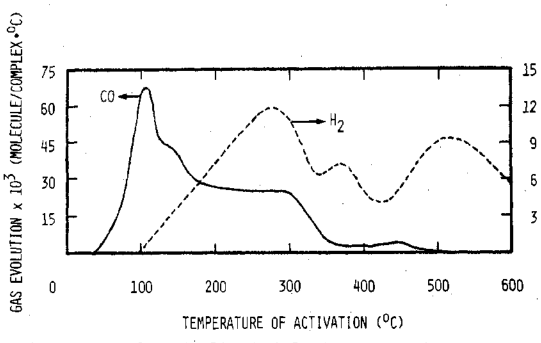

Figure 3. TPDE of $Fe_3(CO)_{12}/Al_2O_3$ (0.098% Fe).

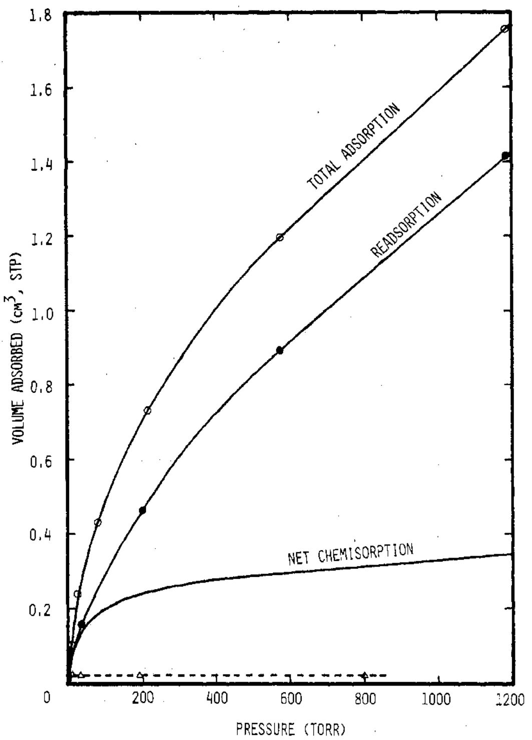

Figure 4. Adsorption of CO on $Fe(CO)_5/Al_2O_3$: solid lines, adsorptions after activation at 120 °C for 30 min; dashed line, net chemisorption after activation at 600 °C for 30 min.

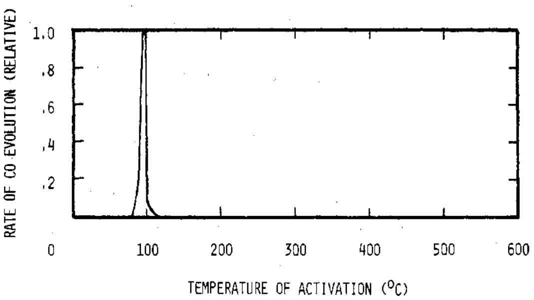

Figure 5. TPDE of unsupported $Fe_2(CO)_9$.

Exposing the $Fe_3(CO)_{12}$ catalyst to CO did not regenerate the deep color of $Fe_3(CO)_{12}$(ads). At all temperatures the recovery of carbonyl was essentially complete in 30 min although the CO flow was continued for ~2 h.

No chemisorbed H_2 was detected on any of the catalysts. The results of the CO adsorption measurements are summarized in Table III and include the background adsorption on Al_2O_3 (H_2 chemisorption was not measured on the catalyst of lines 7 and 8). Adsorption isotherms for $Fe(CO)_5/Al_2O_3$ are shown in Figure 4.

Figures 5 and 6 give the TPDE at $\beta = 5$ °C/min of pure (unsupported) $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ held between plugs

Table III. Dispersion of Catalysts of Supported Fe[a]

catalyst	loading, % Fe	temp of activn, °C	bkgd chemisorpn, cm³ (STP)	chemisorpn on complex, cm³ (STP)	dispersion, %
$Fe(CO)_5$	0.48	120	0.000	0.345	36
$Fe(CO)_5$	0.48	200	0.000	0.149	16
$Fe(CO)_5$	0.48	600	0.014	0.018	1.9
$Fe(CO)_5$[b]	0.48		0.031	0.027	5.6
$Fe_2(CO)_9$[c]	0.50	120	0.008	0.235	24
$Fe_3(CO)_{12}$[c]	0.51	120	0.008	0.234	23
$Fe_3(CO)_{12}$[c]	4.6	120	0.008	1.24	14
$Fe_3(CO)_{12}$[c]	4.6	500	0.014	0.33	3.6
$Fe_3(CO)_{12}$[b,c]	4.6		0.031	0.97	21
Fe	0.33		0.006	0.000 ± 0.001	0.0 ± 0.3
Fe	3.6		0.006	0.050	1.4
Fe	8.5		0.006	0.050	0.6

[a] The chemisorption of the carbonyl catalysts was measured at $P_{CO} = 1200$ torr. The traditional Fe catalysts were calcined for 30 min in flowing O_2 at 400 °C followed by reduction in flowing H_2 for 1 h at 500 °C. [b] Previous catalyst was calcined in flowing O_2 for 30 min at 400 °C followed by reduction with flowing H_2 for 1 h at 500 °C. [c] Dry mix.

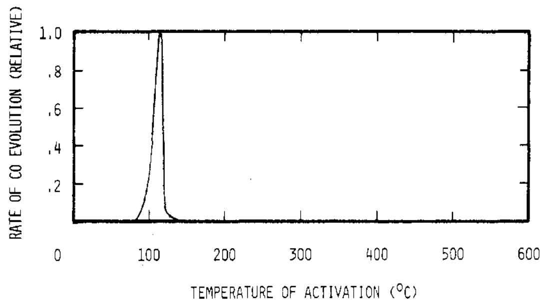

Figure 6. TPDE of unsupported $Fe_3(CO)_{12}$.

of glass wool in a $^1/_4$ in. o.d. Pyrex tube. In each case an Fe mirror was formed and a small quantity of unidentified black solid was left. $Fe(CO)_5$ was recovered in a cold trap downstream of the reactor, corresponding to 65% and 23% of the Fe in $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$, respectively.

Discussion

TPDE. Figures 1 and 3 illustrate that TPDE can reveal changes in the surface chemistry of a catalyst caused by changing the nuclearity of the precursor complex. Both the CO and H_2 portions of the spectra show differences. The shoulder at 140 °C in the spectrum of $Fe_3(CO)_{12}/Al_2O_3$ could be due to some decomposition to form $Fe(CO)_5$(ads) (Figure 1). However, the degree, if any, of such fragmentation must be small: (1) The primary peak of $Fe_3(CO)_{12}$(ads) is at 107 °C, well removed from the peak maximum (138 °C) for $Fe(CO)_5$(ads). (2) The plateau between 200 and 300 °C for $Fe_3(CO)_{12}$(ads) is about 3 times higher than for $Fe(CO)_5$(ads). (3) As shown in Table I, a substantial amount of $Fe(CO)_5$(g) sublimes from the surface during the TPDE of $Fe(CO)_5$(ads), but no $Fe(CO)_5$(g) is detected during the TPDE of $Fe_3(CO)_{12}$(ads).

The TPDE peak for $Fe_3(CO)_{12}$(ads) is unusually broad compared to that of mononuclear complexes.[5-7] It is interesting that whereas in mononuclear carbonyls all of the CO ligands are necessarily terminal, in $Fe_3(CO)_{12}$ there are both terminal and edge-bridging ligands. Furthermore, the ligands are nonrigid,[8] and it is likely that additional rearrangements occur during TPDE which may change the number of terminal and edge- and face-bridging ligands. Thus, cluster complexes inherently have a richness of binding sites, and therefore binding energies, which is not available to metals that only form mononuclear carbonyls.

Integration of the low temperature peak of $Fe(CO)_5/Al_2O_3$ gives an evolution of 3.0 CO/complex. In a separate experiment, $Fe(CO)_5$(ads) was activated for 45 min at 120 °C in flowing He during which time 2.8 CO/complex were evolved and the rate of decomposition decreased 200-fold. Thus, the results suggest, but certainly do not prove, the possible existence of an $Fe(CO)_2$(ads) species. Activation of $Mo(CO)_6/Al_2O_3$ at 100 °C has also been shown to cause the evolution of 3.00 CO/complex, forming $Mo(CO)_3$(ads).[4,7]

Attempts to *impregnate* Al_2O_3 with $Fe_2(CO)_9$ gave unreliable results due to its low solubility and the reactivity of chlorinated solvents. Others have used $CHCl_3$ solutions for the impregnation of various carbonyls.[9,10] Due to the large amounts of CO evolved by reaction of $CHCl_3$ with the Al_2O_3, such studies must be interpreted with caution. Pentane has been shown to be inert with respect to the support.[4] Unfortunately, $Fe_2(CO)_9$ is also not a good candidate for supporting by dry mixing because the combination of its low volatility and low thermal stability may cause it to undergo decomposition characteristic of the bulk before dispersing across the surface:[11]

$$3Fe_2(CO)_9 \xrightarrow{\gtrsim 50\ °C} 3Fe(CO)_5 + Fe_3(CO)_{12} \qquad (1)$$

The TPDE spectra of dry-mixed $Fe_2(CO)_9$, Figure 2, is qualitatively consistent with this reaction. (Compare to the weighted superposition of Figures 1 and 3.) Also, some $Fe(CO)_5$ is recovered from dry-mix runs with $Fe_2(CO)_9$.

In contrast, the TPDE of dry-mixed $Fe_3(CO)_{12}$ is very similar to that obtained by using impregnation with pentane. Thus, even rather low-volatility carbonyls can be supported by this technique as long as the complex has moderate thermal stability. It has also been found that the relatively volatile group 6B hexacarbonyls can be supported by sublimation techniques to yield TPDE and stoichiometry data consistent with the results from runs in which the support was impregnated.[4,6]

A noteworthy characteristic of the TPDE spectra is that decomposition commences at lower temperatures than for the bulk carbonyls (Figures 5 and 6) and continues to much higher temperatures. Thus, *a major role of the alumina is to stabilize subcarbonyl species over a broad range of temperatures.* Similar behavior has been reported for the hexacarbonyls supported on Al_2O_3,[5] but on SiO_2 the hexacarbonyls underwent decomposition in a narrow temperature range.[6]

TPDE at $\beta = 30$ °C/min shifts all peaks to higher temperatures, and theoretically the shift in peak position with β can be used to obtain information on the kinetic parameters of the decompositions.[12] However, it has been shown that more reliable results are obtained if it is assumed that the M–CO bond scission is a unimolecular reaction with a preexponential factor of $10kT_m/h$, where T_m is the temperature of the peak maximum, k is Boltzmann's constant, and h is Planck's constant.[13] Applying this analysis to the first CO peak, one obtains for the activation energy of decomposition E_d = 30 and 28 kcal/mol for $Fe(CO)_5$(ads) and $Fe_3(CO)_{12}$(ads), respectively. Considering the results for the hexacarbonyls on Al_2O_3 and SiO_2,[6] it appears that a value of $E_d \simeq 30$ kcal/mol is typical for the first step in the decomposition of supported carbonyls which are thermally stable at 23 °C.

TPDE of the unsupported carbonyls causes the formation of a low surface area Fe mirror. The TPDE peaks are so narrow as to require an autocatalytic process (peak widths of about 25 and 35 °C are expected for first- and second-order processes, respectively[14]). Catalysis of the decomposition by the metal product is expected. The large recoveries of $Fe(CO)_5$ are also noteworthy, and for the case of $Fe_2(CO)_9$ are reasonably consistent with eq 1.

Oxidation. Extensive decarbonylation is accompanied by the evolution of H_2 for all of the catalysts. For various carbonyl complexes supported on Al_2O_3 or SiO_2 the H_2 has been shown to result from a redox reaction between surface hydroxyl groups (σ-OH) and zerovalent metal (which otherwise would be the product of decarbonylation) which may be approximated as[4,6]

$$M(CO)_j + n(\sigma\text{-OH}) \xrightarrow{\Delta} (\sigma\text{-O}^-)_n M^{n+} + (n/2)H_2 + jCO \tag{2}$$

Thus, a measure of the average ON of a catalyst at any temperature during TPDE can be obtained by integrating the area under the H_2 peak. However, the small evolution of CH_4 represents additional reduction of H^+ and hence oxidation of the metal, so both gas evolutions (as well as the almost negligible evolutions of C_2 hydrocarbons) must be considered in computing an accurate value for the ON. For example, for the fourth catalyst listed in Table I the evolutions of 1.7 H_2 and 0.029 CH_4 per $Fe_2(CO)_9$ imply an increase in oxidation number of 3.4 + 0.17 = 3.6/$Fe_2(CO)_9$, or 1.8/Fe. The excellent agreement between the ON as computed in this manner after TPDE and as found independently by titration with O_2 (Table I) confirms the correctness of the nature of the H_2 and CH_4 evolutions. Thus, we have the important result that *TPDE monitors two parameters which are likely to have great influence on catalytic activity: (1) CO evolution, which roughly monitors the formation of subcarbonyl and possibly coordinatively unsaturated species. (2) H_2 evolution, which monitors the average ON of a supported complex.* Since the CH_4 evolution is very small (and separate experiments show that it occurs at $T > 200$ °C), Figures 1–3 can be used to compute the average ON of the catalysts at various temperatures. For each catalyst at 200 °C ON = 0.2, and after TPDE to 600 °C, ON $\simeq$ 2.0 (Table I). It is interesting to note that the Fe is oxidized by about the same amount regardless of the nuclearity of the complex; i.e., about 3 times as much H_2 *per complex* is evolved during the TPDE of $Fe_3(CO)_{12}$ as compared to the case of $Fe(CO)_5$.

A preliminary report on the activity of $Fe_3(CO)_{12}/Al_2O_3$ for the hydrogenation of propylene is consistent with these results.[15] Activation at low temperatures corresponding to the existence of zerovalent subcarbonyl species resulted in high activity, but activation at temperatures high enough to cause reaction with σ-OH resulted in irreversible loss of activity.

Reversibility. After TPDE to 600 °C no reversibly formed species were detected by exposing the catalysts to a flow of CO at 200 °C. On the basis of the TPDE spectra, fresh catalysts were activated at lower temperatures to give the results shown in Table II. The pair of experiments performed at 90 °C prove that CO is necessary to cleave the $Fe_3(CO)_{12}$ to form $Fe(CO)_5$. Once formed, the highly volatile $Fe(CO)_5$[11] readily sublimes from the support (see also Table I). Consistent with this, $Fe(CO)_5$ is not recovered during the TPDE (in He) of $Fe_3(CO)_{12}$(ads). Also, if during TPDE $Fe_3(CO)_{12}$(ads) primarily formed intermediates common to the TPDE of $Fe(CO)_5$(ads), then it would be expected that above the transition temperature the two TPDE spectra would become identical. This is not observed. It is further known that exposure of Fe powder to CO at 1 atm will not form $Fe(CO)_5$ at a significant rate,[11] so Table II establishes the existence of reversibly formed subcarbonyl species. It has already been noted that $Fe(CO)_2$(ads) is a possible intermediate of some stability during the TPDE of $Fe(CO)_5$(ads). These results are consistent with studies of the hexacarbonyls supported on Al_2O_3 and SiO_2 which showed that reversibly formed subcarbonyl species exist if the carbonyls were activated at temperatures low enough to avoid oxidation by reaction with σ-OH.[4,6]

Dispersion. The data in Table III indicate that iron carbonyls can be used to synthesize catalysts which are 1–2 orders of magnitude more dispersed than obtainable with the traditional technique of catalyst synthesis. Anderson et al. have previously reported the use of $Co_2Rh_2(CO)_{12}$ to obtain a 2.4-fold increase in dispersion over that obtained when SiO_2 was impregnated with the corresponding metal salts.[16] Unfortunately, the exact adsorption stoichiometry on which to base the value of dispersion for the Fe carbonyl catalysts is unknown. However, activation of $Fe(CO)_5/Al_2O_3$ at 120 °C leads to the loss of about 3 CO/Fe, and exposure to flowing CO at elevated temperatures (a condition which will irreversibly drive the reaction toward volatile $Fe(CO)_5$) only forms minor amounts of $Fe(CO)_5$ (Table II), so it would appear that the adsorption stoichiometry must be 2 or less CO adsorbed per surface Fe. In the case of $Mo(CO)_3/Al_2O_3$, it is known that the adsorption of CO occurs stepwise, 1 CO/Mo being rapidly adsorbed at −16 °C and 1 CO/Mo additionally being adsorbed by 100 °C.[17] Hence, the dispersions of the carbonyl catalysts (measured at 0 °C) are computed by assuming an adsorption stoichiometry of 1 CO/Fe. A stoichiometry of 2 CO/Fe would not materially alter the conclusion of the greatly enhanced dispersion of the carbonyl catalysts. For traditional Fe/Al_2O_3 catalysts the adsorption stoichiometry is 1 CO/2 Fe,[18] and it is assumed that this is the more appropriate value to use for the carbonyl-derived catalysts after a redox treatment (such catalysts, of course, are no longer carbonyls). A preliminary communication also used this stoichiometry for the carbonyl catalysts.[19] It should be noted that a small irreversible chemisorption on the Al_2O_3 is also shown in Table III. A similar result has been reported by Gatta et al.[21] and if not corrected for can substantially increase the value computed for the dispersion of catalysts for which the amount of chemisorption on the metal is low.

The higher dispersion of the carbonyl catalysts is explicable in terms of the surface chemistry of traditional catalysts of Fe/Al_2O_3 and the TPDE spectra. Fe/Al_2O_3 (made by impregnation with $Fe(NO_3)_3$) is very difficult to reduce below Fe^{2+}.[1] Thus, at the low loadings which normally favor a high dispersion, chemisorption fails to reveal a dispersed metal because most of the iron is present as Fe^{2+}. Only at very high loadings has the size of the iron crystallites increased sufficiently to minimize the interaction with the support and enable the Fe to regain the reducibility characteristic of the bulk. The large crystallites have a low dispersion. At moderate temperatures of activation the carbonyls provide a direct route to zerovalent Fe, bypassing the difficult reduction step. Kaesz has reported extensive sintering of some supported carbonyl cluster complexes prepared at high loadings.[20]

Heating a supported Fe carbonyl so as to get into the oxidation region lowers its dispersion, lines 3 and 8 of Table III. However, as shown in lines 4 and 9, a redox treatment enhances the dispersion and a high dispersion can be obtained at a high loading. This is potentially particularly important because a deactivated catalyst could likely have its activity regenerated by such redox treatment, a path not available to the carbonyl catalysts.

The shapes of the CO adsorption isotherms for all of the carbonyl-derived catalysts are quite similar to those shown in Figure 4 for $Fe(CO)_5/Al_2O_3$. If the catalysts are only activated at moderate temperatures, the chemisorption continues to rather high pressures, suggesting weaker bonding than for either the carbonyls after high-temperature activation or traditional Fe/Al_2O_3, both of which become saturated at $\lesssim 20$ torr.[3] Surprisingly, after a redox treatment the shape of the isotherm for the 4.6% Fe catalyst resembles that of the original carbonyl catalyst.

The evolution of about 1 H_2/Fe when the complexes are activated at high temperatures requires that essentially all of the Fe interacts with the surface even at elevated temperatures. This is also consistent with the dramatically different TPDE spectra given by the supported and unsupported complexes and the absence of an Fe mirror for the supported complexes. Thus, even though most of the Fe is no longer zerovalent, it is still highly "dispersed". It is possible that supporting carbonyls on materials which cannot oxidize the metal (as a dehydroxylated Al_2O_3[4]) will lead to even higher dispersions by allowing more extensive decarbonylation without oxidation.

Summary. From the foregoing it is clear that the information supplied by TPDE can be invaluable for the designed synthesis of catalysts of supported metals. The technique gives a handle on the development of potential catalytically active sites (coordinative unsaturation) as well as the temperatures and methodology to be used to retain the metals in the low-valent and highly dispersed state. However, it is also clear that the systems are complex, and additional characterization will be necessary to answer some of the residual questions. The use of IR spectroscopy to study some of the specific systems indicated by the TPDE experiments appears particularly promising.

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Registry No. $Fe(CO)_5$, 13463-40-6; $Fe_2(CO)_9$, 15321-51-4; $Fe_3(CO)_{12}$, 17685-52-8; Al_2O_3, 1344-28-1.

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Utilization of a Cationic Ligand for the Intercalation of Catalytically Active Rhodium Complexes in Swelling, Layer-Lattice Silicates

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Triphenylphosphine and the positively charged phosphonium phosphine ligand $Ph_2PCH_2CH_2P^+Ph_2CH_2Ph$ (abbreviated P-P^+) have been shown to react with $[RhCl(COD)]_2$ to give mixed-ligand cationic analogues of Wilkinson-type complexes. The positive charge carried by the phosphonium phosphine ligand allows the complexes to be electrostatically bound between the negatively charged sheets of the swelling, layer-lattice silicate mineral hectorite. The catalyst system derived from a 1:1:1 P-P^+:PPh_3:Rh reaction ratio is active for the hydrogenation of 1-hexene under homogeneous-solution conditions when intercalated in the intracrystal space of the layered silicate. The activity of the intercalated catalyst is about twice that of the homogeneous catalyst in methanol. ^{31}P NMR studies indicate that the phosphonium phosphine ligand is qualitatively similar to triphenylphosphine in its reactivity toward $[RhCl(COD)]_2$. However, the reaction of P-P^+ and $[RhCl(COD)]_2$ at 2:1 and 3:1 P-P^+:Rh ratios generates complexes which are inactive as olefin hydrogenation catalysts. The inactivity of these latter systems is attributed to steric crowding at the rhodium center by two or more of the bulky positively charged ligands. $RhCl(COD)(P\text{-}P^+)$, a cationic analogue of $RhCl(COD)(PPh_3)$, has been isolated as the BF_4^- salt by reaction of P-P^+ and $[RhCl(COD)]_2$ in stoichiometric amounts.

Introduction

It has been demonstrated recently that cationic metal-complex catalysts can be intercalated between the negatively charged sheets of swelling, micalike layered silicates.[2] For example, $Rh(PPh_3)_x^+$ complexes were shown to be active for the hydrogenation of alkenes and alkynes in the intracrystal space of the mineral hectorite. The $Rh(PPh_3)_x^+$/hectorite system exhibited much larger specificity for hydrogenation of terminal olefins vs. internal olefins in methanol than did the solution catalyst.[3] The activity of the mineral-bound catalyst was about 10 times less than that of the homogeneous catalyst for the hydrogenation of 1-hexene, while the activity of this catalyst supported on a cation-exchange resin was approximately 40 times less.[3] In contrast, the activity of $Rh(PPh_3)_x^+$/hectorite for reduction of 1-hexyne was comparable to that of the solution catalyst. One might infer from these

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