Heterogeneous Catalytic Studies With Rhenium Cluster-Based Precursors

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In the 1970's, it was suggested there exists an analogy between small transition metal particles and molecular clusters [1, 1]. The use of metal cluster compounds as precursors for heterogenous catalysts could potentially provide a method for controlling the local composition and microstructure of metal particles on the support [3-5]. This could lead to improved understanding and control of the selectivity and activity patterns from the resulting catalysts. Bimetallic catalysts have been shown to have unique properties and are of significant industrial importance [6]. The exploration of bimetallic cluster compounds as catalyst precursors is of considerable current interest. A bimetallic cluster compound containing rhenium and iridium, [Re₇IrC(CO)₂₃]²⁻, was recently reported [7], and the cluster exists in two isomeric forms. In this work, these two isomers and a pure rhenium-containing cluster, [Re(CO)₃OH]₄, were supported on metal oxide supports. The process of decomposition/activation of the supported compounds was studied by temperature-programmed flow methods and by infrared spectroscopy. Furthermore, certain catalytic properties of the activated materials were examined.

The rhenium cluster, [Re(CO)₃OH]₄, was loaded on Al₂O₃ by incipient wetness from an acetone solution. The sample was activated by temperature programmed decomposition to 773 K in flowing hydrogen. There were no decomposition gas products, CO and CH₄, detected until 650 K. By 480 K, the original cluster appeared to form a surface species consistent with Re(CO)₃{O-Al}{HO-Al} by infrared spectroscopy. Thus, [Re(CO)₃OH]₄ on Al₂O₃ appeared to convert quantitatively to Re(CO)₃{O-Al}{HO-Al} which was stable to 650 K. Above this temperature decomposition began to occur. The formation of this rhenium carbonyl surface species has been observed by Gates and coworkers [8] from supporting H₃Re₃(CO)₁₂ on Al₂O₃ as well as analogous species on MgO and SiO₂.

When previously activated samples, denoted [Re₄]/Al₂O₃, were exposed to CO in the presence of H₂ at 298 K, two overlapping CH₄ desorptions were observed in the subsequent temperature programmed reaction (TPR) profile. The CH₄ peak at 495 K was attributed to a carbon species on Re sites. The formation of CH₄ due to the peak at 495 K had an apparent activation energy of 50-53 kJ/mol. The shoulder to higher temperatures, near 560 K, was attributed to a spillover species, possibly methoxy or formate on the Al₂O₃ surface. The exposure of CO/H₂ at elevated temperatures resulted in the formation of a higher temperature CH₄ evolution centered near 560 K (Figure 1). Work by Falconer and coworkers [9, 10] provided strong evidence that spillover of methoxy to alumina was occurring over Ni/Al₂O₃ or Pd/Al₂O₃ as a result of CO and H₂ treatment at elevated temperatures.

Figure 1. Temperature programmed reaction (TPR) profiles showing the desorption of CH₄ from a 10 minute adsorption of CO/H₂ with exposure at (a) 298 K, (b) 362 K, (c) 408 K, (d) 456 K, and (e) 504 K for [Re₄]/Al₂O₃.
In an attempt to place methoxy groups on the Al₂O₃ surface, CH₃I or CH₃OH was dosed onto activated samples of [Re₄]/Al₂O₃. The resulting TPR profile was similar to the TPR profile produced from high temperature CO and H₂ exposure. This suggests the formation of a methoxy surface species on Al₂O₃ was occurring for the high temperature CO exposures. The use of TiO₂ as a support also led to the formation of a spillover species. The spillover rate appeared to be slower than that for Al₂O₃ supported samples. With SiO₂ as a support there was no evidence for spillover; only methanation from the Re sites was observed, which occurred at the same temperature as for Al₂O₃, 490 K, and with the same apparent activation energy, 50 kJ/mol.

When the mixed metal clusters, [Re₇Ir(CO)₂₃]²⁻ and [Re₅IrC(CO)₁₇(Re(CO)₃)₂]²⁻ (Figure 2), were supported on Al₂O₃ and activated, the resulting catalysts showed differences in activity towards the hydrogenolysis of ethane (Figure 3). The most active catalyst sample was [Re₇Ir(Et₄N)]/Al₂O₃, which achieved a turnover number of 1 mol CH₄/mol "Re₇Ir"/sec at 560 K. The least active catalyst was [Re₇Ir(PPN)]/Al₂O₃, which required a temperature of 685 K to reach an activity of 1 mol CH₄/mol "Re₇Ir"/sec. The other two samples, [Re₅IrRe₂(Et₄N)]/Al₂O₃ and [Re₅IrRe₂(PPN)]/Al₂O₃, showed comparable activities with turnover numbers of 1 mol CH₄/mol "Re₅IrRe₂"/sec at 575 K.

The decomposition of the supported clusters was followed by infrared spectroscopy up to 573 K. All samples formed Re(CO)₃(O-Al){HO-Al} during decomposition together with smaller nuclearity clusters. The formation of Re(CO)₃(O-Al){HO-Al} was quantified by preparing standard samples of [Re(CO)₃OH]₄ on Al₂O₃. The amount of Re(CO)₃(O-Al){HO-Al} formed at 573 K by the bimetallic clusters appeared to correlate with the ethane hydrogenolysis activity of the resulting catalyst, which ultimately was activated at 773 K for 1 hour. For instance, the sample which was most active for ethane hydrogenolysis, [Re₇-Ir(Et₄N)]/Al₂O₃, had produced the largest amount of Re(CO)₃(O-Al){HO-Al} during decomposition, ca. 60% of the available rhenium, whereas the sample which was least ac-
tive, [Re7IrC(CO)23(PPN)]/Al2O3, had resulted in only ca. 40%. The other catalyst samples, [Re5IrRe2(PPN)]/Al2O3 and [Re5IrRe2(ET4N)]/Al2O3, were intermediate in ethane hydrogenolysis activity and in the extent of Re(CO)3(O-Al)(HO-Al)2 formation during the decomposition process.

References


