

Heterogeneous Catalytic Studies With Rhenium Cluster-Based Precursors

Philip Douglas Lane

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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 heterogeneous 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, $[\text{Re}_7\text{IrC}(\text{CO})_{23}]^{2-}$, was recently reported [7], and the cluster exists in two isomeric forms. In this work, these two isomers and a pure rhenium-containing cluster, $[\text{Re}(\text{CO})_3\text{OH}]_4$, 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, $[\text{Re}(\text{CO})_3\text{OH}]_4$, was loaded on Al_2O_3 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 CH_4 , detected until 650 K. By 480 K, the original cluster appeared to form a surface species consistent with $\text{Re}(\text{CO})_3\{\text{O-Al}\}\{\text{HO-Al}\}_2$ by infrared spectroscopy. Thus, $[\text{Re}(\text{CO})_3\text{OH}]_4$ on Al_2O_3 appeared to convert quantitatively to $\text{Re}(\text{CO})_3\{\text{O-Al}\}\{\text{HO-Al}\}_2$ 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 $\text{H}_3\text{Re}_3(\text{CO})_{12}$ on Al_2O_3 as well as analogous species on MgO and SiO_2 .

When previously activated samples, denoted $[\text{Re}_4]/\text{Al}_2\text{O}_3$, were exposed to CO in the presence of H_2 at 298 K, two overlapping CH_4 desorptions were observed in the subsequent temperature programmed reaction (TPR) profile. The CH_4 peak at 495 K was attributed to a carbon species on Re sites. The formation of CH_4 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 Al_2O_3 surface. The exposure of CO/ H_2 at elevated temperatures resulted in the formation of a higher temperature CH_4 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 $\text{Ni}/\text{Al}_2\text{O}_3$ or $\text{Pd}/\text{Al}_2\text{O}_3$ as a result of CO and H_2 treatment at elevated temperatures.

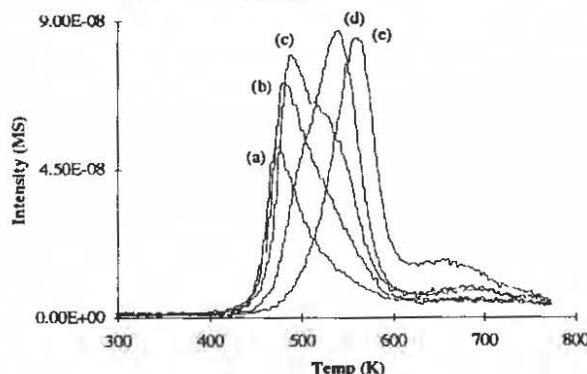


Figure 1. Temperature programmed reaction (TPR) profiles showing the desorption of CH_4 from a 10 minute adsorption of CO/H_2 with exposure at (a) 298 K,

In an attempt to place methoxy groups on the Al_2O_3 surface, CH_3I or CH_3OH was dosed onto activated samples of $[\text{Re}_4]/\text{Al}_2\text{O}_3$. The resulting TPR profile was similar to the TPR profile produced from high temperature CO and H_2 exposure. This suggests the formation of a methoxy surface species on Al_2O_3 was occurring for the high temperature CO exposures. The use of TiO_2 as a support also led to the formation of a spillover species. The spillover rate appeared to be slower than that for Al_2O_3 supported samples. With SiO_2 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 Al_2O_3 , 490 K, and with the same apparent activation energy, 50 kJ/mol.

When the mixed metal clusters, $[\text{Re}_7\text{IrC}(\text{CO})_{23}]^{2-}$ and $[\text{Re}_5\text{IrC}(\text{CO})_{17}(\text{Re}(\text{CO})_3)_2]^{2-}$ (Figure 2), were supported on Al_2O_3 and activated, the resulting catalysts showed differences in activity towards the hydrogenolysis of ethane (Figure 3). The most active catalyst sample was $[\text{Re}_7\text{Ir}(\text{Et}_4\text{N})]/\text{Al}_2\text{O}_3$, which achieved a turnover number of 1 mol CH_4/mol "Re₇Ir"/sec at 560 K. The least active catalyst was $[\text{Re}_7\text{Ir}(\text{PPN})]/\text{Al}_2\text{O}_3$, which required a temperature of 685 K to reach an activity of 1 mol CH_4/mol "Re₇Ir"/sec. The other two samples, $[\text{Re}_5\text{IrRe}_2(\text{Et}_4\text{N})]/\text{Al}_2\text{O}_3$ and $[\text{Re}_5\text{IrRe}_2(\text{PPN})]/\text{Al}_2\text{O}_3$, showed comparable activities with turnover numbers of 1 mol CH_4/mol "Re₅IrRe₂"/sec at 575 K.

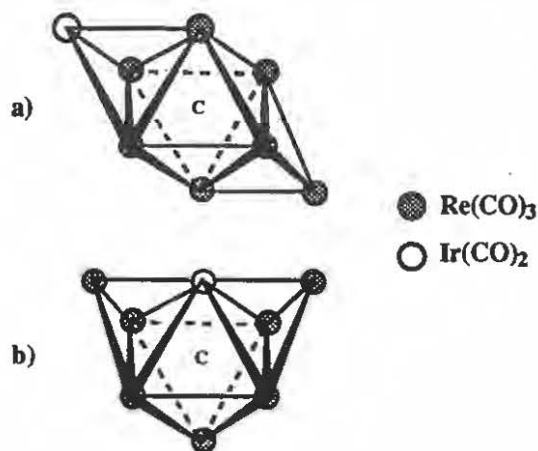


Figure 2. The metal framework structures of (a) $[\text{Re}_7\text{IrC}(\text{CO})_{23}]^{2-}$ and (b) $[\text{Re}_5\text{IrC}(\text{CO})_{17}(\text{Re}(\text{CO})_3)_2]^{2-}$.

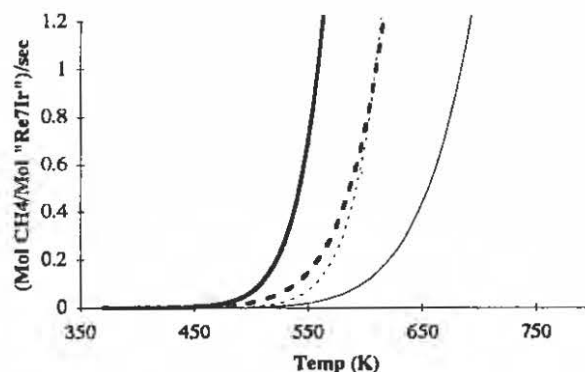


Figure 3. Activity profile for the hydrogenolysis of ethane on $[\text{Re}_7\text{Ir}(\text{Et}_4\text{N})]/\text{Al}_2\text{O}_3$ (---), $[\text{Re}_7\text{Ir}(\text{PPN})]/\text{Al}_2\text{O}_3$ (—), $[\text{Re}_5\text{IrRe}_2(\text{Et}_4\text{N})]/\text{Al}_2\text{O}_3$ (- -), and $[\text{Re}_5\text{IrRe}_2(\text{PPN})]/\text{Al}_2\text{O}_3$ (- -).

The decomposition of the supported clusters was followed by infrared spectroscopy up to 573 K. All samples formed $\text{Re}(\text{CO})_3\{\text{O-Al}\}\{\text{HO-Al}\}_2$ during decomposition together with smaller nuclearity clusters. The formation of $\text{Re}(\text{CO})_3\{\text{O-Al}\}\{\text{HO-Al}\}_2$ was quantified by preparing standard samples of $[\text{Re}(\text{CO})_3\text{OH}]_4$ on Al_2O_3 . The amount of $\text{Re}(\text{CO})_3\{\text{O-Al}\}\{\text{HO-Al}\}_2$ 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, $[\text{Re}_7\text{Ir}(\text{Et}_4\text{N})]/\text{Al}_2\text{O}_3$, had produced the largest amount of $\text{Re}(\text{CO})_3\{\text{O-Al}\}\{\text{HO-Al}\}_2$ during decomposition, ca. 60 % of the available rhenium, whereas the sample which was least ac-

tive, $[\text{Re}_7\text{IrC}(\text{CO})_{23}(\text{PPN})]/\text{Al}_2\text{O}_3$, had resulted in only ca. 40%. The other catalyst samples, $[\text{Re}_5\text{IrRe}_2(\text{PPN})]/\text{Al}_2\text{O}_3$ and $[\text{Re}_5\text{IrRe}_2(\text{Et}_4\text{N})]/\text{Al}_2\text{O}_3$, were intermediate in ethane hydrogenolysis activity and in the extent of $\text{Re}(\text{CO})_3(\text{O-Al})(\text{HO-Al})_2$ formation during the decomposition process.

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