Reduction of Carbon Monoxide and Dioxide by Metal Carbonyls on a Pyrolysed Polymeric Support

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A heterogeneous catalyst consisting of $Ru_3(CO)_{12}$ supported on pyrolysed polyacrylonitrile (PPAN) has been employed in the Fischer–Tropsch reaction and in the methanation of CO_2; a comparison between 2% Ru/PPAN and 2% Ru/Al_2O_3 shows a significantly different product distribution, with the former having improved selectivity for small molecular weight products.

The production of hydrocarbons from synthesis gas *via* the Fischer–Tropsch process has been widely studied. The most common systems use heterogeneous catalysts consisting of a transition metal supported on an inorganic oxide. Although such systems routinely show considerable activity, they suffer from a lack of selectivity, giving rise to a Schulz–Flory product distribution.[1] The selectivity is reported to be altered when catalysts with small metal particles on oxide supports are used, but during the course of the reaction the metal particles migrate on the surface and form large nucleated clusters.[2]

We report here the use of a pyrolysed polymer as a novel support which enables the system to produce low molecular weight hydrocarbons from synthesis gas for long periods of time. These catalysts also exhibit activity comparable to that of reported inorganic-oxide-supported systems for the methanation of CO_2.[3] The support we have been studying, pyrolysed polyacrylonitrile (PPAN), has been previously examined for a variety of uses.[4] In addition to its thermal stability, paramagnetic nature, and semiconductor properties, we viewed the proposed fused pyridine structure (see Figure 1) as a feature making this material particularly attractive for a heavy metal support. This functionality could provide better support binding for metal clusters than the surface oxide or hydroxy groups of the typical inorganic oxide supports.†

Work both in our laboratory and in the literature shows that PPAN is not a uniform-phase polymer. The cyclization proceeds in three dimensions giving rise to a highly cross-linked network, and produces functional groups other than fused pyridine rings. Slow pyrolysis, however, with temperature plateaus at the exothermic regions of the structural transformations (shown from differential scanning calorimetry studies[6]), is reported to maximize the number of fused pyridine moieties. Figure 2 shows the temperature *vs.* time profile used for PAN pyrolysis. Diffuse reflectance infrared spectroscopy (DRIFT) shows the loss of the C≡N stretching at 2240 cm^{-1} and the growth of C=C and C=N

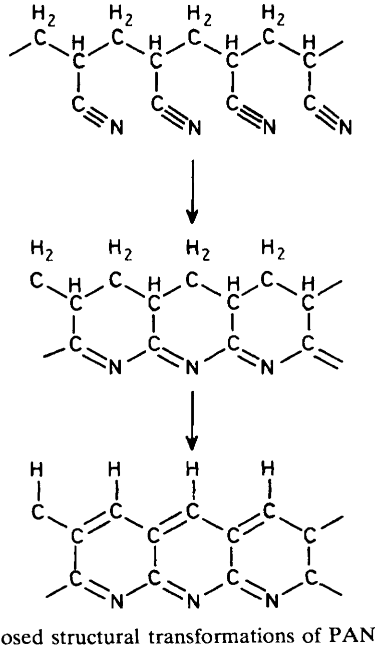

Figure 1. Proposed structural transformations of PAN during pyrolysis.

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† Recent studies have suggested that the condensed pyridine ring functionality does strongly bind metal clusters.[5]

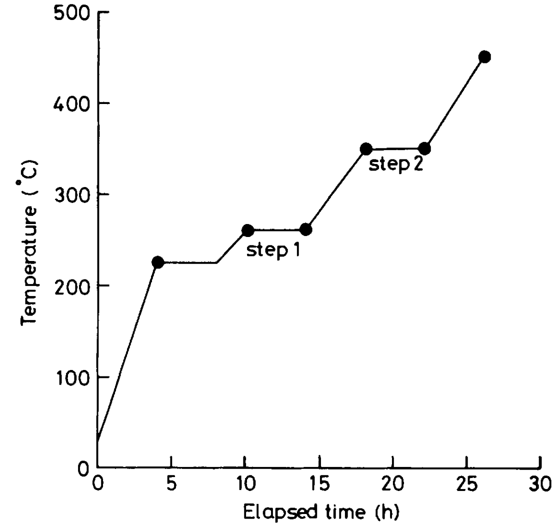

Figure 2. Time *vs.* temperature profile of PAN pyrolysis. The labelled plateaus correspond to the temperature regions where the structural transformations are considered to occur.

stretching bands at 1610 and 1580 cm^{-1}, respectively. The overall spectra agree very well with the literature reports.[6]

The catalysts are prepared by refluxing dissolved $Ru_3(CO)_{12}$ (0.05 g) with a slurry of PPAN (2.45 g) in n-hexane. The n-hexane is then driven off with nitrogen and the solid is dried in vacuum at 60 °C. In a typical catalytic reaction, Ru/PPAN (0.5 g) is put into the reactor,‡ and the system is subjected to nitrogen flow until the reaction temperature is reached and for about 3 h afterwards to allow thermal equilibration. At this point the absence of decomposition products or traces of solvent is verified. Next the $Ru_3(CO)_{12}$ cluster is decarbonylated in hydrogen flow for several hours. During this time, CH_4 is observed in the product stream. When the formation of CH_4 is minimal ($<10^{-9}$ mol), CO/H_2 flow (1:3 ratio) is begun. This leads to rapid formation of hydrocarbon products.

The results of a representative catalytic reaction are shown in Figure 3. The metal/PPAN system reduces CO, producing no detectable quantities of hydrocarbons larger than C_5. Oxygenates other than a trace amount of acetaldehyde, a possible intermediate, were not detected by g.c., g.c.–i.r., or g.c.–mass spectrometry. Also plotted in Figure 3 are the results of an analogous Ru/Al_2O_3 catalytic reaction [catalyst similarly prepared by refluxing $Ru_3(CO)_{12}$ (0.05 g) with Al_2O_3 (2.45 g) in n-hexane]. The shape of the product curves are significantly different, with the Ru/Al_2O_3 displaying the usual broad Fischer–Tropsch distribution while the Ru/PPAN curve drops asymptotically. The absence of products larger than C_5 suggests that either the PPAN support inhibits the formation of large metal aggregates or it is a reactive support playing a role in chain termination. Preliminary work with scanning electron microscopy (SEM) has shown that there is no significant change on the surface of the PPAN catalyst after a catalytic run. This novel product distribution is maintained with a given catalyst for up to six weeks. Furthermore, the catalyst can be cycled back and forth many times with reactant gases and purge gases.

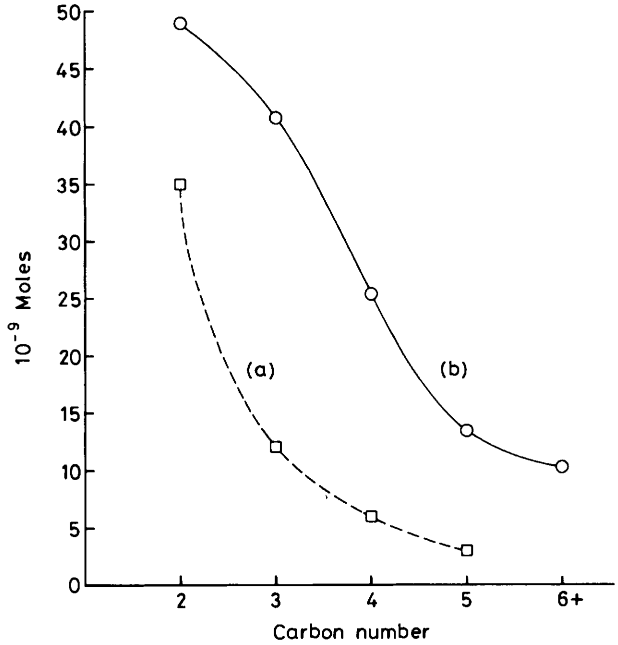

Figure 3. Product distribution of (a) Ru/PPAN *v.* (b) Ru/Al_2O_3. Reactor conditions: 220 °C, 1 atm, 3:1 H_2/CO with total flow 4 ml min^{-1}. The carbon number represents alkene and alkane. The C_{6+} figure for Ru/Al_2O_3 represents the sum of C_6, C_7, and C_8 products. C_1 is not plotted as it is not a Schulz–Flory product, but the values are 6.08×10^{-7} mol for Ru/PPAN and 5.76×10^{-7} mol for Ru/Al_2O_3.

An extensive series of blank experiments has been run. Unmetallated PPAN has been systematically subjected to N_2, H_2, $H_2 + CO$, and $H_2 + CO_2$ gas flows and no products were observed at normal reaction temperatures (220 °C) or temperatures up to 350 °C. PPAN doped with $RuCl_3$ (up to 14% by weight) was similarly found to be unreactive. The reason for this inactivity is that $RuCl_3$ is not reduced under these conditions. Higher temperatures will bring about reduction, but may also lead to undesired structural transformations of the PPAN support and therefore were not further investigated.

We have also examined the methanation of CO_2 with these metal/PPAN systems. With a stoicheiometric ratio of CO_2 and H_2 at 220 °C and 1 atm pressure, the Ru/PPAN system exhibits 8% conversion (mol CH_4 per mol $CO_2 \times 100\%$). From the parameters of our experiment (0.5 g of catalyst and 2 ml min^{-1} CO_2), this corresponds to 2.3×10^{-3} turnovers per second. This value is higher than for some reported CO hydrogenation systems.[7] Methane is the only product unless the reaction is carried out in a large excess of CO_2. Under these conditions small amounts of ethane and propane are also observed.

From a mechanistic standpoint, previous reports suggest that heterogeneous reductions of both CO and CO_2 proceed *via* a carbide intermediate.[8] Similarly, the lack of oxygenated products in this system suggests that CO bond dissociation is occurring. As already mentioned, acetaldehyde is occasionally a trace product and we find that when it is added to the reactant stream it greatly increases the yield of C_3—C_5 hydrocarbons. We are currently using labelled compounds to determine its role.

We have demonstrated that the PPAN support offers important selectivity advantages over the common oxide supports. From an activity standpoint, our conversion rate of 2—3% (total moles of all products per mol CO × 100%) is about ten times less than that of conventional systems. However typical silica or alumina catalysts have surface areas

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‡ The reactor is a fixed bed flow reactor. Temperature is monitored by a thermocouple enclosed in a glass well which is in contact with the catalyst bed. Gas samples can be taken through septa situated both before and after the catalyst bed. Flow rate is measured on the exit gas *via* a bubble meter.

of several hundred m^2 per g while our PPAN systems have a surface area of only 5—8 m^2 per g. An increase in the surface area of the support should improve our catalyst, for surface area is often directly related to activity.[9] We are currently incorporating components such as sucrose and inorganic salts in the pyrolysis step and preliminary studies have shown that these methods can produce an increase in surface area by a factor of ten or more. Work in this area and with other dopants to improve selectivity further is in progress.

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