The Selective Oxidative Dehydrogenation of Propane over Niobium Pentoxide

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It has been found that niobium pentoxide, calcined at temperatures between 500 and 700 °C, exhibits a high selectivity for the oxidative dehydrogenation of propane, although conversion is low; increasing the partial pressure of oxygen increases the conversion without decreasing the selectivity.

Propene and butenes are important intermediates in the petrochemical industry and are normally obtained as products from naphtha crackers. Because of the global abundance of liquefied petroleum gas (LPG), there is increasing interest in the potential use of propane and butanes as sources of the corresponding alkenes. Several processes exist for the catalytic dehydrogenation of the C_3 and C_4 alkanes, but they have the disadvantage of being based on an endothermic equilibrium reaction which requires higher temperatures; under those conditions rapid deactivation of the catalysts takes place due to coking.[1]

The oxidative dehydrogenation of alkanes such as propane is thermodynamically feasible at all temperatures. In principle, it should also be possible to carry out the reaction without problems of carbon deposition; however, complete combustion to give carbon oxides is a possible secondary reaction. The highest selectivity reported to date for the *oxidative dehydrogenation* of propane (60% at a propane conversion of 15%) was obtained with the V_2O_5/MgO catalyst system.[2–4] Although other supports for vanadia have been tested, magnesia-supported materials have been found to be the most selective catalysts; it has been shown that surface V=O species are present on all the other vanadia-based catalysts and it has been suggested that those groups (which are relatively easily reduced) are responsible for the non-selective behaviour.[2]

Niobium belongs to the same group of the periodic system as does vanadium but it is much more inert in its chemistry. Because niobia is less easily reduced than vanadia, we expected that it would have different oxidation properties. Surprisingly little work has been done in which niobium pentoxide has been used as the main catalytic component of selective oxidation catalysts,[5] even though it has been added as a trace component to many catalyst formulations: for example, the addition of niobium oxide to a mixture of vanadium and molybdenum oxides has been shown to improve the behaviour of this system for the oxidative dehydrogenation of ethane to give ethylene.[6] More attention has been paid in the literature to the acidic properties of niobia which has been treated at relatively low temperatures.[7] We report in this communication some preliminary results which show that hydrated niobia calcined at temperatures above 500 °C exhibits a high selectivity for the oxidative dehydrogenation of propane; because the activities of the samples tested were low, attempts were made to prepare more active samples by supporting niobia on α-alumina, and the results of these experiments are also reported.

A series of unsupported niobia materials were prepared by calcining a sample of hydrated niobia at temperatures ranging from 500 to 850 °C. The catalysts were tested, in the form of grains 0.3–0.6 mm in diameter, in a quartz tubular plug flow reactor. The flow to the reactor (space velocity 18000 h⁻¹) consisted of 30% propane and 5 or 10% oxygen, the balance being helium.

Experiments carried out in an empty reactor showed that reaction of propane started at temperatures above about 600 °C. The predominant products under these conditions were propene, ethylene and methane, with minor quantities of CO and CO_2.

Fig. 1 shows the results of two sequences of experiments carried out with the reactor containing a sample of niobia

calcined at 650 °C; the selectivity to propene and the conversion of propane are given as a function of reaction temperature for two partial pressures of oxygen, corresponding to 5 and 10% of the feed stream. The conversion increased steadily with increasing temperature at temperatures above about 480 °C while the selectivity dropped with increasing temperature. The other products were predominantly methane and ethylene, but CO and CO_2 were also formed (see Table 1 discussed below). Increasing the partial pressure of oxygen gave a significant increase in the conversion but, unexpectedly, the selectivity was hardly affected.

Table 1 gives the results of a series of experiments carried out at 550 °C using unsupported nobia samples calcined at various temperatures between 300 and 850 °C. The material calcined at 300 °C had a relatively high area before use but this dropped to 19.2 m² g⁻¹ after use at temperatures up to 610 °C. Increasing the calcination temperature also caused a major decrease in the surface area. The conversion obtained with the sample calcined at 300 °C was low and the selectivity to propene was also relatively very low; this sample also gave relatively high selectivities to CO_x. These results may be due to the presence on the sample calcined at this low temperature of acidic OH groups originating from the hydrated starting material used for the preparation (it is known that Brønsted acidity is the main form of acidity on niobia calcined below 500 °C[8]). In contrast to the results for the sample calcined at 300 °C, samples calcined at temperatures from 500 to 600 °C gave higher propane conversions; the conversions decreased once more for higher calcination temperatures. The samples calcined at temperatures of 500 °C and above gave selectivities of > ca. 75% to propene and the proportions of CO_x in the non-selective products were significantly lower; the proportion of CO_x decreased with an increase in the calcination temperature. For calcination temperatures between about 500 and 700 °C, there was a gradual increase of selectivity to propene which went hand-in-hand with the decrease in conversion, but this trend seemed to be reversed at higher temperatures; the activity and selectivity of the sample calcined at 850 °C were not much different from the
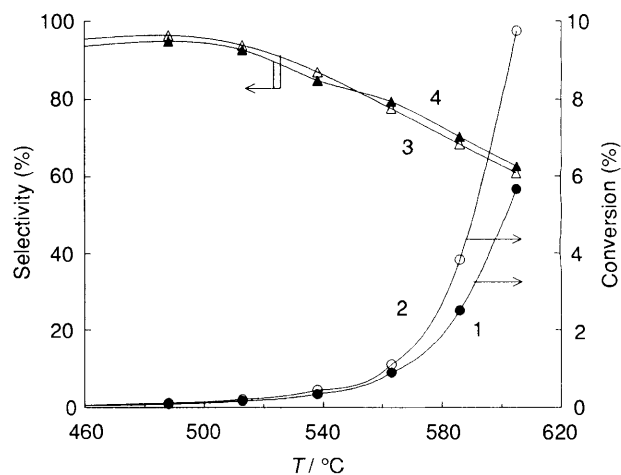

Fig. 1 Propane conversion and propene selectivity on Nb_2O_5 calcined at 850 °C. Lines 1 and 3 for 5% O_2, lines 2 and 4 for 10% O_2.

Table 1 Results of catalyst testing at 550 °C for niobia samples calcined at different temperatures

Calcining temp./°C	Surface area/ $m^2 g^{-1}$	Conversion (mol% propane)	Selectivity (mol%)		
			C_3H_8	$CO_x{}^a$	Cracking[b]
300	108.2[c]	0.56	53.1	43.0	3.8
500	28.5	1.54	77.5	15.6	6.9
570	18.0	1.05	75.2	17.5	7.4
650	9.9	0.62	85.0	6.1	8.9
700	6.8	0.62	82.5	4.9	12.6
850	1.2	0.12	76.9	3.0	20.2
Quartz	0	0.09	60	8	32

[a] $CO + CO_2$. [b] $C_2H_4 + CH_4$. [c] 19.2 $m^2 g^{-1}$ after use up to 610 °C.

corresponding values for a reactor filled with quartz chips (last row, Table 1).

In order to investigate the possibility of increasing the activity of niobium pentoxide by deposition on a high surface area support, a series of experiments was carried out with catalysts prepared on α-alumina (10 $m^2 g^{-1}$). Compared to unmodified α-alumina (conversion 1.6%, selectivity 31%), addition of niobia gave a significant improvement in selectivity, and this appeared to depend on the method of preparation. Deposition of niobia from an oxalate solution by slow precipitation with ammonia seemed to result in a more even distribution of the niobia (selectivity 62%) than did evaporation of the solution in presence of the support (selectivity 42%); in both cases the conversion was 1.2%. The difference in selectivity is probably due to a different degree of spreading of the niobia on the less selective α-alumina. However, the selectivities of the supported samples were in no case as high as that of the equivalent unsupported sample (i.e. the sample calcined at 700 °C, Table 1).

It is as yet unclear why niobium pentoxide is particularly selective for the oxidative dehydrogenation of propane.

According to Iizuka et al.,[9] the surface of niobia, when heated above 500 °C, is almost neutral. Compared to vanadia, niobia is very difficult to reduce; however, it is known to play an important role in the reoxidation of the surface when present in a multicomponent oxide catalyst.[8] The relatively inert surface behaviour, combined with a unique type of interaction with oxygen, is probably responsible for the very selective behaviour of niobia in the oxidative dehydrogenation of propane. Work is currently in progress to try to obtain complete coverage of the α-alumina support and also to examine other potential supports; the indications are that silica may be a suitable material for more detailed work. We have also found indications that suitable promoters improve the activity of the niobia-based materials.

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