Chemical Counting and Characterization of the Active Sites in the Rhenium Oxide/Alumina Metathesis Catalyst

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A method is described for the chemical counting and characterization of the active sites present in the rhenium on alumina metathesis catalyst in the stationary state, which bears out the surface carbene hypothesis, and gives some insight on the catalyst deactivation phenomenon.

Counting the number of active centres in a heterogeneous catalyst remains a goal that is attained only with great difficulties. The poisoning method' *i.e.* the introduction, on a given amount of catalyst, of the exact number of coordinating molecules (*e.g.* carbon monoxide or nitric oxide) for complete catalyst deactivation, or the determination of the number of adsorbed molecules such as alkenes, by IR or Raman spectroscopy, both require some hypothesis concerning the stoichiometry of the interaction of the organic molecules with the active centres and the support.

From this point of view, the metathesis of alkenes catalysed by rhenium oxide on alumina presents some interesting features: (*i*) the reaction is equilibrated, and the organic intermediate species, *i.e.* carbenes, are supposed to remain permanently bound to the surface; (*ii*) the catalyst is active at low temperature, thus allowing easy analytical determinations in the working conditions.

Indirect estimations of the number of active sites present in this catalyst suggest that only a small part of the rhenium is really active for the metathesis reaction.[1] This explains why

Table 1 Counting of the active sites in the Re_2O_7/Al_2O_3 metathesis catalysts[a]

Entry	Re on alumina/ wt %	Thermal activation temperature/°C	1st step Activating alkene	1st step Contact time/h	2nd step Ethylene pressure/MPa	% active Re sites[b]
1	8	520	but-2-ene	2	0.0085	0.20
2	8	520	but-2-ene	2	0.1	0.46
3	8	520	propene	2	0.1	0.43
4	8	520	but-2-ene	2	0.6	0.87
5	8	550	but-2-ene	2	0.01	0.34
6	8	550	propene	2	0.01	0.38
7	8	550	but-2-ene	2	0.1	0.63
8	8	550	but-2-ene	17	0.1	1.07
9	8	550	but-2-ene	74	0.1	1.53
10	5	550	but-2-ene	2	0.1	1.03
11	2	550	but-2-ene	2	0.1	1.79

[a] Catalysts are prepared by dry impregnation of γ-alumina (184 $m^2\ g^{-1}$) with an aqueous solution of $HReO_4$, followed by drying overnight at 120 °C and thermal activation under a dry air flow. [b] Expressed as the % of the total Re on the catalyst.

the physical methods that are commonly used, and which give an overall view of the catalyst, generally fail to give valuable information concerning the true active sites.[2]

The present work proposes a method for the direct counting and characterization of the active sites present in the working catalyst, and in the stationary state. There is evidence that the active sites are not generated at the moment of the thermal 'activation' of the catalyst, but only later, on its first contact with an alkene.[3] The principle of the method is the following. In a first step, active sites are created by contact of the thermally activated catalyst with an excess of a first alkene: the 'activating alkene', but-2-ene or propene in this work. According to the carbene hypothesis, one should expect the formation of two surface carbenes in equal amounts, once the steady state has been reached, see eqn. (1) where (re) stands for a surface rhenium entity. Afterwards, the excess of the activating alkene is removed by pumping out the catalyst under vacuum. Then in a second step, the active sites are reacted with a second alkene, which acts as a developer, ethylene in this work. New alkenes are so generated, which reveal the nature of the carbene surface species, and the amount of which is directly related to the amount of active sites, for example eqn. (2) and all other possible combinations.

$$2(\mathrm{re}) + R^1\text{–}CH{=}CH\text{–}R^2 \rightarrow (\mathrm{re}){=}CH\text{–}R^1 + (\mathrm{re}){=}CH\text{–}R^2 \quad (1)$$

$$(\mathrm{re}){=}CH\text{–}R^1 + R^3\text{–}CH{=}CH\text{–}R^4 \rightarrow (\mathrm{re}){=}CH\text{–}R^3 + R^1\text{–}CH{=}CH\text{–}R^4 \quad (2)$$

This technique has been used previously in the case of the homogeneous metathesis catalyst $WCl_6 + SnMe_4$.[4]

Selected results are given in Table 1. All the experiments have been done at room temperature. In a typical experiment, the Re_2O_7/Al_2O_3 catalyst (60 g, thermally activated) is contacted at atmospheric pressure in a glass flask (250 ml), first with but-2-ene (entry 2) or propene (entry 3) for 2 h, and then, after being treated under vacuum (10^{-2} mmHg, 4 h), with 0.1 MPa ethylene during 15 min. Analysis of the gas over the catalyst shows the presence of propene, generally more than 2 wt%. Blank experiments conducted in the same way with the alumina carrier alone showed the presence of only very small amounts of propene: 0.005 wt% when the activating alkene was but-2-ene, and 0.19 wt% when it was propene (traces of remaining propene after the vacuum treatment). The calculation of the relative amount of active sites is made from the above analysis, taking into account that, according to eqns. (1) and (2), activation with but-2-ene gives an amount of propene equal to the number of active surface rhenium sites, while after activation with propene, vacuum treatment and contact with ethylene, the amount of propene recovered is only half the number of active rhenium sites. Examination of entries 2 and 3, and also 5 and 6 at lower pressure, shows that the same relative quantity of active rhenium is found, whatever the activating alkene. This result would not be expected if the active sites were not carbenes, but for example π-allylic species. On the other hand, the relative amount of active sites is always low, around 0.5% of the total rhenium content. From the catalytic activity determined in the metathesis of propene,[5] the true turn over number (TON) may then be calculated, and falls in the range of 5 to 10 s^{-1}.

In the above sequence of treatment of the catalyst, the pressure of ethylene applied in the second step influences the proportion of active rhenium sites found (entries 1, 2, 4, 5 and 7). This is not unexpected, because the surface reaction involved is nothing more than part of a metathesis reaction, which is an equilibrated reaction. Therefore, it is not surprising that the steps of this reaction are also equilibrated, and an excess of ethylene is thus required to complete the displacement of the surface carbenes.

We have conducted on the catalyst the same sequence of treatment as above, but replacing ethylene by deuteriated ethylene (composition: C_2D_4, 61 wt%, C_2D_3H, 39 wt%, pressure, 0.01 MPa). Activation with either but-2-ene or propene gave again the same proportion of active rhenium sites (respectively, 0.37 and 0.38%), and the propene found in the gas was shown by GC–MS to be labelled at the one position, as expected from active sites consisting of carbene species (estimated composition: $CH_3\text{–}CH{=}CD_2$, 65%, $CH_3\text{–}CH{=}CDH$, 30% $C_3D_3H_3$, 5%, probably arising from some deuterium scrambling).

We have shown in previous work that the deactivation of the catalyst occurs either on a static contact with an alkene or in a dynamic metathesis reaction system.[5] We have thus simulated the ageing of the catalyst by changing the contact time with the activating alkene (but-2-ene, entries 7–9). It is surprising to observe that while the catalyst is well known to deactivate with time in the metathesis reaction, the relative amount of active sites is increasing at the same time. We know, from experiments[3] where the catalyst was contacted with but-2-ene or propene, treated under vacuum according to the normal procedure, and then reacted with an excess of water, that a large amount of the initial but-2-ene or propene remains chemisorbed after the vacuum treatment, possibly as alkenic surface complexes. The quantity of the remaining alkene is approximately four times higher with but-2-ene than with propene. However, the fact that the same relative amount of active rhenium is calculated whatever the activating alkene implies that the remaining part of this alkene is not involved in a superimposed catalytic reaction with ethylene in the second step. On the other hand, the amount of propene which is found is independent of the time of contact with ethylene. It is thus very unlikely that side catalytic reactions are responsible for the higher count number with time. This result may be explained if it is assumed that the overall activity of the catalyst is the product of the number of active sites multiplied by the mean intrinsic activity of one site. The deactivation must then be attributed to a decrease of the mean intrinsic activity of each site, strong enough to overcome a slow increase of the number of sites.

It is also shown, entries 10 and 11, that the proportion of the total rhenium content which is really active is comparatively higher in the low-loaded catalysts.

At the present time, the conclusion is that the method allows the direct determination of the number of active sites in the Re_2O_7/Al_2O_3 metathesis catalyst. It confirms that these active sites are surface rhenium–carbene species that represent only a small part of the total rhenium. Work is now in progress using this method to improve our knowledge of the rhenium-based metathesis catalysts, particularly as concerns the differences observed with various carriers, as well as the effect of the conditions of impregnation and of thermal activation on their activity in the metathesis reaction of light alkenes.

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