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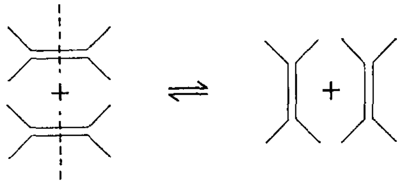
# NOTES

## Reduction and Activity of the Metathesis Catalyst $WO_3/SiO_2$

A wide variety of catalysts derived from W, Mo, or Re have been reported to be active catalysts for the metathesis reaction of alkenes (*1*):



The nature of the ligands and the oxidation number of the metal atom in these compounds appear not to be very critical, and therefore it has been impossible to provide a clear picture of the active site for this reaction. For the $WO_3/SiO_2$ catalyst it has been concluded previously (*1*, *2*) from the "break in" effect that active sites are generated by the interaction of propene with the catalyst. This process is influenced by prior reduction with hydrogen or carbon monoxide. The extent of reduction and the correlation with activity was, however, never quantified. Therefore, we investigated the reduction process for this catalyst gravimetrically while simultaneously measuring activity for the metathesis of propene.

A catalyst containing 3 wt% tungsten oxide on silica (Grace 111, particle size 180–210 μm) was prepared by impregnation with a solution of ammonium paratungstate. After drying at 350 K and heating in flowing air at 825 K the BET surface area was 310 $m^2/g$ and the average pore radius, 5 nm. X-Ray analysis did not show any crystalline compounds. Propene was purified by passing through alumina (Alcoa H 151), a copper catalyst (BASF R3-11) and 3A molecular sieves. Oxygen and hydrogen were dried with 3A molecular sieves.

The apparatus consisted of a Cahn RG electrobalance enclosed in a circulating system of approximately $5 \times 10^{-3}$ $m^3$ volume and a circulating rate of $2 \times 10^{-5}$ $m^3$ $s^{-1}$. A VG Micromass 2 mass spectrometer was attached for analysis of gas composition. Accuracy of the weight measurements was 5 μg on a 50 mg catalyst sample. In all experiments the activity of the catalyst samples was determined at 775 K by introducing a portion of propene which gives in the reaction system a pressure of 2.6 kN $m^{-2}$, and by measuring the conversion after 30 min. For temperature stability a plug of stainless steel turnings was fitted in the hangdown tube beneath the sample bucket. Buoyancy corrections for the weight readings were obtained in a blank experiment with a quartz charge. As indicated by the weight and color change, reoxidation of reduced catalysts proceeds smoothly, but we did not obtain reproducible activities in this manner. Therefore, all experiments were conducted with fresh samples, which were heated in oxygen (26 kN $m^{-2}$) to 875 K, and after renewing the oxygen were kept at this temperature for 15 hr. This was followed by evacuation for 1 hr after which the partial pressure of oxygen was less than $10^{-3}$ N $m^{-2}$. Then, either hydrogen was admitted, followed by another hour of evacuation, or the temperature was lowered

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immediately to 775 K. The propene pressure used in the activity measurements was chosen because at higher pressures we observed only small differences in activity with catalyst samples which were expected to exhibit considerable differences due to the method of pretreatment. We ascribe this to mass diffusion limitations in and around the sample bucket.

The results of the experiments are summarized in Table 1, which shows the activities of differently treated catalyst samples and the level of reduction as derived from the loss of weight. Actually a series of subsequent activity measurements was obtained for each sample. Except for the two samples that were not treated with hydrogen, essentially equal conversions were found in a series of subsequent activity measurements. However, with the two nonreduced samples the conversion obtained during the first activity measurement was only half the value obtained after a few more measurements. This last value is the one recorded in Table 1. This increase in activity was also found in other experiments with nonreduced catalyst samples.

Figure 1 is a logarithmic plot of the reduction of the catalyst with hydrogen at 875 K and a pressure of 100 kN m$^{-2}$. As also found by others (*3*), reduction of tungsten oxide on silica is slow and the straight line indicates that no intermediate oxidation level is significantly stable. X-Ray diffraction patterns differed only for the two most reduced samples from the silica carrier. Here a broad and weak reflection of tungsten metal at $2\theta = 40°$ was observed.

TABLE 1

Correlation between Pretreatment, Stoichiometric Composition of Tungsten Oxide, and Activity

| Pretreatment at 875 K | | Stoichiometric composition of tungsten oxide calcd from the loss of wt | Conversion (%) |
|---|---|---|---|
| (min) | (kN m$^{-2}$ $H_2$) | | |
| None | | | 9 |
| None | | | 7 |
| 1 | 3.9 | | 25 |
| 2 | 26 | Reduction below detection limit | 21 |
| 3 | 100 | | 21 |
| 10 | 100 | $WO_{2.91}$ | 19 |
| 60 | 100 | $WO_{2.47}$ | 11 |
| 540 | 100 | $WO_{1.95}$ | 5 |
| 840 | 100 | $WO_{1.86}$ | 4 |

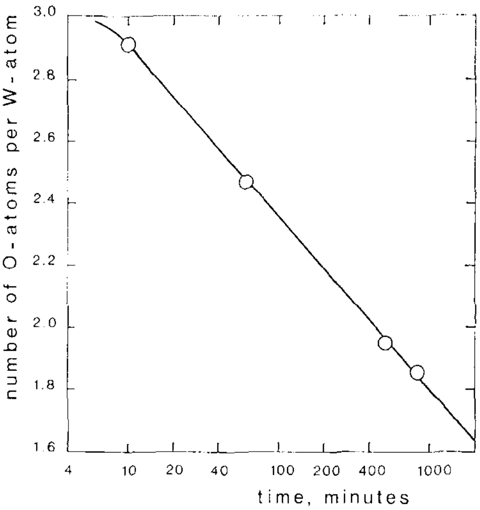

FIG. 1. Stoichiometric composition of tungsten oxide during reduction with hydrogen at 875 K and 100 kN m$^{-2}$.

No weight change as a result of propene admission was observed in any of the experiments. At higher propene pressures, different buoyancy corrections for the reaction products prevent taking accurate weight readings of active catalysts because the gas composition close to the catalyst is uncertain. Where this problem does not exist, as in experiments with ethene, no adsorption is found between 575 and 775 K, and pressures up to 100 kN m$^{-2}$.

The most noticeable result is the very slight reduction that brings about maximum activity. The accuracy of the reduction measurements amounts to 0.05 oxygen atom/tungsten atom. Therefore, the stoichiometric composition of tungsten oxide in the most active sample must lie between $WO_3$ and $WO_{2.95}$. For pure $WO_3$ a number of substoichiometric compounds have been identified (*4*), but because of the large unit cell, these compounds are only conceivable in an extended $WO_3$ lattice, which is not very likely in the irregular and restricted pores of the catalyst and would probably show up in the X-ray diagram of the calcined catalyst. It seems more appropriate to consider the tungsten atoms separately. To obtain a stoichiometric composition of $WO_{2.95}$ one oxygen atom must be missing on 20 tungsten atoms. Because the slightly reduced samples show a considerably larger activity than the samples not treated with hydrogen, it seems reasonable to link this missing oxygen atom to an active site. This is supported by the fact that nonreduced samples exhibit an increase in activity, whereas reduced samples yield a constant conversion from the beginning. Linking the missing oxygen atom to one active site provides a maximum limit to the number of active sites.

It must be pointed out that usually tungsten oxide on silica after calcination in oxygen in assigned the composition $WO_3$. However, ESCA measurements seem to indicate that a considerable fraction of the tunsten atoms should be considered to have a lower valency than six (*3*). Moreover, the tungsten atoms involved in the active sites may, even after evacuation, be blocked by adsorbed oxygen. In that case, hydrogen treatment would have to be described as an efficient method to remove this extra oxygen. However, both complications do not affect the conclusion that at most only 5% of the tungsten atoms in this catalyst are involved in the active sites. This results in a turnover number of 3/s for the most active sample. By extrapolating to our reaction conditions turnover numbers of the same order of magnitude can be derived from data in other studies (*5*, *6*) if the same fraction of tungsten atoms is considered to be active.

Considering the small number of active sites, it is not surprising that no adsorption was detected, and that in the gas phase no products were found from the process that is responsible for the increase in activity in nonreduced samples. This process could be a slow reduction by propene itself, and the low conversion indicates that this reduction with propene at 775 K is even less efficient than the smallest reduction with hydrogen at 875 K. However, experimental evidence given by Luckner and Wills (*2*) indicates that the formation of active sites cannot solely be attributed to a reduction, and must be more complicated. Evidently this did not interfere with our experiments.

The calculated number of active sites is a maximum limit and is based on the detection limit of the balance. The maximum number of active sites is obtained at pretreatment conditions that are far beyond this limit, and it is therefore likely that the number of active sites is even considerably less than 5% of the number of W atoms. In view of the problems this will create in various experimental techniques, it is recommended to look for catalysts with a substantially larger number of sites to add to the elucidation of the picture for the metathesis site.

## REFERENCES

1. Mol, J. C., and Moulijn, J. A., in "Advances in Catalysis" (D. D. Eley, H. Pines and P. B. Weisz, Eds.), Vol. 24, p. 131. Academic Press, New York, 1975.
2. Luckner, R. C., and Wills, G. B., *J. Catal.* **28**, 83 (1973).
3. Biloen, P., and Pott, G. T., *J. Catal.* **30**, 169 (1973).
4. Gebert, E., and Ackermann, R. J., *Inorg. Chem.* **5**, 136 (1966).
5. Luckner, R. C., McConchie, G. E., and Wills, G. B., *J. Catal.* **28**, 63 (1973).
6. Hattikudur, U. R., and Thodos, G., *Advan. Chem. Ser.* **133**, 80 (1974).

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