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J. Chem. Soc., Faraday Trans. 1, 1985, **81**, 1705–1714

Activity of Supported Tungsten Oxide Catalysts for the Metathesis of Propene

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Received 24*th September*, 1984

Published on 01 January 1985. Downloaded by New York University on 25/10/2014 08:27:46.

The activity of several supported tungsten oxide catalysts for the metathesis of propene has been studied under temperature-programmed conditions. WO_3/TiO_2 was found to be active at moderate temperatures; its activity passes through a maximum when the reaction temperature is decreased from 670 to 450 K. WO_3/ZnO is less active and its activity as a function of the reaction temperature goes through a maximum under certain conditions. In contrast to these catalysts and to the earlier reported behaviour of the well known WO_3/Al_2O_3 catalyst, the activity of the WO_3/SiO_2 catalyst steadily increases for reaction temperatures up to 860 K. In this respect the WO_3/SiO_2–Al_2O_3 catalyst behaves like the WO_3/SiO_2 catalyst and not like the WO_3/Al_2O_3 catalyst.

The acidity of the supports has been determined by means of a temperature-programmed desorption technique, using t-butylamine as the adsorbed species. The results of this work do not suggest a relationship between the acidity of the supports and the activity for metathesis.

A maximum in the activity for the metathesis of propene:

$$2CH_3CH{=}CH_2 \rightleftharpoons CH_2{=}CH_2 + CH_3CH{=}CHCH_3 \qquad (1)$$

as a function of the reaction temperature was first found by Banks and Bailey[1] for a CoO–MoO_3/Al_2O_3 catalyst. This feature was later investigated in more detail by Moffat and Clark.[2] Moreover, we have found that the metathesis catalyst WO_3/Al_2O_3 shows a point of maximum as well as of minimum activity for the metathesis of propene as a function of the reaction temperature.[3]

Banks[4] has reported that there seems to be a relationship between the temperature range in which the metathesis catalysts MoO_3/Al_2O_3, WO_3/SiO_2 and WO_3/SiO_2–Al_2O_3 attain maximum metathesis activity (or pass through a maximum) and the range in which the rate of deuterium exchange for the corresponding supports passes through a maximum. This would suggest a functional relationship between the rate of metathesis and the rate of the H–D exchange, the latter being a measure of the acidic properties of the support.

In this paper we present the results of a study of tungsten oxide catalysts on different supports. As well as the well known supports SiO_2, Al_2O_3 and SiO_2–Al_2O_3, we tested TiO_2 and ZnO. The activity of the WO_3/TiO_2 and WO_3/ZnO catalysts for the metathesis of propene was studied as a function of the reaction temperature. The same was done for the WO_3/SiO_2 catalyst, but at a higher temperature range than previously reported.[3] The aim of the present study was to find out whether the occurrence of a maximum in the activity for metathesis as a function of the reaction temperature is a general one and can be considered a characteristic of the active sites involved in the reaction.

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Moreover, the activity of the WO_3/Al_2O_3 and WO_3/SiO_2–Al_2O_3 catalysts for the metathesis of propene was studied as a function of the activation temperature in order to test the hypothesis of a possible relationship between the catalytic activity and the acidity of the supports.

All the supports used and the WO_3/TiO_2 catalyst were also tested for their acidity at various activation temperatures.

EXPERIMENTAL

The experiments were carried out in a conventional fixed-bed microcatalytic flow reactor. The reactor itself was a section of a stainless-steel tubing (8×10^{-3} m internal diameter), placed in a vertical oven, wherein a constant temperature could be provided and maintained.

The gases were first passed through a separate purification section placed on all feed lines leading to the reactor. Alumina (Alcoa H 151) and 3A molecular sieves were used for drying the feed and a Cu/Al_2O_3 catalyst was used to eliminate any oxygen impurity to < 1 ppm.

The product gases were analysed on line by means of a gas chromatograph at room temperature with a $12 \times 3.175 \times 10^{-3}$ m column packed with 30% 2,5,8,11,14-pentaoxapentadecane on Chromosorb P, 149–180 μm, using flame-ionization detection and nitrogen as the carrier gas. The gas-chromatographic signal was real-time processed by a PDP 10/11 computer system, provided with a g.c. signal-integrating program.

The properties of the supports used in this work are given in table 1. From all these supports catalysts containing 6 wt % WO_3 were prepared by wet impregnation. Screened fractions of the supports (180–212 μm) were impregnated with an aqueous solution of ammonium metatungstate (Koch-Light Laboratories, 99.9%) and then dried at 365 K under vacuum. Before testing, the catalysts were calcined in a stream of dry air at 773 K for 6 h unless otherwise stated. The weighted catalyst samples taken for each run were given a second heat treatment (activation) within the reactor in a nitrogen stream for one night.

The acidicity measurements were carried out in a temperature-programmed desorption set up, using t-butylamine (TBA) (Merck, 98%) as the adsorbed species[5] and thermal conductivity/flame-ionization detectors.

RESULTS

ACTIVITY TESTS

A catalyst, different from those normally used in the metathesis reaction (*viz.* WO_3/SiO_2 and WO_3/Al_2O_3), was prepared with TiO_2 as the support. The 6 wt % WO_3/TiO_2 catalyst was calcined at 675 K, activated and tested under temperature-programming conditions by increasing or decreasing the temperature stepwise by 40 K every 30 min (fig. 1). In one experiment the catalyst, activated at 770 K, was studied coming from the low-temperature side. Substantial conversions were only attained when the temperature was raised above 550 K. Clearly, the catalyst went through a break-in for temperatures in the range 550–620 K, as within a 30 min period the conversion of the second sample was always higher than that of the first sample. In three more experiments the catalyst was studied coming from the high-temperature side, for three different activation temperatures, after it had been allowed to go through a break-in at 675 K. A point of maximum activity appears located in the temperature range 490–520 K. The maximum conversion values were found to increase when the activation temperature was decreased from 870 to 770 K.

Fig. 2 shows repeated heating–cooling cycles obtained with the WO_3/TiO_2 catalyst after activation at 770 K. The conversions measured during the cooling leg of the second cycle were much higher than those recorded through the first cooling leg.

Isothermal runs at the lowest temperature of 470 K indicated that the high conversions measured at that temperature could be kept for several hours. Afterwards

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Table 1. Properties[a] of the supports used

	support				
	TiO_2	SiO_2	Al_2O_3	SiO_2–Al_2O_3	ZnO
type	Harshaw Ti–0102–T $3.2\ 10^{-3}$ m	Davison Grace 62	Ketjen CK–300	Ketjen LAC 25	Harshaw
composition	86% TiO_2 14% Al_2O_3	99.9% SiO_2	99.9% Al_2O_3	85% SiO 15% Al_2O_3	100% ZnO
specific surface area/$m^2\ g^{-1}$	78	344	187	618	3
pore volume/$cm^3\ g^{-1}$	0.33	1	0.49	0.7	0.26
chemical composition		trace elements (ppm)			
Al		1–10	—	—	
Ca		5–500	—	—	
Cl		—	100	—	
Cu		1–10	—	—	
Fe		1–10	100	300	
Mg		10–100	—	—	
Mn		1–10	—	—	
Na		—	10	300	
S		—	150	270	
Ti		50–500	—	—	
Zn		10–100	—	—	
Zr		10–100	—	—	

[a] From manufacturers' specifications; blank spaces indicate data not available.

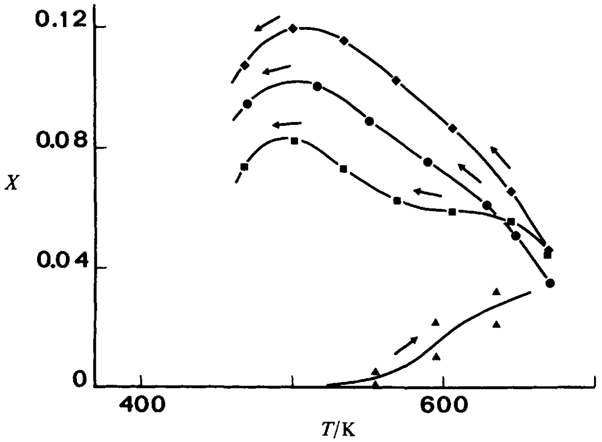

Fig. 1. Plot of catalyst activity, expressed as conversion of propene, X, as a function of the reaction temperature for a 6 wt % WO_3/TiO_2 catalyst. Heating leg after activation at 820 K (▲), cooling legs after activation at 770 (◆), 820 (●) and 870 (■) K. Reaction conditions: contact time, $W/F = 1.89$ kg s mol^{-1}, pressure = 0.2 MPa.

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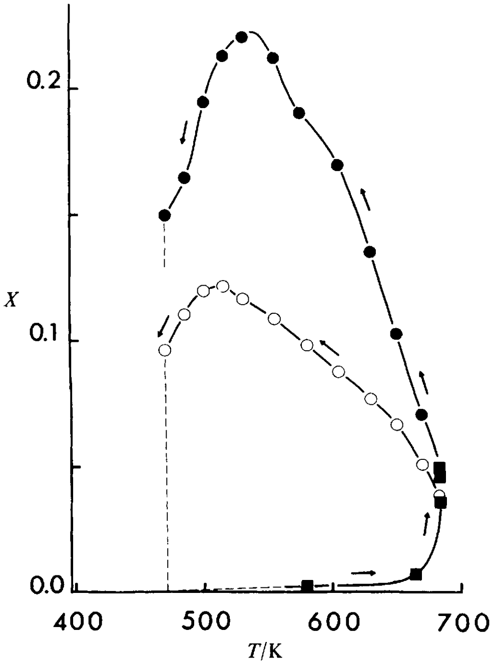

Fig. 2. Plot of catalyst activity, expressed as conversion of propene, X, as a function of the reaction temperature for the 6 wt % WO_3/TiO_2 catalyst activated at 770 K and after attaining steady state at 675 K. ○, First cooling leg; ■, first heating leg and ●, second cooling leg. Reaction conditions: contact time, $W/F = 1.89$ kg s mol^{-1}, pressure = 0.2 MPa.

the catalyst went through a phase of apparently reversible deactivation. The measured deactivation rates for this catalyst were 3.4% h^{-1} of the highest conversion measured after break-in at 675 K and 6% h^{-1} of the highest conversion measured at 470 K.

A 6 wt % WO_3/ZnO catalyst was also tested in the way described above. The results, obtained by increasing (decreasing) the temperature stepwise by 50 K every 30 min, showed that the catalyst is slightly active at temperatures > 600 K. A maximum in activity appeared for an activation temperature of 870 K.

A number of experiments was done to find out whether a maximum appears in the activity of the WO_3/SiO_2 catalyst as a function of the reaction temperature, using 3, 6 and 12 wt % catalysts. Fig. 3 shows a representative plot for the 12 wt % catalyst. For reaction temperatures in the range 675–875 K in no case was a maximum found. In another test the catalyst was found to undergo irreversible deactivation and loose its catalytic activity at temperatures slightly in excess of 875 K.

The supports used in the preparation of all these catalysts were found to be inactive for metathesis.

The rate–temperature relationship for the 6 wt % WO_3/Al_2O_3 catalyst has been reported previously.[3] Fig. 4 shows the effect of the activation temperature on the conversion at 675 K. The catalytic activity increases when the activation temperature is raised. Note that the selectivity for the reaction to primary metathesis products is slightly lower than that of the WO_3/SiO_2 catalyst and decreases when the activation temperature is increased from 770 to 970 K, but from the available data it was estimated to be 95% or better. (The selectivity for the WO_3/SiO_2 catalyst in this study was 99% or better.) The slightly lower selectivity of the WO_3/Al_2O_3 catalyst should

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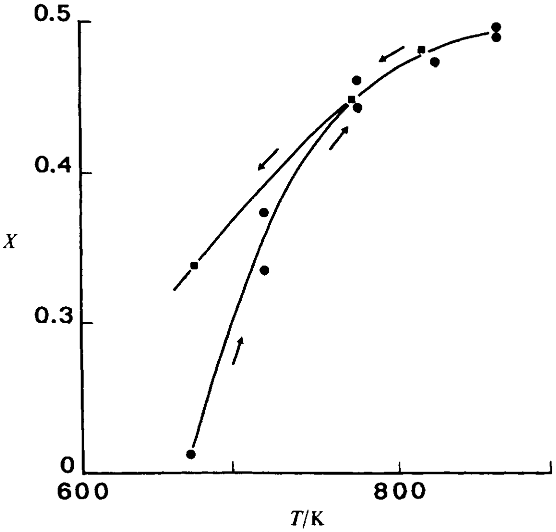

Fig. 3. Plot of catalyst activity, expressed as conversion of propene, X, as a function of the reaction temperature for a 12 wt % WO_3/SiO_2 catalyst after activation at 820 K. Reaction conditions: contact time, $W/F = 3.78$ kg s mol^{-1}, pressure = 0.2 MPa.

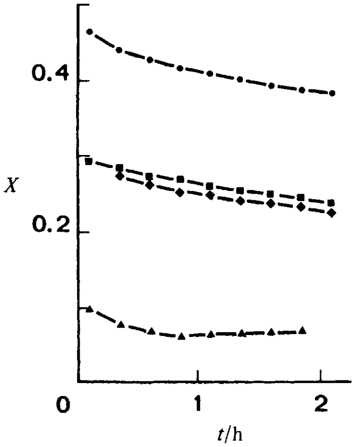

Fig. 4. Plot of the conversion of propene, X, against process time for a 7.4 wt % WO_3/Al_2O_3 catalyst activated at 770 (▲), 870 (◆ and ■) and 970 (●) K. Reaction conditions: contact time, $W/F = 1.89$ kg s mol^{-1}, temperature = 675 K, pressure = 0.2 MPa.

be partly attributed to the action of the support. This support was tested in blank runs at 675 K. The main products of the reaction with propene were ethene and 2-methylpropene, *cis*- and *trans*-but-2-ene in minor quantities and high boiling products. Data from blank runs were used to correct some of the results from the actual runs.

The rate–temperature relationship for the $WO_3/SiO_2–Al_2O_3$ catalyst was studied in a number of experiments. No maxima were found on either the heating or cooling leg of the cycle over the temperature range from 600 to 800 K, at which temperature

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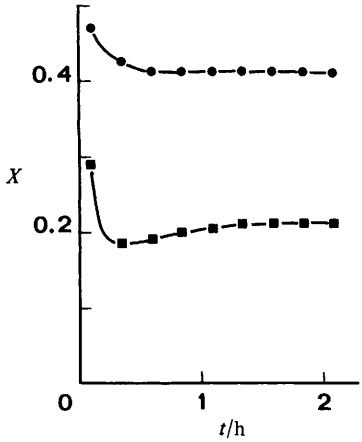

Fig. 5. Plot of the conversion of propene, X, against process time for a 6 wt % $WO_3/SiO_2-Al_2O_3$ catalyst activated at 770 (■) and 870 (●) K. Reaction conditions: contact time, W/F = 1.89 kg s mol^{-1}, temperature = 675 K, pressure = 0.2 MPa.

Table 2. Catalytic activity for catalysts containing 6 wt % catalysts[a]

catalyst	activation, T/K	reaction, T/K	N /s^{-1}	r_0 /10^{-4} mol g^{-1} s^{-1}	r_0^s /10^{-6} mol s^{-1} m^{-2}
		at point of maximum			
WO_3/TiO_2	770	515	0.240	1.62	2.08
WO_3/ZnO	870	710	0.074	0.265	8.83
WO_3/Al_2O_3	820	630	0.166	0.737	0.394
		at 675 K			
WO_3/SiO_2	870	675	3.15	23.6	6.86
	820	675	0.961	4.30	1.25
WO_3/Al_2O_3	870	675	0.425	2.77	1.48
	770	675	0.103	0.501	0.268
$WO_3/SiO_2 \cdot Al_2O_3$	870	675	0.848	7.83	1.27
	770	675	0.414	1.98	0.320

[a] Pressure = 0.2 MPa.

the active sites appeared to undergo irreversible deactivation. This catalyst is thus comparable to the WO_3/SiO_2 catalyst.[3] The effect of the activation temperature on its activity is shown in fig. 5, showing that this catalyst can be more active than the alumina-based one and has no break-in period, as shown by the WO_3/SiO_2 catalyst. The selectivity is comparable.

In order to make the comparison of the various catalysts more complete, conversion values recorded in these and previous tests were used to calculate turnover frequencies and specific rates of the metathesis of propene (table 2). The initial reaction rates given in the last two columns have been calculated on the basis of the rate equation for the carbene model as proposed by Kapteijn *et al.*[6]

From table 2 we can see that the WO_3/TiO_2 catalyst can be much more active than the WO_3/Al_2O_3 catalyst.

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Table 3. Acidity measurements

material	activation temperature /K	number of acid sites/g of support or catalyst Brönsted	number of acid sites/g of support or catalyst Lewis
SiO_2[a]	775	—	2.3×10^{20}
	825	—	2.1×10^{20}
	875	—	2.5×10^{20}
Al_2O_3[a]	775	2.7×10^{19}	1.1×10^{20}
	825	2.8×10^{19}	1.0×10^{20}
	875	2.6×10^{19}	0.9×10^{20}
SiO_2–Al_2O_3[a]	775	1.6×10^{20}	5.2×10^{20}
	825	1.3×10^{20}	4.2×10^{20}
	825	1.2×10^{20}	3.6×10^{20}
TiO_2	775	1.1×10^{20}	2.3×10^{20}
6 wt % WO_3/TiO_2	775	6.3×10^{19}	6.1×10^{19}
	875	7.2×10^{19}	6.2×10^{19}
ZnO	775	—	1.5×10^{18}
	875	—	1.2×10^{18}

[a] The values for these catalysts are in general agreement with results reported by B. Scheffer, P. Grimberg and J. A. Moulijn, to be published.

At a reaction temperature of 675 K the WO_3/SiO_2 catalyst appears to be more active than those based on alumina or silica–alumina. The activity of this catalyst appears to be much more dependent on the activation temperature, whereby we estimate that its activity for an activation temperature of 770 K would be comparable to that of the alumina- or silica–alumina-based catalysts. On the basis of the initial reaction rates it appears that the alumina-based catalyst is more active than the silica–alumina-based catalyst. However, the two catalysts appear to have approximately the same activity when this is expressed on a unit-surface-area basis.

ACIDITY MEASUREMENTS

The results of the acidity measurements are shown in table 3. On the basis of these results the supports can be classified in order of decreasing Brönsted acidity at 775 K as follows:

$$SiO_2\text{–}Al_2O_3 > TiO_2 > Al_2O_3$$

while the classification for the Lewis acidity at 775 K is

$$SiO_2\text{–}Al_2O_3 > TiO_2 \approx SiO_2 > Al_2O_3 > ZnO.$$

Van Roosmalen *et al.*[7] found silica to contain little Lewis acidity, and this mainly associated with the aluminium impurity. The high value for SiO_2 in table 3 is due to a large amount of physisorbed t-butylamine. Further, SiO_2 was found to contain no Brönsted-acid sites.

ZnO was also found to contain no Brönsted acidity. Its Lewis acidity is lower than that of Al_2O_3 by a factor 100, but its specific surface area is also lower by as much. The peak corresponding to the Lewis-acid sites appears as a convolution of two peaks: a large one in the temperature range 375–425 K and a smaller one in the temperature range 515–535 K.

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Al_2O_3 also shows a convolution of two peaks: a large one in the temperature range 355–375 K and a smaller one in the temperature range 475–485 K. The location of these peaks does not shift when the activation temperature is increased. The trend of total acidity of Al_2O_3 in this work as a function of the activation temperature is dissimilar from that reported by Tanabe.[8]

SiO_2–Al_2O_3, like alumina, is found to contain both Lewis- and Brönsted-acid sites. The peak corresponding to the Lewis sites is not a convolution of two smaller ones and the peak corresponding to the Brönsted sites is located at a lower temperature, an indication that silica–alumina contains stronger acidity.

A change in the activation temperature seems to affect only the Lewis acidity of alumina, but both the Brönsted and Lewis acidity of silica–alumina. The Lewis acidity of the WO_3/TiO_2 catalyst appears to be lower than that of the original support by a factor of four, while the Brönsted acidity is lower by a factor of two. The change in activation temperature seems to affect only the Brönsted acidity of this catalyst. At the higher activation temperature, the peak corresponding to the Brönsted acid is located at a lower temperature, possibly an indication of stronger Brönsted-acid sites.

DISCUSSION

Because of the complexity it is impossible to come to a general theory for the relationship between catalytic activity for metathesis and the structural properties. Apart from the parameters defining the catalytic activity in general, the following should be considered as critically important for the metathesis reaction: (*a*) the reducibility of the catalyst, (*b*) the stability of the reduced species, (*c*) the acidity of the support and/or of the corresponding catalyst, (*d*) the precursor surface structures and (*e*) the type and concentration of the surface hydroxyl groups.

In this article we restrict ourselves to the case of the tungsten oxide catalysts for the metathesis of propene.

For the chemistry of the break-in or activation process, reference should be made to two previous articles.[3, 9] The beneficial effect of the increased activation temperature on the catalytic activity of the WO_3/Al_2O_3 and WO_3/SiO_2–Al_2O_3 catalysts should be attributed to the loss of catalytic amounts of O and OH surface species from one or more tungsten oxide surface compounds, as was also observed in the case of WO_3/SiO_2 catalysts.[3]

CATALYTIC ACTIVITY AS A FUNCTION OF THE REACTION TEMPERATURE

The appearance of a maximum in the catalytic activity as a function of the reaction temperature appears to be a frequent occurrence in the metathesis of propene over a solid catalyst, as has been shown with various supported WO_3 catalysts. The WO_3/TiO_2 catalyst, having a maximum in the temperature range 490–520 K, can be compared with the WO_3/Al_2O_3 catalyst, which has a maximum at *ca.* 630 K.[3] At 500 K the WO_3/TiO_2 catalyst is more active than the WO_3/Al_2O_3 catalyst at 630 K. Explanations for the appearance of a maximum can be found in a special relationship between the activation energy for the metathesis and the heat of adsorption of propene, or in a reversible change in the number of active sites taking place when poisons or fragments needed for the reaction are adsorbed or desorbed.[3]

In contradiction to the behaviour of the WO_3/Al_2O_3 (fig. 4) and WO_3/SiO_2[3] metathesis catalysts, however, the activity of the WO_3/TiO_2 catalyst increases when the activation temperature is decreased. The results of fig. 2 indicate a relationship between the observed maxima and the catalytic activity. As the maximum becomes more pronounced in the second cycle, showing higher catalytic activity, and the

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deactivation rate is moderate and higher at the point of maximum, we conclude that deactivation does not vitiate such results. This catalytic system is active in a temperature range where the WO_3/SiO_2 catalyst shows negligible activity, and therefore it is promising for practical applications.

The WO_3/ZnO catalyst showed a maximum in activity as a function of the reaction temperature for an activation temperature of 870 K. The point of maximum is located at a higher temperature than in the previous case.

The presence of a maximum in the activity as a function of the reaction temperature occurs so generally in the case of the metathesis catalysts[3] as to prompt the idea that it is a characteristic property of the active sites involved in this reaction. There are, however, exceptions preventing us reaching this conclusion. One exception is provided by the WO_3/SiO_2 catalyst. For this catalyst the activity for the metathesis reaction does not pass through a maximum even when the reaction temperature is raised as high as 860 K. At that temperature the catalyst can work efficiently and selectively without any sign of a break-down. Another such exception is provided by the WO_3/SiO_2–Al_2O_3 catalyst.

RELATIONSHIP BETWEEN CATALYTIC ACTIVITY AND THE ACIDITY OF THE SUPPORTS

The Brönsted acidity of the TiO_2, Al_2O_3 and SiO_2–Al_2O_3 supports does not seem to play a role in the metathesis reaction. This conclusion is based on the following considerations. Among these supports, TiO_2 yields the most active catalyst and yet it is not the most acid. The number of Brönsted-acid sites remains constant (Al_2O_3) or decreases (SiO_2–Al_2O_3) when the activation temperature is increased, while the catalytic activity of the corresponding catalyst increases in both cases. It is surprising that the Brönsted acidity of the WO_3/TiO_2 catalyst is lower than that of the original support and increases with the activation temperature. The fact that at the higher activation temperature the catalyst is less active suggests that the Brönsted acidity present in this catalyst plays no role in the metathesis reaction. Therefore we cannot accept, in our case, the suggestion made by Laverty *et al.*[10] that strong Brönsted-acid sites play an important role in metathesis. When a proton is needed for the formation of the initial metal carbene (the suggested intermediate in metathesis), a more likely source seems to be a Lewis site located on the transition-metal ion, carrying an alkene molecule, as proposed by Van Roosmalen and Mol,[9] or a product molecule originating from the reduction of the alkene.

Furthermore, the classification of the various supports on the basis of decreasing Lewis acidity does not correspond to their classification on the basis of decreasing activity. Therefore we conclude that the Lewis acidity of the carriers is not directly involved in the metathesis reaction. This conclusion is further strengthened by the fact that the Lewis acidity is seen to decrease with increasing activation temperature, while the catalytic activity of the corresponding catalyst increases. The WO_3/TiO_2 catalyst does not fit in this pattern, but its behaviour does not contradict the conclusion.

We thank Mr B. Scheffer for his assistance with the acidity measurements.

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