LETTERS TO THE EDITOR

New Active Heterogeneous Olefin Metathesis Catalyst Based on Molybdenum Oxotetrachloride

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We demonstrated earlier [1, 2] that molybdenum pentachloride (MoCl_5) reacts with the surface hydroxyl groups of silica gel to release 2 mol of HCl per mole of molybdenum, forming two covalent bonds: $(\text{Si}-\text{O})_2\text{MoCl}_3$. This catalyst in combination with tetramethyltin (SnMe_4) as a cocatalyst is highly active in the metathesis of olefins, including 1-hexene:

where $\text{R} = \text{C}_4\text{H}_9$.

The initial rate of this reaction at 25°C is up to $70 (\text{mol 1-hexene}) (\text{mol Mo})^{-1} \text{s}^{-1}$.

Here, we report the synthesis of still more active metathesis catalysts based on silica gel-immobilized molybdenum oxotetrachloride (MoOCl_4) and SnMe_4 .

The interaction of MoOCl_4 with two hydroxyl groups of silica gel yields an inactive catalyst precursor, as distinct from what is observed for MoCl_5 . By decreasing the immobilization temperature and raising the silica gel precalcination temperature, it is possible to increase the proportion of sites in which the molybdenum atom is bound to the surface by a single bond: $\text{Si}-\text{O}-\text{MoOCl}_3$. This enhances the activity of the catalyst (table) and changes its color from yellow-orange to dark claret.

Obviously, raising the silica gel calcination temperature decreases the number of hydroxyl groups on the

SiO_2 surface, thus lowering the probability of a MoOCl_4 molecule reacting with two silanol groups. As catalysts (table, samples 1–4) were stored in argon in sealed tubes, they gradually lost their original color, turning yellow-orange, and this was accompanied by a decrease in their activity. Only sample 5 did not change its color and activity during storage. It was demonstrated that the decline in the activity of the catalysts and the changes in their color with time are due to the interaction between immobilized MoOCl_4 and free hydroxyl groups of silica gel with evolution of an additional amount of HCl.

A comparison between the activity of the molybdenum oxotetrachloride-based catalysts (table) and the activity of the molybdenum pentachloride-based catalyst (see above) suggests that samples 3–5 of the former are 1.8–2.2 times more active than the latter.

REFERENCES

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$\text{MoOCl}_4/\text{SiO}_2$ catalysts containing 5 wt % Mo: synthetic conditions and activity in 1-hexene metathesis

Sample no.	SiO_2 calcination temperature, $^\circ\text{C}^*$	MoOCl_4 immobilization temperature, $^\circ\text{C}$	$n(\text{HCl})/n(\text{Mo})$, mol/mol	Color of the catalyst	Initial 1-hexene metathesis rate,** $(\text{mol 1-hexene})(\text{mol Mo s})^{-1}$
1	300	80	1.72	Yellow-orange	21
2	300	22	1.41	Orange	59
3	350	22	1.35	Red-orange	130
4	400	22	1.28	Claret	148
5	460	22	1.02	Dark claret	159

* Calcination for 4 h at a residual pressure of 5×10^{-4} Torr.

** $T = 25^\circ\text{C}$.