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The Metathesis of Hexenes over Tungsten Oxide on Silica in the Presence of Hydrocarbons with Functional Groups

The catalytic olefin metathesis reaction is broadly applicable to simple olefins, but its extension to olefins with functional groups has met with limited success (*1–10*). Metathesis of the latter olefins may be inhibited, under conditions favorable for the metathesis of simple olefins, by such factors as steric hindrance, electronic influences on the double bond by a vicinal group, and adsorption and mobility characteristics of the heterosubstituted olefins over heterogeneous catalysts; most often, however, metathesis is prevented by deactivation of the catalyst by the functional group (*2*). Therefore, in order to define the scope of a metathesis catalytic system, it is necessary to determine the influence of different functional groups on its activity, before other factors can be scrutinized.

In this note we report a study of the influence of hydrocarbons containing halogens, nitrogen, or sulfur on the metathesis activity of tungsten oxide on silica. This catalyst is of interest because it operates at high temperatures (above 300°C) and, therefore, is considered resistant to poisoning by polar molecules (*1*).

Small amounts, generally 2 volume percent (see Table 1), of heterosubstituted alkanes or arenes were added to 2-hexene, and their effect on the metathesis conversion of the hexene was measured. The experiments were carried out at 673°K and at atmospheric pressure in a single-pass continuous-flow system, with a fixed catalyst bed in a tubular (7-mm-i.d.) quartz reactor (*11*). The temperature was measured in the center of the catalyst bed. One cubic centimeter of fresh catalyst was used in each test. The catalyst, 6.8% tungsten trioxide on silica (20/40 mesh, S.A. = 350 m^2/g) (*11*), was activated in the reactor at 873°K, first in a stream of dry air for 1 hr, then in a stream of carbon monoxide for 30 min. The catalyst was flushed with nitrogen after the air treatment for 10 min, and after the CO treatment while the catalyst was cooled to 673°K.

The heterosubstituted hydrocarbon was blended with the hexene, and the blend was added with a syringe pump at the rate of 12 cm^3 of liquid/hr; the contact time (catalyst void volume/flow rate) was ca. 0.3 sec. The reactor effluent was collected for 1 hr in a trap cooled to 197°K. The reactant mixture and the products were analyzed by gas chromatography and mass spectrometry. Hexene-2 (Phillips Pure Grade) was purified by percolation under nitrogen through activated alumina and magnesium oxide. The additives listed in Table 1 were commercial samples; they were purified by percolation

TABLE 1

Effects of Functional Groups on the Olefin Metathesis Activity of $WO_3 \cdot SiO_2$

Additive	Vol%	% Hexene conversion	% Additive recovered
None		57	
Fluorohexane	2	0	n.d.[a]
Chlorohexane	2	3	6
Bromohexane	2	8	0
Iodohexane	2	11	4
Fluorobenzene	2	55	100
	10	32	100
Chlorobenzene	2	22	100
Bromobenzene	2	4	100
Iodobenzene	2	<1	99
Hexanenitrile	2	12	n.d.
Benzonitrile	2	11	100
Hexylamine	4	30	n.d.
Nitrobenzene	2	0	40
Hexanethiol	2	0	0
Butyl sulfide	2	0	82
Thiophene	2	45	96

[a] n.d., not determined.

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through activated alumina, molecular sieves, and magnesium oxide.

In four tests made at regular intervals in the course of this work conversion of the neat hexene to metathesis products ranged from 53 to 62%; the average conversion was 57%. All the additives caused a decrease in the metathesis activity of $WO_3 \cdot SiO_2$, and some deactivated the catalyst completely. The hexene conversions obtained in the presence of the additives are listed in Table 1.

The haloalkanes inhibited severely the metathesis of hexene. The inhibiting effects increased regularly from the iodo compound, with reduced metathesis by more than 80%, to the fluoro compound which destroyed activity altogether. With the haloarenes, which underwent little or no decomposition, the opposite trend was observed; fluorobenzene showed the least inhibiting influence of all compounds tested, chlorobenzene was a moderate inhibitor, bromobenzene and iodobenzene were strong poisons.

The effects produced by hexanenitrile and those produced by benzonitrile were very similar; both compounds reduced hexene conversion markedly and by about the same amount. Hexylamine also inhibited hexene metathesis though much less severely than the nitriles. Similar inhibition by hexylamine has been reported by Gangwal and Wills (*12*), who observed that injection of a primary or secondary amine into a propylene feed stream enhanced temporarily the disproportionation of propylene over $WO_3 \cdot SiO_2$, while protracted addition of the amine led to deterioration of catalytic activity.

One of the three sulfur compounds tested, hexanethiol, decomposed completely during the experiment yielding hydrogen sulfide, that is known to deactivate $WO_3 \cdot SiO_2$ (*13*). Butyl sulfide also destroyed metathesis activity, although most of the sulfide was recovered unchanged. Thiophene caused only a moderate decrease in hexene conversion.

The influence of the acetylenic group on the olefin metathesis activity of $WO_3 \cdot SiO_2$ was also determined. Pent-2-yne, whose disproportionation is catalyzed by $WO_3 \cdot SiO_2$ (*14*), inhibited strongly the metathesis 2-hexene.

These results illustrate the principal difficulties associated with the metathesis of olefins with functional groups over high-temperature catalysts. On the one hand, many heterosubstituted hydrocarbons undergo thermal or catalytic decomposition. Moreover, the compounds themselves or their decomposition products may react with the catalyst altering its metathesis activity; for example, the metathesis activity of $WO_3 \cdot SiO_2$ is destroyed by exposure to H_2S (*13*) and enhanced after exposure to HCl (*15*). On the other hand, the high operating temperature provides only limited resistance to catalyst poisoning by those compounds which do not decompose. Thus, bromobenzene and iodobenzene, which were recovered essentially unchanged, were stronger poisons than their alkyl counterparts, which decomposed.

Despite these difficulties, some heterosubstituted olefins may undergo metathesis over $WO_3 \cdot SiO_2$. Although all the functional groups investigated reduced the metathesis activity of $WO_3 \cdot SiO_2$, a few were only moderate inhibitors. Alkenes containing the latter groups should, at least in limited concentrations, participate in the metathesis reaction, unless their participation is prevented by factors other than catalyst deactivation. This point is illustrated by the following example.

In view of the limited poisoning effects produced by fluorobenzene, we investigated the reaction of pentafluorophenylpropene and 2-hexene over $WO_3 \cdot SiO_2$. The experimental conditions and the procedure were the same as those used in the experiments described previously. The feed contained 90% by volume 2-hexene and 10% of a mixture of the two double bond isomers of pentafluorophenylpropene (see Table 2); in one of the isomers the pentafluorophenyl group is attached di-

TABLE 2

Products of the Cometathesis of Pentafluorophenylpropene and 2-Hexene

Pentafluorophenyl-alkene fraction	Wt%	
	Reactants	Products
$(C_6F_5)-C=C-C$	37.0	37.2
$(C_6F_5)-C-C=C$	63.0	42.6
$(C_6F_5)-C-C=C-C$	0	10.5
$(C_6F_5)-C-C=C-C-C$	0	1.4
$(C_6F_5)-C-C=C-C-C-C$	0	8.3

rectly to an olefinic carbon; in the other the double bond and the pentafluorophenyl group are separated by a $-CH_2$-group.

Pentafluorophenylpropene inhibited the metathesis of 2-hexene more severely than fluorobenzene; the conversion of 2-hexene to self-metathesis products was 14%. There was no evidence that 1-pentafluorophenylpropene reacted; however, the hexene underwent cometathesis with 3-pentafluorophenylpropene, 32% of which was converted to the products listed in Table 2. It is clear in this instance that the failure of 1-pentafluorophenylpropene to participate in the metathesis reaction is not a consequence of catalyst deactivation, but reflects steric and/or electronic effects of the pentafluorophenyl group.

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