Olefin metathesis on supported rhenium catalysts activated by γ-irradiation

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Abstract

A new approach to the activation of Re_2O_7/Al_2O_3 and $Re_2O_7/Al_2O_3 \cdot SiO_2$ for low-temperature olefin metathesis has been developed. After heating in oxygen and then in vacuum at 873 K, the catalysts were subjected to γ-irradiation from a ^{60}Co source in the presence of methane, butane, or carbon monoxide at ambient temperature. IR data revealed that, upon γ-irradiation, reduced Re species (metal ions in lower oxidation states and rhenium carbonyls) were produced. After evacuation at 293 or 423 K, catalytic activities of the γ-irradiated samples for olefin metathesis at 293 K were measured. The turnover frequencies (TOF) in propene metathesis for the Re-catalysts irradiated in CH_4 or C_4H_{10} were found to be approximately one order of magnitude higher than those for the unirradiated catalysts. The TOF for the catalysts irradiated in CO significantly increased after treatment with cyclopropane at 293 K. In the liquid-phase metathesis of hex-1-ene, turnover numbers as high as 1100–2700 mol C_6/mol Re (selectivity 90–98%) were obtained for the irradiated catalysts. It is suggested that γ-irradiation in the presence of alkanes induces a series of chemical transformations of the supported metal ions and can produce surface metal–carbene complexes which are active intermediates in metathesis.

Keywords: Rhenium–alumina catalyst; Propene; Hex-1-ene metathesis; Activation; γ-irradiation

1. Introduction

Alumina-supported rhenium oxide is one of the most active and stable catalysts for the metathesis of olefins at low temperatures [1,2]. At present a number of procedures are known for increasing the activity of this catalyst: (i) adding another transition-metal oxide (MoO_3, V_2O_5, or WO_3), (ii) phosphating or borating the support, (iii) using silica–alumina instead of pure alumina as a support, and (iv) promoti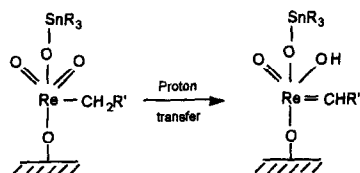ng the catalyst by treatment with a tetraalkyltin or a tetraalkyllead compound. The last treatment results in a significant enhancement in metathesis activity. It has been suggested that this effect is associated with the formation of organorhenium intermediates according to the following scheme [3]:
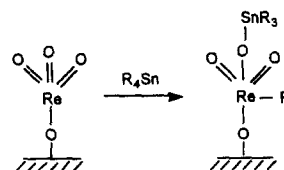
Supposedly, the Re-alkyl complexes formed can further isomerize via a proton transfer to

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yield Re-carbene complexes, which play a role as active sites for olefin metathesis [4]:

$$
\begin{array}{ccc}
\text{SnR}_3 & & \text{SnR}_3 \\
| & & | \\
O \diagdown \overset{O}{\underset{|}{\diagup}} O & \xrightarrow[\text{transfer}]{\text{Proton}} & O \diagdown \overset{O}{\underset{|}{\diagup}} OH \\
\text{Re} - \text{CH}_2\text{R'} & & \text{Re} = \text{CHR'} \\
| & & | \\
O & & O \\
\text{/////} & & \text{/////}
\end{array}
$$

Thus, treating the original catalysts with R_4Sn or R_4Pb appreciably increases the concentration of active sites on the surface and thereby enhances their activity. Unfortunately, this procedure has substantial drawbacks. For instance, it is necessary to carry out repeated treatment with organometallic promoters to regenerate the catalyst after deactivation. This applies for all subsequent activation cycles. Hence, considerable amounts of heavy metals (Sn, Pb) accumulate on the catalyst, and finally, it completely and irreversibly loses its activity. Sn-and Pb-containing organic substances are highly toxic, and their presence on the catalysts is extremely undesirable, since they can also be incorporated into the reaction products. It is therefore of interest to search for alternative methods for activating Re-containing metathesis catalysts which do not entail the introduction of heavy metals.

Earlier we developed a new efficient method for the activation of molybdena/silica metathesis catalysts [5,6]. This method involved low-temperature photoreduction of MoO_3/SiO_2 in carbon monoxide, during which supported Mo^{6+} ions are reduced to Mo^{4+}, followed by chemisorption of a carbene-donor compound such as cyclopropane, methylcyclopropane, or cycloheptatriene. These compounds interact with Mo^{4+} to form Mo–carbene complexes on the catalyst surface. Highly active catalysts for the metathesis of simple and functionalized olefins were obtained as a result of this two-step treatment. Instead of UV irradiation, ^{60}Co γ-irradiation can be used for MoO_3/SiO_2 activation [7]. The aim of the present study is to determine

whether or not γ-irradiation can be applied for the activation of $Re_2O_7/Al_2O_3 \cdot SiO_2$ and Re_2O_7/Al_2O_3 catalysts.

2. Experimental

2.1. Catalyst preparation and activation

The catalysts were prepared by impregnating the supports with aqueous solutions of ammonium perrhenate (Johnson Matthey, JMC 836 Specpure) followed by drying in air at 383 K. γ-Al_2O_3 (Ketjen CK 300, $S_{N2} = 208$ m^2/g, particle size 180–250 μm) and silica–alumina (Akzo, 24.3% of Al_2O_3, $S_{N2} = 374$ m^2/g, particle size 180–250 μm) were used as supports. Re_2O_7 contents in the samples were 3 and 6 wt%.

A weighed portion of the catalysts was placed in a quartz ampoule connected to a vacuum line and heated in oxygen (200 Torr) at 823 K under static conditions for 2 h and then evacuated for 1 h at the same temperature. Following this, 400 Torr of CH_4, n-C_4H_{10} or CO were admitted, and the ampoule was then sealed off. The samples were γ-irradiated from a ^{60}Co source at ambient temperature until the dose of approximately 100 Mrad was attained. After γ-irradiation the samples were evacuated and transferred into small breakable glass balls without exposure to air.

Thermal reduction in CO or H_2 was carried out in a static circulation system at a gas pressure of 80–100 Torr at 673 K. The reduction products were trapped at liquid nitrogen temperature. Photoirradiation in CH_4 was performed using unfiltered light of a high-pressure mercury lamp DRSh-1000 (1 kW).

2.2. Reagents

Propene and cyclopropane were purified by a triple freeze-thaw cycle with intermediate evacuation at 77 K.

Hydrogen, carbon monoxide, and methane were freed from oxygen and other admixtures by passing them through a column filled with Cr^{2+}/SiO_2.

Pure grade hex-1-ene was refluxed over KOH for 2 h and a middle fraction was collected by distillation ($\sim$ 80%) which was then refluxed over CaH_2 for 2 h. This procedure was repeated twice. Finally, hex-1-ene was distilled under Ar.

2.3. Measurements of catalytic activities in propene and hex-1-ene metathesis

Catalytic activities in both reactions were measured at room temperature. In propene metathesis, the gaseous mixture was circulated through the catalyst bed (0.15–0.2 g) in a volume of 570 cm³ (initial propene pressure was 44 Torr). The compositions of gaseous mixtures were determined using a UTI-100C quadruple mass-spectrometer connected to the circulation system through a leak valve.

Hex-1-ene metathesis was carried out under Ar in a reactor equipped with a magnetic stirrer and connected to a burette for measuring the amounts of ethene evolved. A breakable glass ball with a catalyst sample (0.15–0.2 g) was broken in the reactor under the layer of hex-1-ene (10 cm³), the magnetic stirrer was then switched on, and the amounts of ethene evolved were measured at different time intervals. In some experiments, after attaining hexene conversions of $\sim$ 50%, another 10 cm³ of hexene was added. The metathesis products were analyzed with a LKhM-8D gas chromatograph.

2.4. Spectroscopic measurements

IR diffuse reflectance spectra were recorded on a Perkin-Elmer 580B instrument in the 2300–1900 cm^{-1} range using a home-made attachment. For optical measurements, the samples were placed in quartz cuvettes supplied with CaF_2 windows.

3. Results

3.1. Catalytic activities of γ-irradiated $Re_2O_7/Al_2O_3 \cdot SiO_2$ and Re_2O_7/Al_2O_3 in propene metathesis

In the present work, we studied the effect of preliminary γ-irradiation of 3 and 6 wt% $Re_2O_7/Al_2O_3 \cdot SiO_2$ and Re_2O_7/Al_2O_3 in carbon monoxide, methane, and n-butane on their catalytic activities in propene metathesis. The corresponding data are summarized in Table 1. The specific activities of the catalysts were determined in the following way. Linear transforms for each kinetic curve $x_{but} = f(t)$, where x_{but} is the butene fraction in the gas mixture and t is the reaction time, were plotted in the coordinates $\ln[1 + (0.5\sqrt{K_{eq}} - 1)\ x_{but}]/[1 - (0.5\sqrt{K_{eq}} + 1)x_{but}] - t$, where K_{eq} is the equilibrium constant of the propene metathesis reaction. This equation was obtained earlier [8] assuming a Langmuir–Hinshelwood mechanism for propene metathesis. Typical linear transforms for 6 wt% $Re_2O_7/Al_2O_3 \cdot SiO_2$ activated by various procedures are shown in Fig. 1. Specific activities of the catalysts (TOF) were determined from the slopes of the straight lines.

As seen from Table 1, the catalytic activities of the samples irradiated in CH_4 and C_4H_{10} are approximately one order of magnitude higher than those of untreated samples (compare Runs 2, 3, 9 and 12 with Runs 1, 8, and 11). This effect is most pronounced for 6 wt% Re_2O_7/Al_2O_3.

γ-Irradiation in CO somewhat decreases the activity (Run 4). However, after cyclopropane adsorption, the activity sharply increases. This effect is even more pronounced after evacuation of the γ-irradiated sample at 423 K (Run 5). This is probably due to the removal of adsorbed radiolysis products at elevated temperatures, as a result of which subsequent cyclopropane chemisorption is more efficient.

The activities of the γ-irradiated catalysts decrease as the metathesis reaction proceeds. Thus, for example, exposure of 6 wt%

$Re_2O_7/Al_2O_3 \cdot SiO_2$, pre-$\gamma$-irradiated in CH_4 or CO, to an equilibrium mixture of the metathesis products for 1 h reduces the activity by a factor of ~ 20 (Runs 3 and 5). However, after evacuation at 423 K, the activity again increases and almost reaches its initial value. Hence, the decrease in activity is reversible and probably due to adsorption of the metathesis products which block the active sites.

The activities of the catalysts thermally reduced in CO at 673 K or in H_2 at 723 K (Runs 6, 10, and 14), as well as those of the samples photoirradiated in CH_4 (Run 7) were also measured. These treatments do not give rise to highly active catalysts. Moreover, after photoreduction or thermal reduction in H_2, the activities are even smaller than those of the original untreated samples. These reduction procedures evidently do not yield rhenium ions in the valent states necessary for the formation of catalytically active sites.

γ-Irradiated samples are sensitive to oxygen: following exposure to O_2 at room temperature, their activity diminishes drastically (Run 2). As indicated above, the active sites for propene metathesis are stable at 423 K. However, they are irreversibly destroyed at higher temperatures (573 K) (Run 9).

A characteristic feature of the γ-irradiated $Re_2O_7/Al_2O_3 \cdot SiO_2$ catalysts is the occurrence of side reactions, which somewhat decreases their selectivity. Small amounts of C_5–C_8 alkenes are found, which are most likely formed by cross-metathesis of propene and but-1-ene.

Table 1
Catalytic activities of $Re_2O_7/Al_2O_3 \cdot SiO_2$ and Re_2O_7/Al_2O_3 in propene metathesis ($T = 293$ K, $P_0(C_3H_6) = 44$ Torr, γ-irradiation dose 100 Mrad)

Run No.	Treatment [a]	Specific activity (TOF) (mol C_3H_6/mol Re s) $\times 10^3$
	6 wt% $Re_2O_7/Al_2O_3 \cdot SiO_2$	
1	None	7.5
2	γ-irradiation in CH_4, evacuation at 293 K	100
	Exposure to O_2 (10 Torr, 2 min)	4.8
3	γ-irradiation in n-C_4H_{10}, evacuation at 493 K	95
	Readmission of C_3H_6 onto the sample after 1 h of the reaction	5.5
	Evacuation at 423 K for 1 h	75
4	γ-irradiation in CO, evacuation at 293 K	3.8
	Cyclopropane adsorption at 293 K	42
5	γ-irradiation in CO, evacuation at 423 K, cyclopropane adsorption at 293 K	67
	C_3H_6 readmission onto the sample after 1 h of the reaction	3.0
	Evacuation at 423 K for 1 h	60
6	Thermal reduction in CO at 673 K for 1 h	12
	Cyclopropane adsorption at 293 K	12
7	Photoreduction in CH_4 at 293 K for 2 h	5.7
	3 wt% $Re_2O_7/Al_2O_3 \cdot SiO_2$	
8	None	9.3
9	γ-Irradiation in CH_4, evacuation at 293 K	71
	Evacuation at 573 K for 1 h	2.3
	Reoxidation in O_2 at 823 K for 1 h	7.0
10	Thermal reduction in H_2 at 723 K for 1 h	1.0
	6 wt% Re_2O_7/Al_2O_3	
11	None	1.2
12	γ-Irradiation in CH_4, evacuation at 293 K	140
	C_3H_6 readmission onto the sample after 1 h of the reaction	12
	Evacuation at 423 K for 1	110
13	γ-Irradiation in CO, evacuation at 423 K, cyclopropane adsorption at 293 K	95
14	Thermal reduction in CO at 623 K for 0.5 h	1.8

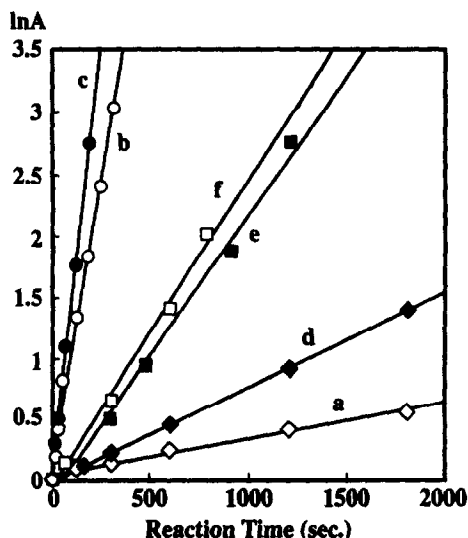[a] The catalysts were pretreated in oxygen (100 Torr) at 823 K for 2 h (see Section 2).

Fig. 1. Linear transforms of the kinetic curves for propene metathesis on 6 wt% $Re_2O_7/Al_2O_3 \cdot SiO_2$ plotted in the coordinates $\ln A = \ln[1 + (0.5\sqrt{K_{eq}} - 1)x_{but}]/[1 - (0.5\sqrt{K_{eq}} + 1)x_{but}] - t$: a – sample γ-irradiated in CO, evacuated at 293 K; b – sample γ-irradiated in CO, evacuated at 293 K, cyclopropane is adsorbed; c – sample γ-irradiated in CO, evacuated at 423 K, cyclopropane is adsorbed; d – sample c after exposure to the reaction mixture for 1 h, evacuation at 293 K and C_3H_6 readmission; e – unirradiated sample; f – sample thermally reduced in CO at 673 K.

The latter is probably produced by the double-bond shift in but-2-ene, the major product of propene metathesis. It should be emphasized that the metathesis selectivity is higher for γ-irradiated Re_2O_7/Al_2O_3.

It is evident from Table 1 that cyclopropane treatment of γ-irradiated $Re_2O_7/Al_2O_3 \cdot SiO_2$ and Re_2O_7/Al_2O_3 results in an appreciable increase in their catalytic activities. By analogy with the earlier studied Mo^{6+}/SiO_2 catalysts photoreduced in CO [5,6], we can assume that rhenium–carbene complexes are produced by cyclopropane adsorption. We attempted to estimate the number of adsorption sites. The number of cyclopropane molecules adsorbed on a γ-irradiated 6 wt% $Re_2O_7/Al_2O_3 \cdot SiO_2$ sample after evacuation at 423 K was determined to be 2.1×10^{19} g^{-1}.

The number of cyclopropane molecules adsorbed on the γ-irradiated support alone was 6.3×10^{18} g^{-1}. Thus, the number of cyclopropane molecules adsorbed on reduced rhe-

nium species is 1.5×10^{19} g^{-1} or 9.9% of the total rhenium content in the sample. Similar measurements were performed for a 6 wt% (Re_2O_7/Al_2O_3 sample γ-irradiated in CO. The numbers of cyclopropane molecules adsorbed on irradiated and on untreated samples were 2.0×10^{19} and 6.4×10^{18} g^{-1}, respectively, i.e., the number of sites capable of cyclopropane adsorption is 9.1% of the total rhenium content in the sample. Hence, about 10% of the rhenium species adsorbs cyclopropane and could yield carbene complexes. However, this is only an upper estimate for the number of Re-carbene sites due to the plausible occurrence of side reactions (for example, isomerization of cyclopropane to propene).

3.2. Catalytic activities of γ-irradiated $Re_2O_7/Al_2O_3 \cdot SiO_2$ and Re_2O_7/Al_2O_3 catalysts in liquid-phase hex-1-ene metathesis

The activities of γ-irradiated $Re_2O_7/Al_2O_3 \cdot SiO_2$ and Re_2O_7/Al_2O_3 in liquid-phase hex-1-ene metathesis are given in Table 2. The most important characteristics of the catalysts is their productivity, i.e., the number of moles of hex-1-ene converted on 1 mole of Re until complete deactivation of the catalyst (TON). The productivities of all the studied catalysts fall in the interval from 1000 to 2700 regardless of the activation procedure. A comparison with literature data shows that the productivities of the γ-irradiated samples are not inferior to those activated by treatment with organometallic promoters. For instance, the maximum productivity of 2.8% $Re(acac)_3/Al_2O_3$ activated by $Pb(Et)_4$ in hex-1-ene metathesis at 50°C and at the olefin/Re = 5000 ratio is 1460 mole of hexene per 1 mole of Re [9]. It should be also noted that the γ-irradiated support alone is completely inactive (Table 2, Run 7), which indicates that γ-irradiation in CO and alkanes is an efficient method of catalyst activation.

An analysis of the data of Table 2 reveals that the selectivity relative to C_{10} production (dec-5-ene) is substantially dependent on the

Table 2
Catalytic activities of $Re_2O_7/Al_2O_3 \cdot SiO_2$ and Re_2O_7/Al_2O_3 in hex-1-ene metathesis ($T = 293$ K, hexene/Re = 2000–3000, γ-irradiation dose 100 Mrad)

Run No.	Treatment	Reaction time (h)	C_6 conversion (%)	Product composition (%)							Selectivity to C_{10} (%)	Productivity (TON) (mol C_6/mol Re)
				C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}		
				6 wt% $Re_2O_7/Al_2O_3 \cdot SiO_2$								
1	γ-irradiation in CO, evacuation at 293 K, cyclopropane adsorption at 293 K	48	42.1	2.2	57.9	3.2	0.8	3.4	32.3	0.2	90.2	1130
2	γ-irradiation in CH_4, evacuation at 293 K	1	46.1	2.0	53.9	1.2	0.4	2.0	40.3	0.2	94.2	1150
		48	81.8	2.6	18.2	11.0	3.5	15.0	48.5	0.7	66.7	1710
3	γ-irradiation in C_4H_{10}, evacuation at 293 K	1	27	1.6	73.0	0.8	0.1	1.3	23.1	0.1	96.1	920
				3 wt% $Re_2O_7/Al_2O_3 \cdot SiO_2$								
4	γ-irradiation in CH_4, evacuation at 293 K [a]	1	30.3	2.5	69.7	1.0	0.2	1.7	24.8	0.1	94.5	1600
		48	66.6	3.0	33.4	7.4	1.7	11.0	42.9	0.4	76.3	2740
				6 wt% Re_2O_7/Al_2O_3								
5	γ-irradiation in CH_4, evacuation at 293 K	1	58.8	0.2	41.2	0.2	0.1	1.1	57.2	–	98.6	1050
		24 [b]	52.0	0.2	48.0	0.2	0.1	1.0	50.5	–	98.5	2000
6	γ-irradiation in CO, evacuation at 423 K, cyclopropane adsorption at 293 K	1	46.0	0.1	54.0	0.1	0.1	0.1	44.6	–	98.6	1050
		24 [b]	40.6	0.2	59.4	0.2	0.1	1.1	39.0	–	98.5	1860
				$Al_2O_3 \cdot SiO_2$								
7	γ-irradiation in CH_4, evacuation at 293 K	1		Traces								

[a] Repeated γ-irradiation after heating the sample in O_2 and then in a vacuum at 823 K.
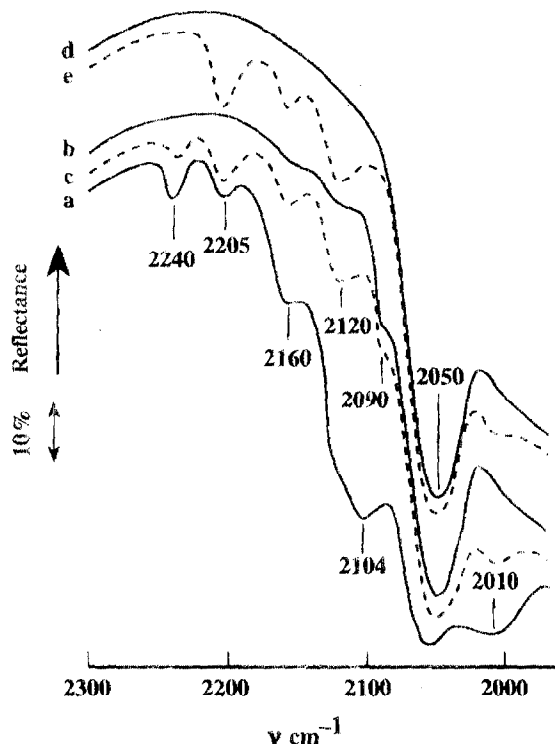[b] Another 10 cm³ of hex-1-ene is added.

Fig. 2. Diffuse reflectance IR spectra of 6 wt% $Re_2O_7/Al_2O_3 \cdot$ SiO_2 after: a – γ-irradiation in CO (recorded in the presence of 20 Torr CO in the gas phase); b – sample a after evacuation at 423 K; c – sample b after admission of 20 Torr CO; d – sample c after evacuation at 573 K; e – sample d after admission of 20 Torr CO.

contact time of the catalyst with the substrate. It is higher than 94% for shorter contact times (1 h), but the selectivity to C_{10} for Re_2O_7/Al_2O_3 $\cdot SiO_2$ for longer contact times (24–48 h) decreases markedly (Runs 2 and 4). This is apparently due to the double-bond shift catalyzed by the acid sites of the support. The resulting isomerization products then metathesize yielding a whole variety of products ranging from C_5 to C_{11}. However, the selectivity of Re_2O_7/Al_2O_3 samples (Runs 5 and 6) remains high enough even for longer contact times (24 h).

3.3. Diffuse reflectance IR spectra of γ-irradiated $Re_2O_7/Al_2O_3 \cdot SiO_2$ and Re_2O_7/Al_2O_3

Fig. 2a shows the IR spectrum of a 6 wt% $Re_2O_7/Al_2O_3 \cdot SiO_2$ sample γ-irradiated in CO in the range of CO stretching vibrations (2300–

2000 cm^{-1}). The spectrum is rather complex and consists of a series of absorption bands which complicate unambiguous interpretation. Nevertheless, some of the absorption bands (ABs) can be reliably assigned.

The two higher frequency ABs (at 2205 and 2240 cm^{-1}) can be detected only in the presence of CO in the gas phase. They completely disappear after evacuation of the sample at 293 K, whereas the intensities of other bands do not change significantly. The bands reappear after admission of CO. These bands can be attributed to CO molecules weakly adsorbed on two different types of sites on the $Al_2O_3 \cdot SiO_2$ surface, probably on aprotic sites of the support [10] and/or on radiation-induced defects. The lower frequency ABs in Fig. 2a (at 2160, 2104, 2050, 2010, and a shoulder at 2120 cm^{-1}) should be assigned to complexes of CO with reduced rhenium species produced during γ-irradiation in CO. The thermal stability of these complexes differs significantly. The most stable complex is characterized by an AB at 2050 cm^{-1}. The intensity of this band remains almost unchanged upon evacuation of the sample even at 573 K (Fig. 2d), whereas the other bands already vanish at 423 K (Fig. 2b). The 2050 cm^{-1} band can be attributed to rhenium tricarbonyl complexes, which were earlier identified on alumina and silica surfaces and characterized by two major IR ABs at ~ 2030 and 1915–1920 cm^{-1} [10–15]. The latter band is beyond the limit of our IR measurements because of the strong light absorption by $Al_2O_3 \cdot SiO_2$. The surface tricarbonyl complexes were found to be thermally stable, because in situ IR measurements have shown that CO loss occurs only at temperatures exceeding 573 K [12].

The lowest frequency band at 2010 cm^{-1} which disappears upon evacuation at 423 K and reappears after CO admission can be attributed to CO adsorbed on metal rhenium in a linear form [10]. The ABs at 2160, 2120 and 2104 (2090) cm^{-1} in Fig. 2a and 2c, which behave similarly to the one at 2010 cm^{-1}, most likely belong to CO complexes with reduced rhenium

ions. It is generally accepted that the lowering of CO stretching-vibration frequencies in M^{n+}...CO complexes is associated with an increase in the electron-donor ability of the metal ions, i.e., the lower the oxidation state, the lower the frequency. Taking this into account, we can assign ABs at 2160, 2120, and 2104 (2090) cm^{-1} to Re^{n+} carbonyl complexes, where $n \leq 6$. The actual oxidation state of the rhenium species cannot be deduced more precisely from the present data.

The question arises as to which of the ABs observed can be attributed to those Re ions which are the precursors of the active sites in metathesis. To answer this question, we can compare the spectrum of the $Re_2O_7/Al_2O_3 \cdot SiO_2$ sample γ-irradiated in CO, evacuated at 423 K and then exposed to CO (Fig. 2c), with the spectrum of the same sample, which was recorded after evacuation at 573 K and CO readmission (Fig. 2e). The former corresponds to the active catalyst (see Tables 1 and 2), whereas the latter is characteristic of the completely deactivated catalyst. The major difference between the two spectra is the absence of a weak AB at 2090 cm^{-1} in the spectrum of the deactivated sample [1]. This band could correspond to CO complexes with those Re^{n+} ions that yield the carbene-type transient structures involved in metathesis. The valence state of these ions cannot be unambiguously deduced from the IR spectra. However, taking into consideration the relatively low ν_{CO} value in the complex and the presence of two higher frequency bands in the spectrum in Fig. 2c (at 2160 and 2120 cm^{-1}), we can assume that the rhenium in this complex has an oxidation state lower than 6 + or even 5 + .

The IR spectrum of Re_2O_7/Al_2O_3 γ-irradiated in methane recorded in the presence of CO (Fig. 3) is similar to that of $Re_2O_7/Al_2O_3 \cdot SiO_2$. The background of the support is less
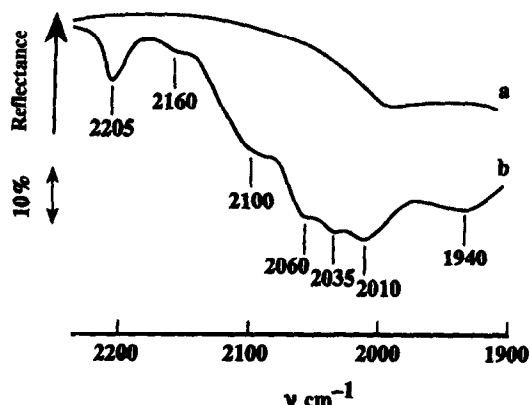

Fig. 3. Diffuse reflectance IR spectra of 6 wt% Re_2O_7/Al_2O_3 after: a – γ-irradiation in CH_4 and evacuation at 293 K; b – after admission of 20 Torr CO.

intense in the latter spectrum, and thus, the recording could be extended to lower wavenumbers. The ABs at 2160 and 2100 cm^{-1} are assigned to Re^{n+}...CO complexes, whereas those at 2060, 2035, 2010 and 1940 cm^{-1} are attributed to rhenium carbonyls and linearly bonded CO on metal rhenium clusters.

After cyclopropane adsorption at 293 K on $Re_2O_7/Al_2O_3 \cdot SiO_2$ and Re_2O_7/Al_2O_3 γ-irradiated in CO, we could not find any new ABs in the range of C–H stretching vibrations (2800–3000 cm^{-1}). Thus, we were not able to detect possible formation of π-complexes or $Re^{n+} =CH_2$ after cyclopropane adsorption by IR.

4. Discussion

The present study allows us to unambiguously conclude that γ-irradiation of rhenium catalysts in the presence of CO and alkanes causes reduction of supported rhenium ions, which originally have an oxidation state of 7 + . This emerges from the IR spectra of γ-irradiated $Re_2O_7/Al_2O_3 \cdot SiO_2$ and Re_2O_7/Al_2O_3 recorded under CO atmosphere, in which a set of ABs arising from complexes of CO with reduced Re ions can be clearly seen (Figs. 2 and 3). Radiation reduction occurs non-selectively and leads to the formation of rhenium ions in various oxidation states.

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[1] The absence of AB at 2240 cm^{-1} in the spectrum in Fig. 2e is most likely associated with the annealing of the sites for physical adsorption of CO as a result of heating at 573 K.

For 6 wt% $Re_2O_7/Al_2O_3 \cdot SiO_2$ γ-irradiated in CO, we were able to determine the mean oxidation state of rhenium by measuring the amount of CO_2 formed during irradiation. This value was found to be 6.3, i.e., the reduction is not very pronounced. Thermal reduction of 6 wt% $Re_2O_7/Al_2O_3 \cdot SiO_2$ in CO proceeds much more deeply: the mean oxidation states for rhenium in this case were 5.9 and 5.1 at 623 and 673 K, respectively.

Photoreduction of the rhenium catalysts in CO turned out to be inefficient. No CO_2 or other photoreduction products were found. This can be explained by proposing that an excited charge-transfer complex, which could be formed as a result of photon absorption, deactivates very rapidly and thus has extremely low probability for reacting with any reducing molecules.

The following reaction scheme can be assumed for the radiation reduction in CO:
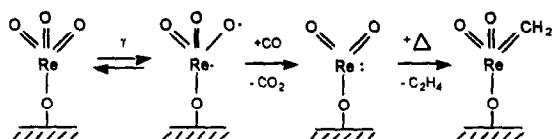
The energy of a γ-quantum is mainly absorbed by the support [2] and further transferred to the surface rhenium species. An excited charge-transfer complex which is formed in this process reacts with CO molecule yielding CO_2 and, thus, Re^{7+} is reduced to Re^{5+}. The latter can react with cyclopropane giving rise to $Re=CH_2$ carbene complexes active in metathesis. This explains a sharp increase in the activity and productivity in metathesis of γ-irradiated in CO samples after cyclopropane treatment (Tables 1 and 2). An analogous reaction of photoproduced Mo^{4+} ions with cyclopropane on the

silica surface has been thoroughly studied in [5,6]. Taking into account a rather high mean oxidation state of rhenium in the catalysts reduced by γ-irradiation ($Z = 6.3$) and the fact that less than 10% of the reduced Re ions can adsorb cyclopropane to yield carbene complexes (see Section 3.1), we can conclude that only a small fraction of the rhenium is involved in the metathesis reactions.

Upon γ-irradiation in alkanes, Re-carbenes are formed by the following hypothetical scheme:
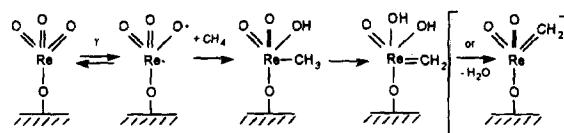
A key step in the above scheme is the interaction of methane (or alkane) molecule with the excited Re-complex, which results in the formation of the $Re-CH_3$ (or Re–R) bond. Possibly, $Re=CH_2$ (or Re = R') is yielded by the subsequent proton transfer or by the elimination of a molecule of water.

The above schemes for radiation reduction and formation of Re-carbenes are only hypotheses; they do not account for all the experimental data obtained (for example, formation of reduced rhenium ions in various valence states). Nevertheless, they can explain the effect of cyclopropane treatment and activation under irradiation in the presence of alkanes.

It is of interest to compare specific activities for the γ-irradiated catalysts and those obtained earlier with the same catalysts but under different reaction conditions, i.e., in a fixed-bed flow reactor at a higher pressure and reaction temperature [16]. According to [16], TOFs in propene metathesis at 323 K at a $C_3H_6:N_2$ ratio of 1:2 ($P = 1.5$ atm) are equal to 100×10^{-3} and 130×10^{-3} s^{-1} for 6 and 3 wt% $Re_2O_7/Al_2O_3 \cdot SiO_2$, respectively, and to 10×10^{-3} s^{-1} for 6 wt% Re_2O_7/Al_2O_3. A comparison of these values with the TOF for the untreated catalysts

(Table 1, Runs 1, 8, and 11) reveals qualitative agreement between the two series of data, that is $Re_2O_7/Al_2O_3 \cdot SiO_2$ is much more active than Re_2O_7/Al_2O_3. However, there is no quantitative consistency between the above results, probably, due to a higher reaction temperature [16] (by 30 K) and to the difference in the reaction conditions. It should, however, be emphasized that the TOF for γ-irradiated $Re_2O_7/Al_2O_3 \cdot SiO_2$ and Re_2O_7/Al_2O_3 do not differ appreciably.

Thus, we can draw the conclusion that γ-irradiation under a reducing atmosphere is an efficient method for the activation of rhenium-containing catalysts. It allows repeated use of the same catalyst samples after their complete deactivation. This is achieved by second, third, and further γ-irradiations of the samples preheated at high temperatures in oxygen. A certain drawback of the γ-irradiated $Re_2O_7/Al_2O_3 \cdot SiO_2$ catalysts is the occurrence of side reactions (double-bond shift in alkenes on acid sites), which somewhat reduces the selectivity of metathesis. Re_2O_7/Al_2O_3 is free of this drawback.

Acknowledgements

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