Journal of Catalysis **192**, 374–380 (2000)
doi:10.1006/jcat.2000.2843, available online at http://www.idealibrary.com on IDEAL®

Tungsten Catalysts Supported on Activated Carbon

II. Skeletal Isomerization of 1-Butene

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Received October 25, 1999; revised February 1, 2000; accepted February 10, 2000

Tungsten catalysts supported on activated carbon were used in the isomerization reaction of 1-butene. The results obtained were compared with those of other tungsten catalysts supported on Al_2O_3, SiO_2, and TiO_2. When the catalysts supported on activated carbon were pretreated in He flow, at either 623 or 748 K, the activity to produce isobutene increased linearly with the surface acidity of the catalysts, and the specific activity after pretreatment at 623 K was higher than that after pretreatment 748 K. The activity to produce isobutene did not decrease with reaction time and no dimerization by-products were obtained. After the pretreatments at 973 and 1223 K, there was a loss of activity with reaction time, and by-products from the dimerization of butenes appeared. The presence of water vapor in the reaction mixture was also studied. The catalysts supported on Al_2O_3, SiO_2, and TiO_2 and pretreated under the same conditions, at both 623 and 748 K, showed a decrease in activity to produce isobutene with reaction time and the catalyst supported on Al_2O_3 was the most active. Results show the importance of the support in these kinds of catalysts and seem to indicate that the activated carbon, due to its surface basicity, moderates the surface acidity of the tungsten oxide particles. Therefore, with a lower surface acidity of the catalyst it has an activity similar to that found with the Al_2O_3–W catalysts but without deactivation. © 2000 Academic Press

Key Words: **tungsten catalysts; carbon support; isomerization of 1-butene.**

INTRODUCTION

Skeletal isomerization of C_4 hydrocarbons can be efficiently catalyzed by the binary oxides of W, Mo, and Al (1–10). These materials are highly selective but are deactivated very quickly (11).

The surface active sites present on the above oxides, responsible for the skeletal isomerization of 1-butene, must be of the Brønsted type to produce a rapid isomerization, and their acid strength should not be too strong (1, 12). The presence of very strong surface acid sites of the Brønsted type brought about an excessive formation of by-products (6). Lewis surface acid sites seem to be less important in this reaction (4, 6).

It has been shown recently (1, 3, 6, 11, 13, 14–24) that the skeletal isomerization of 1-butene to produce isobutene was selectively achieved by a monomolecular mechanism, whereas the by-products of the reaction were produced through a bimolecular mechanism, which involved the dimerization of butenes and isobutene followed by breakdown of the octenes formed. Therefore, the dimerization must be suppressed on these catalysts in order to avoid the formation of by-products that deactivate them.

According to the above information the catalysts to be used in the skeletal isomerization of 1-butene should have Brønsted surface acid sites of moderate strength and a composition and/or structure that eliminates or strongly suppresses the formation of dimers or polymers and carbonaceous residues that deactivate the catalysts. Thus, recently there was an important breakthrough in the skeletal isomerization of 1-butene with the use of microporous materials with proper channel dimensions and pore structure as well as acidity (1, 11, 13, 16, 19, 22, 25, 26). The high selectivity to isobutene and catalytic activity of these materials can be explained by their shape selectivity. These are selective since intermediates leading to by-products cannot be formed freely inside their pores and channels due to their dimensions. Also, deactivation is slow because polymerization is also restricted (11, 17).

Tungsten trioxide is a quite effective catalyst for the skeletal isomerization of 1-butene since its surface has more suitable acid sites than other binary oxides (12). Thus, WO_3 has been used supported on TiO_2, Al_2O_3, SiO_2, and ZrO_2 as catalyst in the above reaction (5, 7, 8, 27–29) and, recently, a tungsten oxide carbon aerogel (9) has also been used. Results of this last study showed that the by-products of dimerization were not obtained and that the isobutene yield was around 40% at 448 K. Therefore, this WO_3 catalyst was more active and selective than others reported in the literature. These results could indicate that the carbon support favors the formation of isobutene in comparison

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0021-9517/00 $35.00

to others used previously. For this reason, we started this study to determine the effects of catalyst preparation, their tungsten content, and pretreatments given to them on the activity and selectivity of tungsten catalysts supported on activated carbon, whose preparation and characterization had been studied previously (30). Results found with these catalysts will be compared with those obtained with other tungsten catalysts supported on Al_2O_3, SiO_2, and TiO_2 and which were also prepared by us.

EXPERIMENTAL

Tungsten catalysts supported on activated carbon have been described elsewhere (30). Al_2O_3 and SiO_2, both supplied by Merck, and TiO_2 by Fluka, all of them with a particle size between 63–200 μm, were also used as supports. The catalysts were prepared by impregnation with an aqueous solution of ammonium tungstate to give a 5% metal loading. These catalysts were also pretreated in He flow between 623 and 748 K before their characterization and use in the reaction. They were characterized by N_2 adsorption at 77 K, XRD, and TPD of adsorbed ammonia (30).

The isomerization of 1-butene was performed in a quartz microreactor at atmospheric pressure with 0.2 g of catalyst, and using a continuous N_2 flow (60 $cm^3\ min^{-1}$) containing 1% 1-butene (by volume). The reaction temperatures ranged between 323 and 373 K. Products were analyzed by gas chromatography using a flame ionization detector and a GS-alumina capillary column supplied by J&W Scientific (50 m × 0.53 mm). Prior to studying the isomerization of 1-butene the catalyst was heat treated in He flow at temperatures ranging between 623 and 1223 K for 4 h. Once this treatment was finished, the catalyst was cooled to the reaction temperature and the He flow switched to the reaction mixture, which passed through the catalyst for 30 min before analysis of the reaction products. Between two activity measurements at different temperatures the catalyst was cleaned by passing He. Activity measurements at different temperatures were measured by both increasing and decreasing the reaction temperature.

Activity to obtain a determined species, r_x, was obtained from the general Eq. [1],

$$r_x = F_{1\text{-butene}}\, C_x / W, \qquad [1]$$

where $F_{1\text{-butene}}$ is the 1-butene flow through the catalyst in moles per minute, C_x is the conversion of 1-butene to species x, and W is the weight of the catalyst in grams.

Apparent activation energy was obtained by applying Arrhenius's equation to the activity data obtained at different temperatures.

RESULTS AND DISCUSSION

Tungsten Catalysts Supported on Activated Carbon

Results of product distribution and activity to produce isobutene, r_{IB}, at 343 K and apparent activation energy to produce this hydrocarbon in the temperature range 323–363 K after the catalysts were previously heated at 623 and 748 K, in He flow for 4 h, are compiled in Tables 1 and 2. The catalysts were not deactivated during the experiments and the support alone (without tungsten), after its heat treatment at the above temperatures, did not give any activity within the reaction temperature range studied.

Product distribution obtained after the pretreatments at 623 and 748 K shows that isobutene, IB, was the main product obtained followed by *trans*-2-butene, T2B, and in much lower amounts its cis isomer, C2B. Neither C_3–C_5 nor C_2–C_6 by-products were obtained, which would come from dimerization of butenes. Therefore, the bimolecular mechanism must be suppressed and the reaction on these catalysts follows a monomolecular mechanism which produces both the skeletal and double bond isomerization (1, 3, 6, 11, 13, 14–24). Both isomerization reactions seem to need surface acid sites of different strength. Thus, in tungsten oxide catalysts supported on Al_2O_3 (7), the skeletal isomerization was suppressed when the strong acid groups were eliminated and the activity for double bond isomerization was, therefore, sustained.

TABLE 1

Product Distribution (%) and Activity of the Catalysts to Produce Isobutene, r_{IB}, at 343 K

Catalyst	r_{IB}, μmol g^{-1} min^{-1}	E_a (IB), kJ mol^{-1}	Isobutene	*trans*-2-Butene	*cis*-2-Butene	Cis/trans
W4.8	5.46	40.9 ± 0.8	68.6	28.8	2.6	0.09
W9.1	11.67	46.1 ± 1.8	60.6	38.9	0.5	0.01
W14.9	20.29	48.0 ± 1.5	61.6	37.5	0.9	0.02
W23.1	38.20	43.7 ± 1.2	59.9	39.6	0.5	0.01
HW6.1	7.55	26.6 ± 1.2	65.6	32.5	1.9	0.06
HW15.1	40.81	37.8 ± 0.8	63.6	35.3	1.1	0.03

Note. Apparent activation energy to produce isobutene in the temperature range between 323–363 K. Pretreatment temperature, 623 K for 4 h in He flow.

TABLE 2

Product Distribution (%) and Activity of the Catalysts to Produce Isobutene, r_{IB}, at 343 K

Catalyst	r_{IB}, μmol g^{-1} min^{-1}	E_a (IB), kJ mol^{-1}	Isobutene	*trans*-2-Butene	*cis*-2-Butene	Cis/trans
W4.8	1.04	49.1 ± 2.4	60.0	30.0	10.0	0.33
W9.1	2.18	47.9 ± 0.9	60.3	34.5	5.2	0.15
W14.9	4.44	47.7 ± 1.7	61.4	34.9	3.7	0.11
W23.1	6.39	47.4 ± 2.7	59.8	38.5	1.7	0.04
HW6.1	2.08	45.7 ± 2.1	62.3	32.1	5.6	0.17
HW15.1	11.49	47.7 ± 2.2	60.6	38.9	0.5	0.02

Note. Apparent activation energy to produce isobutene in the temperature range between 323–363 K. Pretreatment temperature, 748 K for 4 h in He flow.

Tables 1 and 2 show that the cis/trans ratio was lower than the unit, decreasing when the tungsten content of the catalyst increased, and increasing when the pretreatment temperature was increased from 623 to 748 K. An increase in the reaction temperature also produced a decrease in the above ratio. The values of the cis/trans ratio seem to depend on the nature of the surface acid sites (Brønsted or Lewis), their strength, and the isomerization mechanism (31–33). Thus, it has been suggested that in the isomerization reactions carried out with 12-heteropolyacids 12-phosphotungstic acid and 12-silicotungstic acid, formation of the cis isomer was favored by the weaker acid sites (33, 34). Results found with the activated carbon-supported tungsten catalysts could indicate that they did not present acid sites weak enough to produce the cis isomer.

Activity for isobutene formation, r_{IB}, increased with the W content of the catalyst and, in Fig. 1, its relationship with the total surface acidity of the catalysts is shown. The values of the parameters of the straight lines found are compiled in Table 3. They have a very high correlation coefficient and the results indicate that r_{IB} exclusively depended on the surface acidity and was independent of the method of preparation of the catalysts. These results are different from those found by Gielgens *et al.* (7) with tungsten oxide catalysts supported on Al_2O_3 and containing up to 30% WO_3. Thus, these authors found a sharp increase in r_{IB} when the WO_3 content was increased from 7 up to 15%. They indicated that the formation of IB needs doublet active sites which are formed by dimer, WO_4^-, species. Moreover, the above authors (7) also indicated that a high concentration of surface active sites led to a deactivation of the WO_3/Al_2O_3 catalysts due to carbonaceous residues induced by the polymerization of isobutene. This deactivation was not found with our catalysts. All these results could be due to the different nature of the supports used: activated carbon versus alumina.

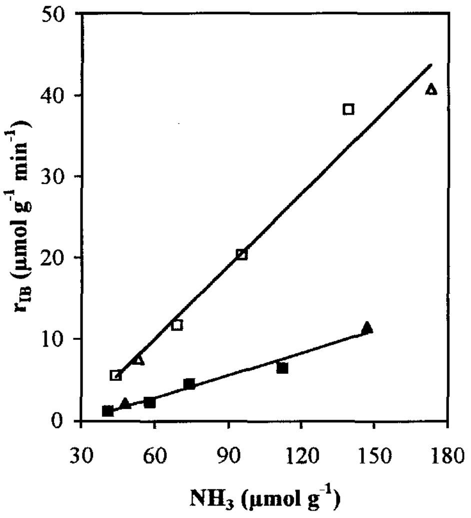

FIG. 1. Variation in activity to obtain isobutene at 343 K against the total surface acidity. □, series W; Δ, series HW. Open symbols, pretreatment at 623 K. Solid symbols, pretreatment at 748 K.

The slope of the straight lines found is a measure of the activity of the catalysts per surface acid site, i.e., the specific activity, and it depends on the pretreatment temperature applied to the catalysts. Thus, this was about 3 times lower at 748 K than at 623 K, which suggests that the most active sites to produce IB were eliminated when the treatment temperature increased within the above range. Finally, the surface acid sites which are inactive in the formation of IB did not change with the pretreatment temperature, as shown in column 4 of Table 3.

The apparent activation energy to obtain IB did not change with the tungsten content nor with the pretreatment temperature in the case of catalysts from series W. However, for the catalysts from series HW and at a pretreatment

TABLE 3

Parameters of the Straight Lines in Fig. 2

$T_{\text{pretreatment}}$, K	Correlation coefficient	Slope, min^{-1}	NH$_3$ ($r_{IB} = 0$), μmol g^{-1}
623	0.9741	0.30	26
748	0.9689	0.09	28

TABLE 4

Effect of Water Vapor on the Product Distribution (%) and Activity of the Catalysts W14.9 and HW15.1 To Produce Isobutene, r_{IB}, at 343 K

Catalyst	P_{H_2O}, Torr	Product distribution IB	T2B	C2B	Cis/trans	r_{IB}, μmol g^{-1} min^{-1}	E_a (IB), kJ mol^{-1}
W14.9	0	61.4	34.9	3.7	0.11	4.44	47.7 ± 1.7
W14.9	4.6	61.1	22.2	16.7	0.75	2.22	62.4 ± 1.8
W14.9	23.8	58.3	20.9	20.8	1.00	1.50	68.7 ± 2.7
HW15.1	0	60.6	38.9	0.5	0.01	11.49	47.7 ± 2.2
HW15.1	4.6	64.4	25.4	10.2	0.40	4.08	67.2 ± 1.6
HW15.1	23.8	65.4	23.1	11.5	0.50	1.74	74.6 ± 2.1

Note. Apparent activation energy to produce isobutene in the temperature range between 323–363 K. Pretreatment temperature, 748 K for 4 h in He flow.

temperature of 623 K, E_a (IB) was much smaller than in the case of the others series and increased with the tungsten content. An increase in the pretreatment temperature up to 748 K produced an increase in E_a (IB), which now presented a value similar to that of the series W.

The effect of the presence of water vapor in the reactant mixture on the catalytic behavior of several catalysts was also studied. Table 4 shows, as an example, the results obtained with catalysts W14.9 and HW15.1. The increase in the water vapor pressure in the reactant mixture brought about a marked increase in both the cis/trans ratio and the E_a (IB) values, as well as a marked decrease in the r_{IB} value. Gielgens *et al.* (7) found that the presence of water vapor in the reactant mixture increased the selectivity to produce IB with WO_3 catalysts supported on Al_2O_3. They explained their results as being due to the possible creation of new –OH groups by the presence of H_2O. However, the same authors (7) also indicated that with the same catalysts the presence of H_2O also influences the carbonaceous deposits produced during the reaction. When pure Al_2O_3 or that modified with Cl, Br, or I was used, the selectivity to produce IB decreased with the presence of H_2O in the reactant mixture (4). Results obtained with our catalysts indicate that the presence of H_2O in the reactant mixture brought about a decrease both in the number of surface active sites (decrease in r_{IB}) and in their acid strength (increase in E_a (IB)). Thus, there was probably a loss of the more active surface sites, which would be those of strong acidity, due to the deposition on them of carbonaceous residues favored by the presence of H_2O in the reactant mixture as above commented. The loss of these stronger acid groups could explain the increase in the cis/trans ratio with the P_{H_2O}, since the weaker acid groups, which remained on the surface of the catalyst, would favor the formation of the cis isomer (33, 34).

Some selected catalysts were also studied in the isomerization reaction of 1-butene after their heat treatments in He flow at 973 and 1223 K for 4 h. In this case, the support alone was also inactive. Results obtained with the catalyst W14.9 are shown in Tables 5 and 6. In both cases there was (i) a large decrease in r_{IB} with reaction time, essentially during the first 60 min, (ii) formation of by-products C_3–C_5 and C_2–C_6, and (iii) an increase in the cis/trans ratio with reaction time, which reached values higher than unit. Thus,

TABLE 5

Product Distribution (%) and Activity To Produce Isobutene, r_{IB}, at 323 K with the Catalyst W14.9

t, min	r_{IB}, μmol g^{-1} min^{-1}	Product distribution IB	T2B	C2B	Ethene	Hexene	Propene	Pentene	Cis/trans
30	30.71	36.5	53.8	0.2	0.6	0.9	4.1	3.8	0.01
65	12.02	43.3	47.0	0.7	0.4	1.4	1.1	6.1	0.01
100	4.23	46.7	39.4	4.1	0.2	1.7	0.3	7.5	0.10
135	2.07	53.7	24.4	12.2	0.2	1.8	—	7.7	0.50
170	1.60	57.0	20.1	16.8	0.1	1.1	—	4.8	0.84
205	1.31	56.3	20.1	20.1	0.2	0.6	—	2.7	1.00
240	1.22	58.0	17.8	22.3	0.1	0.3	—	1.4	1.25
275	1.13	56.6	18.9	23.6	0.1	0.2	—	0.7	1.25

Note. Pretreatment temperature, 973 K for 4 h in He flow.

TABLE 6

Product Distribution (%) and Activity To Produce Isobutene, r_{IB}, at 323 K with the Catalyst W14.9

		Product distribution							
t, min	r_{IB}, μmol g^{-1} min^{-1}	IB	T2B	C2B	Ethene	Hexene	Propene	Pentene	Cis/trans
30	21.63	40.7	57.7	0.5	0.1	0.2	0.2	0.7	0.01
65	2.36	48.8	37.1	9.8	0.4	0.8	0.1	3.1	0.26
100	0.76	44.2	22.1	27.6	0.6	1.2	0.1	4.3	1.25
135	0.57	44.2	14.7	36.8	0.6	0.8	—	2.8	2.50
170	0.57	48.7	8.1	40.6	0.5	0.4	—	1.5	5.01
205	0.47	44.7	8.9	44.7	0.5	0.3	—	0.8	5.02

Note. Pretreatment temperature, 1223 K for 4 h in He flow.

these results indicate that the dimerization of butenes took place by a bimolecular mechanism, which after the breakdown of the octenes yielded the C_3–C_5 and C_2–C_6 fractions. The amounts of C_2 and C_3 are, in general, lower than those of C_6 and C_5, respectively, which could be due to the decomposition of the former hydrocarbons on the surface of the catalysts leaving carbonaceous residues that block the stronger active sites, producing a decrease in r_{IB} and an increase in the cis/trans ratio with reaction time.

It was shown elsewhere (30) that when the pretreatment temperature of the activated carbon-supported tungsten catalysts increased between 623 and 1223 K there was a decrease in total surface acidity, and tungsten oxides in which the oxidation state of tungsten was below (VI) appeared. Even at 1223 K metallic tungsten and tungsten carbides appeared. The presence of these tungsten species is probably responsible for the dimerization and polymerization of butenes, bringing about the deposition of carbonaceous residues and the loss in catalytic activity.

Tungsten Catalysts Supported on SiO_2, Al_2O_3, and TiO_2

Tungsten catalysts supported on SiO_2, Al_2O_3, and TiO_2 had a 5% metal loading and were pretreated at 623 and 748 K, since at these temperatures the catalysts from series W and HW showed the higher activity and did not undergo deactivation during their time in reaction. Surface characteristics of these catalysts are shown in Table 7.

Surface area, S_{N_2}, did not change with the heat treatment between 623 and 748 K and the catalyst supported on SiO_2 had the highest S_{N_2} value. The total surface acidity decreased when the pretreatment temperature increased. These catalysts have a tungsten content similar to that of catalyst W4.8. Therefore, the total surface acidity decreased in the following order:

$$Al_2O_3\text{–W} \gg SiO_2\text{–W} > \text{W4.8} \approx TiO_2\text{–W}.$$

XRD of these catalysts showed the diffraction peaks of WO_3 only in the case of SiO_2–W; in the remaining catalysts only the diffraction peaks corresponding to the support appeared, which in the case of TiO_2 was anatase.

Results of the isomerization reaction of 1-butene with these catalysts, previously heat treated at 623 K in He flow for 4 h, are compiled in Tables 8 to 10. The activity of the catalyst Al_2O_3–W to obtain IB was much higher than that for the other two catalysts, SiO_2–W and TiO_2–W. In all cases the r_{IB} value decreased with reaction time, which was different from that recorded for the catalysts supported on activated carbon. IB was the main product obtained

TABLE 7

Surface Characteristics of Tungsten Catalysts Supported on Al_2O_3, SiO_2, and TiO_2 after Their Heat Treatments in He Flow at Different Temperatures for 4 h

Catalyst	$T_{\text{treatment}}$, K	S_{N_2}, m^2 g^{-1}	NH_3, μmol g^{-1}
Al_2O_3–W	623	118	373
Al_2O_3–W	748	120	294
SiO_2–W	623	250	116
SiO_2–W	748	247	99
TiO_2–W	623	8	43
TiO_2–W	748	9	38

TABLE 8

Product Distribution (%) and Activity To Produce Isobutene, r_{IB}, at 323 K with the Catalyst Al_2O_3–W

		Product distribution			
t, min	r_{IB}, μmol g^{-1} min^{-1}	Isobutene	*trans*-2-Butene	*cis*-2-Butene	Cis/trans
35	20.76	76.9	22.7	0.4	0.02
70	17.82	78.6	20.9	0.5	0.02
140	14.46	79.9	19.5	0.6	0.03
210	12.27	80.4	18.9	0.7	0.04
350	9.45	80.4	18.2	1.4	0.08
560	6.99	80.8	17.3	1.9	0.11

Note. Pretreatment temperature, 623 K for 4 h in He flow.

TABLE 9

Product Distribution (%) and Activity To Produce Isobutene, r_{IB}, at 323 K with the Catalyst SiO_2–W

		Product distribution			
t, min	r_{IB}, μmol g^{-1} min^{-1}	Isobutene	*trans*-2-Butene	*cis*-2-Butene	Cis/trans
35	2.03	69.1	23.6	7.3	0.02
70	1.01	79.2	20.8	—	—
140	0.48	81.8	18.2	—	—
210	0.32	85.7	14.3	—	—
385	0.16	90.9	9.1	—	—

Note. Pretreatment temperature, 623 K for 4 h in He flow.

TABLE 10

Product Distribution (%) and Activity To Produce Isobutene, r_{IB}, at 323 K with the Catalyst TiO_2–W

		Product distribution			
t, min	r_{IB}, μmol g^{-1} min^{-1}	Isobutene	*trans*-2-Butene	*cis*-2-Butene	Cis/trans
35	1.86	66.7	23.5	9.8	0.42
70	1.15	65.6	21.9	12.5	0.57
140	0.71	68.4	21.1	10.5	0.50
315	0.44	80.0	20.0	—	—
490	0.38	87.5	12.5	—	—

Note. Pretreatment temperature, 623 K for 4 h in He flow.

followed by T2B, the cis/trans ratio being smaller than unit.

The higher r_{IB} values of the catalyst Al_2O_3–W in comparison with those of the other catalysts are probably due to the higher total surface acidity of this catalyst. Deactivation with the time of reaction could be due to the formation of carbonaceous deposits from the polymerization of butenes as has been shown to occur with other similar catalysts (7, 8). In support of this, in the case of catalyst Al_2O_3–W, which had the highest activity, its color was initially white and after 560 min of reaction at 323 K it was black.

Results obtained indicate the importance of the support in this reaction. Thus, the initial activity (at 35 min), r_{IB}, of the catalyst Al_2O_3–W was quite similar to that of catalyst W14.9, also pretreated at 623 K (Table 1), although in this last case its surface acidity (95 μmol g^{-1}) was about 4 times lower than that in the case of the Al_2O_3–W catalyst and close to that of the SiO_2–W catalyst. Furthermore, the W14.9 catalyst behaved in a different way from the other catalysts, since it was not deactivated during the reaction time. These results could indicate that the carbon support, due to its basicity (pH_{PZC} 10.2), moderated the surface acidity of the tungsten oxide particles, in such a way that the tungsten catalysts supported on the activated carbon presented the proper surface acidity to have, with a smaller total surface acidity, an activity similar to that of catalyst Al_2O_3–W, and with a surface acidity similar to that of SiO_2–W, to have an activity about 10 times higher than that of this last catalyst, and without deactivation with reaction time.

Results obtained when the catalysts were pretreated at 748 K are compiled in Tables 11 to 13. Here, the initial activity (at 35 min), r_{IB}, increased in catalyst Al_2O_3–W and decreased in the other two. The r_{IB} values also decreased with reaction time. However, in the case of catalyst Al_2O_3–W this was not so marked as it had been in the above heat treatment. This is probably because the decrease in surface acidity (about 20%) with the increase in pretreatment temperature produced a reduced formation of carbonaceous residues. The product distribution of catalyst Al_2O_3–W showed the formation of by-products from the dimerization of the butenes.

The initial r_{IB} of catalyst Al_2O_3–W pretreated at 748 K was not comparable to that of any of the catalysts from series W and HW. However, it was comparable to those of catalysts HW15.1 and W23.1 pretreated at 623 K, although in these last samples the surface acidity was lower and also these were more stable to deactivation with reaction time.

TABLE 11

Product Distribution (%) and Activity To Produce Isobutene, r_{IB}, at 323 K with the Catalyst Al_2O_3–W

		Product distribution							
t, min	r_{IB}, μmol g^{-1} min^{-1}	IB	T2B	C2B	Ethene	Hexene	Propene	Pentene	Cis/trans
35	46.14	83.33	16.19	0.13	0.02	0.01	0.18	0.12	0.01
70	42.87	84.26	15.19	0.17	0.02	0.01	0.18	0.13	0.01
140	37.75	84.49	15.54	0.22	0.02	0.01	0.17	0.12	0.01
210	36.27	85.46	14.00	0.24	0.03	0.02	0.14	0.10	0.02
350	30.87	85.92	13.53	0.33	0.02	0.02	0.11	0.08	0.02
560	22.90	85.26	14.16	0.40	0.02	0.03	0.08	0.06	0.03

Note. Pretreatment temperature, 748 K for 4 h in He flow.

TABLE 12

Product Distribution (%) and Activity To Produce Isobutene, r_{IB}, at 323 K with the Catalyst SiO_2–W

		Product distribution			
t, min	r_{IB}, μmol g^{-1} min^{-1}	Isobutene	*trans*-2-Butene	*cis*-2-Butene	Cis/trans
35	0.32	95.2	4.8	—	—
70	0.16	90.9	9.1	—	—
245	0.16	93.8	6.2	—	—

Note. Pretreatment temperature, 748 K for 4 h in He flow.

CONCLUSIONS

The activity of the tungsten catalysts supported on activated carbon, previously heat treated in He flow at 623 and 748 K, did not decrease with reaction time and increased linearly with the total surface acidity of the catalysts. The specific activity of the catalysts after the pretreatment at 623 K was higher than that after 748 K. The product distribution, in both cases, showed that the main product was isobutene, followed by *trans*-2-butene, with a cis/trans ratio smaller than unit. No by-products from the dimerization of the butenes were found. The presence of water vapor in the reactant mixture reduced the activity for isobutene formation, and increased both the activation energy to obtain isobutene and the cis/trans ratio.

Pretreatment of the above catalysts at 973 and 1223 K brought about a loss in activity with reaction time. Product distribution showed that by-products from the dimerization of butenes were also obtained, which would explain the loss in activity. The formation of dimers, and probably polymers, could be due to the presence in the tungsten oxide particles of other tungsten atoms with an oxidation state below (VI), as was shown by XRD and XPS.

In the case of the tungsten supported on Al_2O_3, SiO_2, and TiO_2 and pretreated at 623 and 748 K, the most active was Al_2O_3–W pretreated at 748 K followed by the same catalyst pretreated at 623 K. However, with all these catalysts there was a loss of activity to obtain isobutene with reaction time.

TABLE 13

Product Distribution (%) and Activity To Produce Isobutene, r_{IB}, at 323 K with the Catalyst TiO_2–W

		Product distribution			
t, min	r_{IB}, μmol g^{-1} min^{-1}	Isobutene	*trans*-2-Butene	*cis*-2-Butene	Cis/trans
35	1.16	75.9	17.2	6.9	0.40
70	0.69	76.5	17.6	5.9	0.33
140	0.48	81.8	18.2	—	—
315	0.32	85.7	14.3	—	—
455	0.26	83.3	16.7	—	—

Note. Pretreatment temperature, 748 K for 4 h in He flow.

Results obtained show the importance of the support in these catalysts. Thus, it seems that the activated carbon, which had a basic surface, moderated the surface acidity of the tungsten oxide particles in such a way that, with a lower surface acidity, the catalyst had an activity similar to that of catalyst Al_2O_3–W but with no deactivation with reaction time.

ACKNOWLEDGMENTS

This work was supported by DGESIC Project no. PB97-0831.

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