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Oligomerization of 2-Methylpropene and Transformation of 2,4,4-Trimethyl-2-Pentene over Supported and Unsupported Perfluorinated Resinsulfonic Acid Catalysts[1]

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Oligomerization of 2-methylpropene was studied with two types of supported (on alumina and on silicon carbide) as well neat perfluorinated resinsulfonic acid catalysts. The heterogeneous reactions were carried out over the solid acid catalysts in a continuous flow reactor at temperatures between 85 and 170°C under atmospheric pressure. Under the studied conditions (85 to 105°C, 1 atm pressure, *WHSV*: 1–3 g/g · h) all catalysts studied are suitable for oligomerization of 2-methylpropene. Product distributions show regular temperature dependence: upon increasing temperature the molecular weight of oligomers decreases, with no difference in the selectivity of the catalysts. Transformation of 2,4,4-trimethyl-2-pentene in the liquid phase at room temperature shows surprising selectivity using either the hydrated or dehydrated forms of the resinsulfonic acids. In the case of the hydrated forms of the acids, only double bond isomerization takes place. With dehydrated acids oligomerization as well as isomerization occurs. Above 50°C the selectivity is lost.

INTRODUCTION

Perfluorinated resinsulfonic acids are efficient and versatile heterogeneous acid catalysts. Their acid strength is comparable to 100% sulfuric acid. The fluorocarbon polymer acids are chemically resistant and stable up to 200–250°C. They are effective in most acid catalyzed transformation (*2*). At the same time they have the disadvantage that their surface areas compared to those of more common heterogeneous acid catalysts (metal oxides, alumino–silicates, zeolites, etc.) are very low (0.5–2m^2/g). The acidic sites which are incorporated into the fluorocarbon matrix are not readily accessible to the reactants and thus the reaction rates are limited by diffusion. This problem can be minimized by reducing the particle size of the resin. For example, the reactivity of a 120-mesh resin is nearly seven times greater than that of a 30-mesh resin in the alkylation of phenol with 1-decene (*3*). Finely powdered catalysts, however, are usually inconvenient to use in contact catalytic processes, particularly in continuous flow systems. Another way of increasing of the surface area is to support the catalysts on suitable solid carriers. This often-used method was also applied to perfluorinated resinsulfonic acid catalysts. For example, McClure and co-workers used Nafion-H resin supported on different carriers (alumina, silica, silica–alumina, and porous glass) for the alkylation of 2-methylpropane with olefins and for the isomerization of hexane. It has been found that the activity of a 1% Nafion-H on Chromosorb-T is 2.5 times greater than that of 5% Nafion-H on silica and about 12 times greater than that of the unsupported Nafion-H resin (*4*). In another example, in several aromatic alkylation re-

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actions it was found that the supported Dow perfluorinated resinsulfonic acid catalyst (Dow XU-40036) had a much higher efficiency than unsupported 10–30-mesh solid polymer pellets (*3*).

The oligomerization of 2-methylpropene is probably the earliest known polymerization (*5*). The polymerization of propene and butenes was one of the *first* commercial catalytic processes in the petroleum industry. Because 2-methyl-propene is a very reactive olefin (*6*), its acid catalyzed oligomerization takes place with almost any electrophilic catalysts. For instance, liquid acids such as sulfuric acid, phosphoric acid, alkanesulfonic acids, etc., and solid acids such as activated clays, silica–alumina cracking catalysts, zeolites, metal oxides, or mixed oxides are all effective. The most widely used commercial catalyst is "silicophosphoric" acid, sometimes called "solid phosphoric acid" (prepared by mixing 85% orthophosphoric acid with kieselguhr and calcinated at temperature from 180 to 300°C). The oligomerization process is carried out from 100 to 250°C and pressures from 10 to 40 atm (*7, 8*).

More recently several catalysts and processes were introduced for improved oligomerization of 2-methylpropene. Zeolites such as mordenite, erionite, pentasil, type L and Y (*9*), surface modified ZSM types (*10*), CeY (*11*), etc., were found to be particularly effective. Moreover, graphite intercalates (*12*), tantalum halide/oxide–metal oxide systems (*13*), porous silica impregnated with aluminum hydride (*14*), fluorinated alumina (*15*), cationic exchange resins (*16–18*), benzylsulfonic acid siloxane (BSS) (*19*), boron trifluoride on alumina (*20*), Nafion-H (*21*), etc., have also been used.

The oligomerization of 2-methylpropene can be carried out either in the liquid or gas phase, in continuous flow, batch or semibatch reactors, in the temperature range between 50 and 300°C, under atmospheric or elevated pressure sufficient to maintain the liquid state.

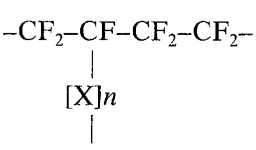
The products of oligomerization usually consist of dimers, trimers, and tetramers (used as blending agents for gasolines). The ratio of oligomers is variable and the composition depends on the temperature. Generally with increasing temperature the molecular weight of the oligomers decreases. The *dimer* fraction under conditions when secondary transformation, principally isomerization, does not take place, consist of 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene with a ratio of about 4 to 1 (*22*). An investigation of the isomers present in the *trimer* fraction has shown that they consist of approximately 55% 4-methylene-2,2,6,6-tetramethylheptane, 35% 2,2,4,6,6-pentamethyl-3-heptene, and about 5% each of 2,4,4,6,6-pentamethyl-1-heptene and -2-heptene (*23*). In the *tetramer* fraction 2,2,4,6,6,8,8-heptamethyl-4-nonene(51%), 4,4,6,6-tetramethyl-2-neopentyl-1-heptene(37%), and 2,2,4,6,6,8,8-heptamethyl-3-nonene(12%) were identified by ^{13}C NMR (*24*).

EXPERIMENTAL

Catalysts and Materials

In our investigations three solid catalyst provided by the DOW Chemical Co. (XUS-40036.01, XUS-40036.02 and XU-40036.04), and DuPont's Nafion-H resin were used.

XU-40036.04 (designated subsequently as 04) is an unsupported perfluorinated resinsulfonic acid which is similar in structure to Nafion-H, only the side chains carrying sulfonic acid groups are shorter:



$$\begin{array}{l}-CF_2-\underset{\displaystyle\underset{\displaystyle O-CF_2CF_2SO_3H}{\displaystyle\underset{|}{\displaystyle\underset{|}{[X]n}}}}{CF}-CF_2-CF_2-\end{array}$$

DuPont Nafion-H: $n = 1, 2, 3 \ldots$
Dow resin: $n = 0$
X: CF_2CF_2

The equivalent weight of this polymer 800 g/eq and was used as small pellets.

XUS-40036.01 (01) is the 04 resin supported on 1/16″ α-alumina spheres. The resin content is 12 wt% and the acid capacity approximately 0.1 meq/g.

XUS-40036.02 (02) is the 04 resin supported on 1/4″ hollow cylinders of silicon carbide. It has a very low surface area, (approximately 0.02 m^2/g), the acid capacity of the dry catalyst is 0.20–0.22 meq/g, resin content is 18 wt%. The form of the 02 catalyst was not suitable for our studies, thus before use it was broken into small pieces similar in dimension to the 01 catalyst.

2-Methylpropene was obtained from Matheson (99% purity); 2,4,4-trimethyl-2-pentene was from the Aldrich Co. (99% purity) and used without any further purification.

Apparatus and Experiments

Experiments were carried out in a usual fixed bed flow reactor (200 × 12 mm glass tube), which was electrically heated. During experiments the reactor temperature did not deviate by more than ± 1°C. The reactor was charged with 3 g catalyst. Fresh catalysts were used for each experiment in order to standardize the conditions. After the pretreatment (1 h at 150°C in dry He, flow rate 10 ml/min) the reactor was kept at the temperature of experiments, which varied between 85 and 170°C. The gaseous reactants were introduced via flow controller from pressure cylinders. The flow rate was usually 40 ml/min (i.e., 1.9 g/g · h weight hourly space velocity /*WHSV*/), or was varied between 15 and 60 ml/min (*WHSV*: 1–2.8). The liquid reactant was introduced via a syringe pump, *WHSV*: 1.2 g/g · h.

The products emerging from the reactor were condensed in cold traps: the liquids at 0°C, the gasses at −60°C, and analyzed by GC and GC/MS. Individual compounds were identified on the basis of their retention time (in comparison with authentic samples), or using an MS library search method. In cases where these methods were not successful in accounting for the large number of similar compounds, we identified the compounds by their molecular weight based on GC/MS.

The transformations of 2,4,4-trimethyl-2-pentene were carried out in an autoclave (volume 50 ml), which was charged with 0.5 g catalyst and 5 ml reactant and stirred magnetically.

Mass spectras were obtained using a FINNIGAN MAT INCOS 50 GC/MS system. The VARIAN 3400 gas chromatograph was equipped with a 30-m DB-5 (J&W) capillary column. The composition of the reaction products was determined by a VARIAN 3300 gas chromatograph equipped with a 30-m DB-1 (J&W) capillary column and flame ionization detector (carrier gas (He) pressure 14 psi; temperature program: at 100°C 5 min isotherm then increases to 200°C with 10°C/min heating rate).

RESULTS AND DISCUSSION

Effect of Catalyst Pretreatment

Pretreatment of catalysts usually has a very important effect on activity and selectivity in heterogeneous catalysis. The acidity of the perfluorinated resinsulfonic acid polymers mainly depends on their water content. The Hammett acidity of dry Nafion-H has been estimated to be in the superacidic range (*1*), which makes it comparable to or stronger than 100% sulfuric acid. In our studies pretreatment was used to reduce the water content and increase acidity, as well as to standardize the catalysts.

Catalysts pretreated in different ways (at 150, 170, and 200°C in continuous flow of dry helium or in vacuum of >0.1 mmHg for 1 h) did not show any difference in the activity and selectivity of the oligomerization of 2-methylpropene. The 04 catalyst (unsupported resin) lost 19 wt% water at 150°C in vacuum. More and co-workers reported that in their experiments the resin with 909 equiv. wt. absorbed ca. 25% water (*25*). Actually, the untreated catalysts show similar activity and selectivity above 100°C as do the pretreated ones. This is not surprising because dry 2-methylpropene itself can also dehydrate the resin at this temperature. Further (*vide infra*) the acid strength of the hydrated form is also sufficient to

TABLE 1

Temperature and Catalyst Dependence of the Oligomerization Products of 2-Methylpropene

Temperature (°C): Catalyst:	85				105				130				170			
	01	02	04	Naf	01	02	04	Naf	01	02	04	Naf	01	02	04	Naf
Conversion (%)	72.1	71.2	37.5	54.0	64.5	65.3	43.2	52.0	57.7	61.3	48.6	51.1	71.0	66.8	36.8	59.5
Products (wt%)																
C_5–C_7	2.9	2.5	0.6	0.8	2.3	2.8	2.1	2.0	4.6	4.3	3.3	2.8	4.2	6.4	5.5	4.9
C_8	37.8	24.7	28.2	28.6	40.1	40.8	38.8	44.9	63.6	58.6	50.0	57.8	79.6	74.5	69.1	70.6
C_9–C_{11}	3.2	0.7	1.1	0.9	4.5	2.4	2.5	2.8	5.6	3.9	5.5	2.9	1.8	3.3	4.5	4.2
C_{12}	50.5	64.1	61.9	61.6	46.1	49.6	50.7	47.2	25.3	33.2	36.4	36.1	14.4	15.7	20.2	19.3
C_{13}–C_{15}	1.2	0.9	1.2	1.3	3.0	0.9	1.6	1.0	—	—	2.3	—	—	—	0.3	0.6
C_{16}	4.4	7.1	7.0	6.8	4.9	3.5	4.3	2.1	0.9	—	2.5	0.4	—	—	0.4	0.7

Note. Flow rate: 40 ml/min, first hour.

catalyze the oligomerization of 2-methylpropene at appropriate temperatures.

On the other hand, the water content of the resin has a significant effect on the transformation of 2,4,4-trimethyl-2-pentene.

Oligomerization of 2-Methylpropene

Products of the oligomerization of 2-methylpropene are complex mixtures of the possible isomeric dimers, trimers, and tetramers and of compounds which are formed by secondary isomerization and fragmentation transformations. Moreover, there are many pseudo-equilibria among the monomers, dimers, trimers, tetramers, etc. It is worthwhile to note that more than 125 compounds could be separated in the reaction mixtures by gas chromatography, but only 18 were present in an amount higher than 1%. Variation of the product distribution with temperature and with catalyst is summarized in Table 1 (average results of the first on-stream hour) and Table 2 (average results of the 20th on-stream hour). The ratio of the oligomers essentially depends on the temperature. As is generally the case, with increasing temperature the ratio of trimers and tetramers decreases and the ratio of the fragmentation increases (Table 1). Using the 02 catalyst the changes are in Fig. 1. Up to 110°C, under atmospheric pressure, the products are in the liquid state. 2-Methylpropene is soluble in this liquid phase and this is advantageous for forming higher molecular weight oligomers and also increases the conversion. This may be the reason for the unexpected temperature dependence of the conversion was observed during the first

TABLE 2

Temperature and Catalyst Dependence of the Oligomerization Products of 2-Methylpropene

Temperature (°C): Catalyst:	85				105				130				170			
	01	02	04	Naf	01	02	04	Naf	01	02	04	Naf	01	02	04	Naf
Conversion (%)	70.5	68.9	32.7	53.2	61.8	57.0	39.8	40.6	37.3	36.8	29.5	33.4	20.0	19.3	14.4	17.0
Products (wt%)																
C_5–C_7	2.0	1.8	0.4	0.7	2.1	2.1	1.4	1.3	1.0	1.9	2.5	1.5	1.0	1.6	3.7	2.1
C_8	26.4	22.9	28.2	29.1	32.6	41.6	34.8	41.5	57.9	46.9	48.7	48.6	78.7	71.2	63.2	65.8
C_9–C_{11}	3.2	0.7	0.4	0.8	3.7	1.6	2.0	1.9	1.5	3.0	4.9	3.1	1.3	1.7	5.0	3.8
C_{12}	60.0	66.9	63.7	61.7	54.8	49.8	51.7	51.5	36.9	47.5	40.3	43.3	19.0	25.3	27.6	27.0
C_{13}–C_{15}	2.1	0.8	0.6	0.6	1.8	0.5	4.8	1.1	0.8	0.4	1.7	1.4	—	0.2	0.2	0.6
C_{16}	6.3	6.9	6.7	7.1	4.9	4.4	5.3	2.7	1.9	0.3	1.9	2.1	—	—	0.3	0.7

Note. Flow rate: 40 ml/h, 20th hour.

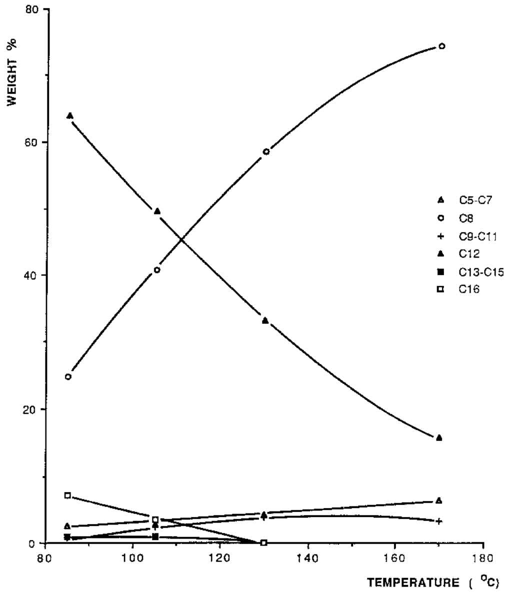


FIG. 1. Temperature dependence of product distribution over 02 catalyst (1st hour).

hour (see Fig. 4.). The conversion with elevating temperature first decreases then increases. At 170°C the ratio of dimers and trimers is particularly advantageous for use as a fuel blending agent, but at this temperature the lifetime of the catalysts is limited.

The primarily formed dimers (2,4,4-tri-methyl-1-pentene and 2,4,4,-trimethyl-2-pentene with a ratio of about 4 to 1) undergo increasing skeletal isomerization with increasing temperature (Fig. 2). Under similar condition using HY zeolite catalyst neither skeletal isomerization nor fragmentation takes place (*26*). This difference between the resinsulfonic acid and the zeolite may be explained by their different acid strength. The acid strength of the Nafion-H-type resins is higher than that of the HY zeolite (*27*).

We also studied the effect of the flow rate. One typical example is shown in Fig. 3. Either the ratio of trimers and tetramers or the conversion decreases with increasing flow rate.

On the basis of the comparison of the results which are summarized in Tables 1 and 2, it seems that the aging of the catalysts does not affect significantly the composition of the oligomerization products. The ability of the catalysts to cause fragmentation decreases, and the ratio of trimers and tetramers increases with prolonged aging, but these effect are not significant.

The supports used (alumina and silicon carbide) are effectively inert under the reactions conditions towards the oligomerization of 2-methylpropene.

The studied catalysts did not show any significant deviation in selectivity (Table 1). Since they all are similar perfluorinated resinsulfonic acids with inert supports, this was expected. The activity of the catalysts depended mainly on the available surface area of the resin. The conversions obtained using the same amount of the catalysts (3 g) are shown in Fig. 4 (average of the first hour of the runs) and in Fig. 5 (average of the 20th hour of the runs). The supported catalysts show significant advantages, as they posses much greater activity per unit of resin present than the unsupported catalysts, substantially lowering the amount of resin required. The efficiency of the resin per unit may be characterized by the α-factor which is defined as

$$\alpha = \frac{WHSV \cdot C}{y}$$

$WHSV$: weight hourly space velocity
C: conversion (%)
y: resin content of the catalyst (wt%).

The α-factors of the catalysts studied are summarized in Table 3. The difference between the α-factors of the two supported catalysts may be explained by their different resin content. The layer of the resin on silicon carbide is thicker than on alumina, therefore less surface area is available for the reactant. The α-factor of the 01 catalyst may probably be further increased with lower resin content.

The deactivation of the catalysts shows significant dependence on the temperature. With increasing temperature the lifetime rapidly decreases (Fig. 6). In this respect,

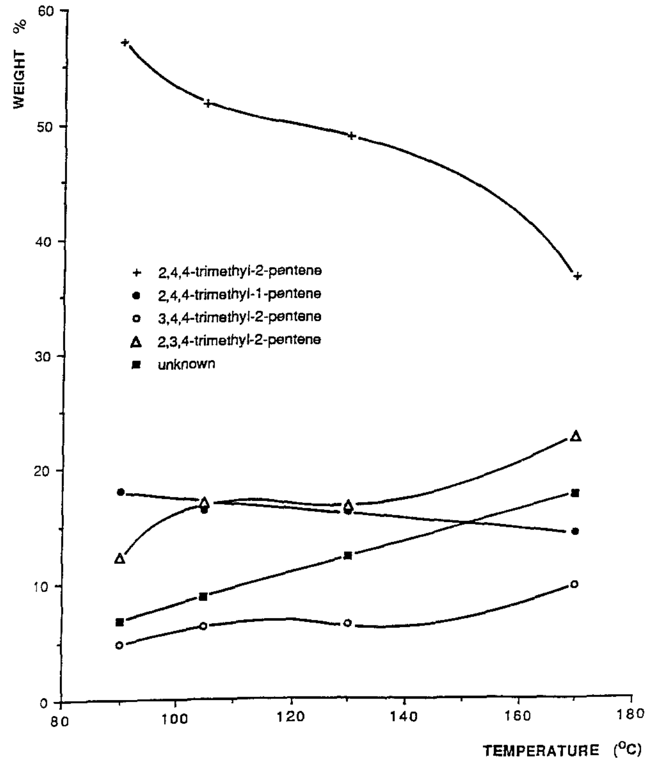


FIG. 2. Temperature dependence of dimer distribution over 02 catalyst.

the supported and unsupported catalysts do not show any difference (Fig. 5). As is usual with heterogeneous catalytic processes, liquid reactants have a beneficial effect on the lifetime.

There may be three possible reasons for the deactivation of the perfluorinated resinsulfonic acid catalysts. First, higher molecular weight oligomers or polymers can be formed and deposited on the surface hindering the reactants from contact with the acid sites. This effect would be expected mainly at lower temperatures because these favor formation of higher oligomers. Second, esterification of the sulfonic acids with 2-methylpropene can take place (*28*). Third, the most probable reason for the deactivation is coke deposit formation on the catalyst surface. This increases with temperature, and, indeed, deactivation is faster at higher temperatures. All the originally white catalysts darken above 130°C. The deactivated catalysts cannot be reactivated by simple washing with organic solvents (ethanol, aceton, ether, etc.) or steam treatment up to 200°C.

TABLE 3

α-Factors of Catalysts Studied at 85°C

Catalyst	01	02	04	Nafion-H
α	12.0	7.9	0.8	1.1

Transformation of 2,4,4-Trimethyl-2-Pentene

As previously noted, the transformation of 2,4,4-trimethyl-2-pentene at room temperature shows significant dependence on the water content of the catalysts. Under these conditions, 2,4,4-trimethyl-2-pentene

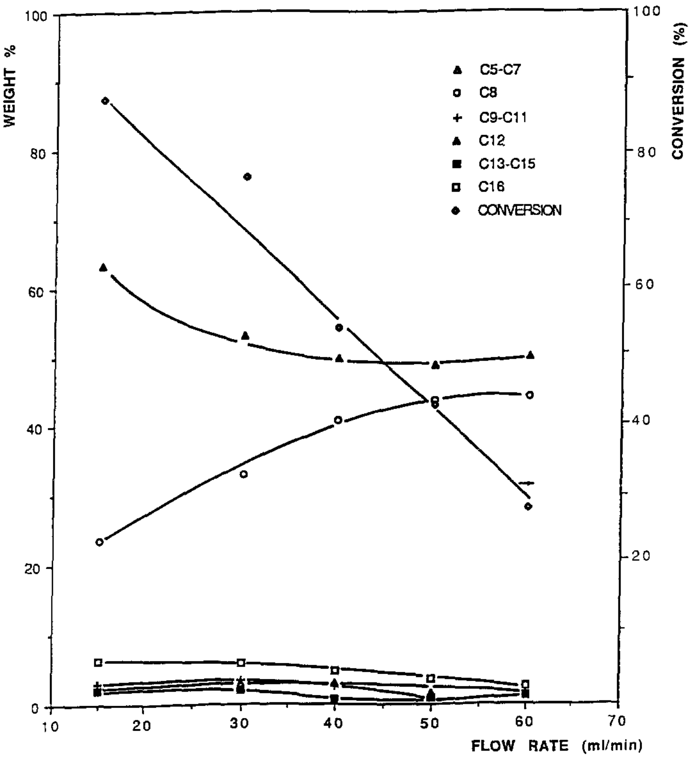


FIG. 3. Distribution of oligomerization products of 2-methylpropene as a function of flow rate 02 catalyst, at 105°C.

can isomerize to 2,4,4-trimethyl-1-pentene and dimerize to tetraisobutylenes. As seen from the data summarized in Table 4, conversions without pretreatment (drying) of the catalysts are extremely low. The unsupported resin without pretreatment is practically inactive. More important is the effect on the selectivity. The untreated, hydrated catalysts do not show any oligomerization ability at 20°C. 2-Methylpropene in contrast

TABLE 4

Transformation of 2,4,4-Trimethyl-2-Pentene at 20°C

Catalyst		Conversion (wt%)		Isomerization		Oligomerization	
		I	II	I	II	I	II
01	A	69.4	98.7	25.6	5.7	43.8	93.0
01	U	9.4	68.7	9.4	68.1	—	0.6
02	A	41.5	96.6	31.6	14.9	9.9	81.7
02	U	0.5	12.0	0.5	12.0	—	—
04	A	0.3	3.1	0.3	3.1	—	—
04	U	—	—	—	—	—	—

Note. A: activated (at 150°C under 0.1 mmHg pressure for 1 h); U: untreated; I: reaction time 1 h; II: reaction time 20 h.

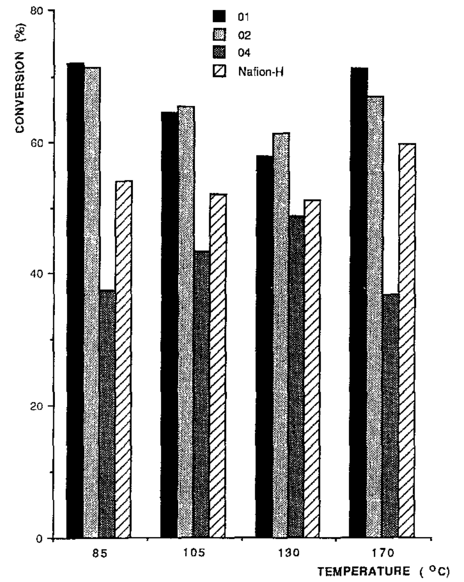


FIG. 4. Temperature dependence of the conversion (first hour).

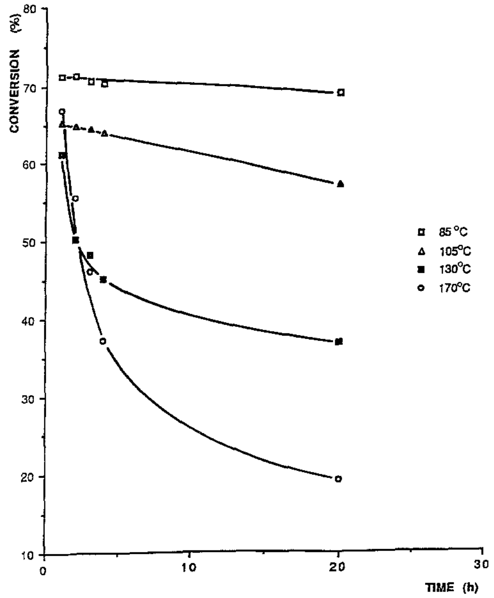


FIG. 6. Time dependence of activity of catalyst 02 at different temperature.

can be readily oligomerized with 65–70% sulfuric acid at 0°C (*7*). Sulfuric acid of this concentration has an approximate acidity of H_0: -5– -6 (*29, 30*). We thus can conclude that the hydrated forms of the perfluorinated resinsulfonic acids have comparable acidity, which is sufficient for the double-bond isomerization, but not for the oligomerization of 2,4,4-trimethyl-2-pentene at room temperature.

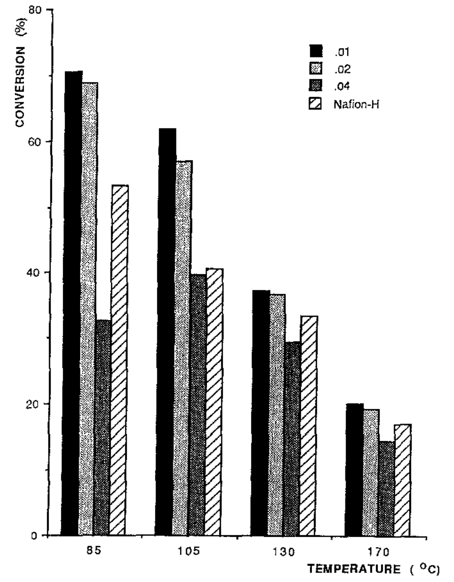
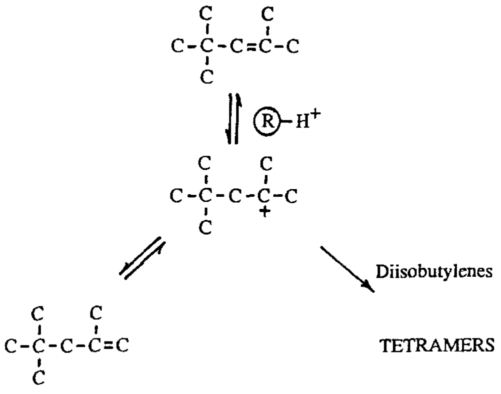


FIG. 5. Temperature dependence of the conversion (20th hour).

One possible explanation for the observed behavior may be the lifetime of the formed carbocationic intermediates common in both transformations (Scheme 1). The dou-



SCHEME 1

TABLE 5

Transformation of 2,4,4-Trimethyl-2-Pentene with 04 Catalyst (Reaction Time 20 h)

Temperature (°C)		Product distribution (wt%)				
		Conversion (wt%)	C=C bond isom.	Skeletal isom.	Trimers (fragm.)	Tetramers
50	A	94.2	22.4	1.2	0.5	70.1
50	U	20.0	18.4	—	—	1.6
70	A	95.8	16.6	2.7	2.6	73.9
70	U	92.2	27.1	1.6	3.8	59.7

ble-bond isomerization, as an intramolecular transformation, probably necessitates much a shorter lifetime of the carbocationic intermediates than the oligomerization, which is intermolecular. The lifetime of carbocations increase with increasing acid strength. The difference between the acid strength of the hydrated and dehydrated forms of the resinsulfonic acids may be sufficient to account for the observed results.

Double-bond isomerization decreases with increasing temperature, and skeletal isomerization and fragmentation become more predominant, as can be seen from the data of Table 5. The same trends observed in Table 5 are also found in heterogenuos gas-phase reactions at higher temperatures, as can be seen from the data summarized in Table 6.

The data show that the ratio of 2-methylpropene, diisobutylenes and triisobutylenes is similar, whether isobutylene or 2,4,4-trimethyl-2-pentene is reacted. The differences may be explained by the different flow rates.

CONCLUSIONS

Dow Chemical perfluorinated resinsulfonic acid and DuPont Nafion-H catalysts were studied and show similar activity and selectivity during the oligomerization of 2-methylpropene. Under appropriate conditions (85 to 105°C, 1 atm pressure, *WHSV*: 1–3 g/g · h) all studied catalysts are suitable for oligomerization of 2-methylpropene.

Supporting the resinsulfonic acids on alumina or silicon carbide supports has no effect on their catalytic properties. The supported catalysts, however, show greater activity per unit of resin than the unsupported ones. Below 100°C, the investigated catalysts did not suffer noteworthy deacti-

TABLE 6

Transformation of 2,4,4-Trimethyl-2-Pentene with 02 Catalyst

Temperature (°C)	Product distribution (wt%)					
	C_4	C_5–C_7	C_8	C_9–C_{11}	C_{12}	C_{16}
85	1.3	—	61.1	0.9	18.6	18.1
105	8.8	3.5	62.1	4.5	18.8	2.4
130	11.3	6.8	55.8	5.9	20.2	—
150	16.0	10.4	46.7	10.6	16.3	—
170	32.8	10.8	41.4	6.2	8.8	—

Note. Conditions: flow reactor, *WHSV*: 1.7 g/g · h.

vation after 20 h on-stream time. Above 130°C, the lifetime of the catalysts is greatly limited.

Product distribution of the oligomerization of 2-methylpropene shows similar temperature dependence as with other electrophilic catalysts. With increasing temperature, the molecular weight of oligomers decreases. At 170°C, the equilibrium distribution is 3.7 : 4.7 : 1 = monomer : dimers : trimers.

The transformation of 2,4,4-trimethyl-2-pentene at room temperature shows significant dependence on used hydrated or dehydrated resinsulfonic acid catalysts and thus the acidity of the catalysts. In the case of hydrated ones only double-bond isomerization takes place. With dehydrated resinsulfonic acids both isomerization and oligomerization occur. From these results it is indicated that the Hammett acidity of the hydrated resinsulfonic acids is comparable to 65–70% H_2SO_4, whereas the dehydrated resinsulfonic acid is comparable to or stronger than 100% H_2SO_4.

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