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Transformation of Ethylene over a Molybdena–Alumina Catalyst Reduced with Hydrogen

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The transformation of ethylene was investigated at 40°C over a catalyst containing 9.1 wt% MoO_3 on γ-alumina, reduced with hydrogen at 550°C. A study was made on catalysts without reversibly adsorbed hydrogen, with hydrogen adsorbed at 550 and at 40°C, and catalysts oxidized with water vapor and oxygen at 550°C. Polymerization, dimerization of ethylene and its metathesis with 2-butene were observed. The initial rate of the reactions increased upon the effect of hydrogen adsorbed at 40°C. The initial rate of dimerization increased and that of metathesis decreased due to hydrogen adsorbed at 550°C, while the rate of polymerization decreased due to hydrogen adsorbed at 550°C or to hydrogen present in the ethylene. The rate of dimerization was suppressed and the rate of polymerization was increased due to oxidation with water vapor of the reduced catalyst.

INTRODUCTION

In propylene metathesis the activity of a MoO_3/Al_2O_3 catalyst reduced with hydrogen or carbon monoxide depends on the degree of reduction (*1–5*). The surface coverage with hydrogen has an even more remarkable effect on the behavior of the catalyst reduced in an identical manner (*6, 7*). At low reaction temperatures (0–55°C) hydrogen adsorbed below 100°C increases the activity and stability of the catalyst; at higher temperatures (80–120°C) it increases initial activity and restores the activity of aged catalysts. Hydrogen adsorbed at higher temperatures decreases the activity of the catalyst at any reaction temperature.

The ratio of ethylene to butenes produced by the metathesis of propylene over a reduced catalyst differs from unity (*5*), and the difference depends on the conditions of second hydrogen treatment of the catalyst. Therefore we studied the transformation of ethylene and 2-butenes over a reduced MoO_3/Al_2O_3 catalyst under the conditions of propylene metathesis described previously (*4–6*). The present paper deals with the transformation of ethylene.

METHODS

Catalyst. The catalyst consisted of 9.1 wt% MoO_3 on Ketjen CK 300 γ-Al_2O_3 (particle size 0.2–0.4 mm). Preparation of the catalyst involved impregnation of the support with molybdic acid (Merck, commercial grade) dissolved in dilute ammonium hydroxide, then drying at room temperature by evacuation, and calcination at 550°C in dry air stream for 24 hr. Surface areas of support and catalyst calculated from nitrogen adsorption isotherms were 214 and 205 m^2/g, respectively.

Reagents. Commercial oxygen was passed through a trap cooled with liquid nitrogen and an adsorber filled with activated clinoptilolite to remove water and hydrocarbon contamination. Nitrogen was passed through a trap cooled with liquid nitrogen and a tube filled with Ridox Reagent (Fischer Scientific Co.) to remove traces of water and oxygen. Hydrogen was purified by a Matheson hydrogen purifier

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containing a palladium alloy diffusion element. Polymerization grade ethylene was liquefied at liquid nitrogen temperature, then evacuated and distilled from a container cooled with dry ice–methanol. The ethylene contained 30 ppm ethane as impurity.

Equipment and procedures. The experiments were carried out in a closed glass circulation system. The U-shaped quartz reactor (volume: 20 ml) could be separated from or connected to the circulation and vacuum systems by greaseless "O" ring taps. The reactor could be evacuated by using a two-stage mercury diffusion pump and liquid nitrogen cold trap to 1×10^{-4} Torr (1 Torr = 133.3 N/m^2). It was heated by a thermostat with air circulation, maintaining the reactor temperature in the range of ±0.5°C. During ethylene transformation reactor temperature was controlled by a water thermostat (±0.2°C). The circulation system (volume: 270 ml) was separated from the gas inlet and an independent vacuum system by greaseless "O" ring taps. Substantial parts of the circulation system (a mercury manometer and mixer of 200 ml volume) was thermostated to the temperature of ethylene transformation. The mixer was used as a cold trap in the course of catalyst pretreatment and desorption processes.

Catalyst pretreatment. In the catalyst reduction–reoxidation experiments 0.6 g of catalyst was used, and 1 g in ethylene transformation experiments. Since reproducibility upon regeneration was good, the same catalyst was used in all experiments. First the catalyst was heated in dry air for 8 hr at 550°C, and the desired amount was measured into the reactor. Then the reactor was heated to 550°C, oxygen was recirculated for 2 hr through it, and the mixer was cooled with liquid nitrogen. The reactor was cooled in oxygen to room temperature and evacuated for 1 hr.

Catalyst hydrogenation. The reactor was closed and thermostated to 550°C. 800 Torr of hydrogen was fed in the circulation system, while the mixer was thermostated to 40°C. Then the mixer was cooled with liquid nitrogen, and the hydrogen was circulated for 2 hr through the reactor. The reactor was evacuated for 1 hr at 550°C or, in some experiments, at 40°C.

For the determination of hydrogen consumption, the mixer in the circulation system was thermostated again to 40°C, and the pressure of hydrogen and water, released during reduction, was recorded. After the mixer was cooled once more with liquid nitrogen, hydrogen was pumped off, and the pressure of water was recorded at 40°C.

In ethylene transformation experiments the circulation system was evacuated after reduction without the determination of hydrogen consumption. The reduced catalyst evacuated at 550°C for 1 hr was the standard catalyst (SC) used generally in metathesis and ethylene transformation experiments. In some cases the SC was treated with hydrogen or water before ethylene admission.

Second hydrogen treatment of the catalyst. The reactor containing the SC was cooled to the temperature of ethylene transformation, then hydrogen was recirculated for 0.5 hr as above. Before the admission of ethylene, hydrogen was evacuated from the reactor for 2 min.

Oxidation of the catalyst with water. For ethylene transformation experiments the SC was flushed at 550°C for 2 hr with nitrogen saturated at 40°C with water vapor. Then the reactor was evacuated for 1 hr at the same temperature. For the determination of water consumption and of the amount of hydrogen evolved, reoxidation was carried out with recirculation of wet nitrogen. Ten microliters of water was injected into the circulation system and freezed twice with dry ice–methanol for degassing, then the circulation system was filled with nitrogen. The nitrogen–water vapor mixture was recirculated through the reactor for 3 hr. In the first 2 hr of recirculation the mixer was thermostated at 40°C, and in the last 1 hr was cooled with liquid nitrogen. The amount of unreacted water and the hydrogen evolved was determined as described above. The amount of hydrogen formed was determined also by gas chromatography.

Determination of ethylene transformation. The reactor was evacuated before admission of ethylene at 40°C. The starting pressure of ethylene in the circulation system was 800 Torr. The change of pressure was recorded with a mercury manometer and the composition of the gas phase was determined by gas chromatographic analysis. Samples of 40 μl were taken every 10 min, separated at 20°C on a 3-m column containing Choromosorb P coated with 20% dibenzilamine, and the chromatogram was recorded with a flame ionization detector. Air infiltration through the septum was avoided by maintaining higher than atmospheric pressures in the circulation system. No drop of the pressure was observed owing to leakage. After 1 hr the "O" ring taps of the reactor were closed and the reaction was stopped by cooling the reactor with dry ice–methanol.

Desorption studies. A given amount of nitrogen was recirculated through the reactor and the mixer, which was cooled with liquid nitrogen. The temperature of the reactor was increased to 300°C, and the nitrogen was recirculated at this temperature for 0.5 hr. The amount of hydrocarbons desorbed was calculated from the change in pressure, while the composition of the gas phase was determined by gas chromatographic analysis. After desorption at 300°C, desorption at 450°C was carried out in a similar way.

Oxidation of the catalyst. Oxygen was recirculated through the reactor and the mixer, which was cooled with liquid nitrogen. The temperature of the reactor was raised from 25 to 550°C, and at this temperature oxygen was recirculated for 2 hr. Oxygen consumption in the reduction–reoxidation experiments was determined by the method described for hydrogen uptake. The catalyst was kept overnight in dry oxygen flow at 550°C.

RESULTS

Reduction-Reoxidation of the Catalyst

The results of reduction and reoxidation of the catalyst are summarized in Table 1. The amount of hydrogen consumed in the course of reduction is identical with H_2 consumption reported in a previous publication (*9*). The amount of water collected during reduction was found to be greater than obtained in previous experiments. The difference in the amount of water collected can be explained by the larger capacity of the trap used in our current investigations. The amount of hydrogen desorbed during evacuation at 550°C corresponds to the amount calculated previously according to the method of Hall (*8*) by subtracting twice the amount of oxygen consumed in reoxidation from the amount of hydrogen consumed in reduction.

The hydrogen adsorbed reversibly (*8, 10*) by the catalyst after reduction was only partially removed by evacuation at 40°C. Most of the hydrogen adsorbed at 550°C can be removed only at higher temperatures. The adsorption of 0.005 mole

TABLE 1

Reduction–Oxidation of the Catalyst[a]

Treatment of the catalyst after reduction	$[H_2]^b$	$[W]^c$	$2[O_2]^d$	$[H_2^D]^e$	$[W^*]^f$
	mole/mole MoO_3				
Evacuation at 550°C	1.297	0.735	0.988	0.309	
Evacuation at 40°C	1.225	0.728	1.170	0.055	
Oxidized with water vapor	1.252	0.732	0.616	0.611[g]	0.336

[a] 0.6 g of 9.1% MoO_3/Al_2O_3 reduced and oxidized at 550°C for 2 hr. Initial pressure of hydrogen and oxygen 750 Torr.

[b] Hydrogen consumed in reduction.

[c] Water released in reduction.

[d] Oxygen consumed in oxidation.

[e] Hydrogen desorbed in evacuation after reduction and calculated according to Hall (*8*) as $[H_2^D] = [H_2] - 2[O_2]$.

[f] Water consumed in oxidation = hydrogen developed and determined with gas chromatograph.

[g] The amount of hydrogen desorbed during evacuation and developed from water.

H_2/mole MoO_3 was observed at 40°C in the second hydrogen treatment of the SC. This result is in good agreement with that obtained by the temperature-programmed desorption method (TPD) (*7*). By this method the desorption of 0.002 and 0.009 mole H_2/mole MoO_3 was determined from the catalyst after treatment with hydrogen at 0 and 120°C, respectively.

The reduced catalyst can be partially reoxidized with water as described earlier by Massoth (*11*) and in our previous publication (*9*). Good agreement was achieved between the amount of water consumed and the amount of hydrogen evolved calculated either from the increase of pressure in the circulation system or from gas chromatographic data.

Transformation of Ethylene over Reduced Catalyst Evacuated at 550°C

At 40°C the formation of propylene and butenes was observed by means of gas chromatographic analysis (Fig. 1). In the first sample, taken after 5 min, propylene, 1-butene, and 2-butenes were obtained in nearly equimolar quantities. Later propylene content increased considerably, while the amount of 2-butenes decreased to a constant level. The amount of 1-butene increased continuously and reached a constant level at a value higher than 2-butenes.

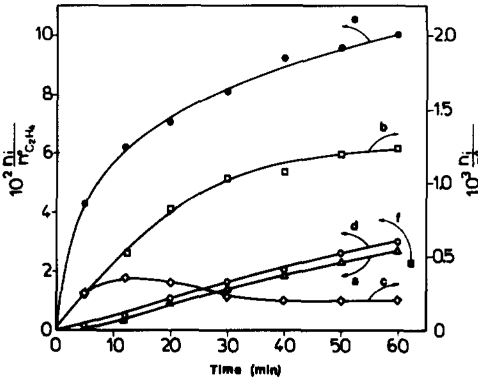


FIG. 1. Transformation of ethylene at 40°C over a reduced catalyst evacuated at 550°C. (a) propylene; (b) 1-butene; (c) 2-butene formed; (d) extent of dimerization; (e) extent of polymerization; (f) amount of hydrocarbons desorbed at 300°C.

First rapid, then slower continuous ethylene uptake was observed. No ethylene bound to the catalyst was recovered on elution with nitrogen, even at 300°C. In 1 hr the total uptake was 2.3 mole ethylene/mole MoO_x, and 0.4 mole hydro-

TABLE 2

Composition of Gas Phase Desorbed from the Catalyst[a]

Component	Catalyst evacuated at 550°C		Catalyst evacuated at 40°C		Catalyst treated with hydrogen at 40°C		Ethylene + 15% hydrogen		Catalyst oxidized with water vapor	
	300°C	450°C	300°C	450°C	300°C	450°C	300°C	450°C	300°C	450°C
C_2H_6	0.09	2.06	0.10	1.32	0.03	2.10	0.04	0.71	0.06	2.24
C_2H_4	12.05	1.90	16.03	1.35	10.46	1.84	13.39	0.79	0.03	1.82
C_3H_8	—	0.26	0.02	0.21	0.07	0.26	0.06	—	—	0.18
C_3H_6	6.39	0.68	0.61	0.44	3.65	0.68	6.02	0.26	1.11	0.77
$n\text{-}C_4H_{10}$	—	0.12	0.05	0.07	—	0.09	0.15	—	—	0.07
$1\text{-}C_4H_8$	0.42	0.27	0.64	0.14	0.28	0.24	0.50	—	0.11	0.30
trans-$2\text{-}C_4H_8$	1.84	0.14	3.66	0.07	1.52	0.09	1.89	—	0.40	0.12
cis-$2\text{-}C_4H_8$	0.78	—	1.69	0.08	0.73	0.11	0.94	—	0.22	0.12
C_5H_{10}	0.54	—	0.11	—	—	—	—	—	0.05	—
Σ	22.11	5.43	22.91	3.68	16.74	5.41	22.99	1.76	1.98	5.62

[a] 10^{-3} mole hydrocarbon/mole initial ethylene eluted with nitrogen and collected in a trap cooled with liquid nitrogen for 0.5 hr at 300°C, after that for 0.5 hr at 450°C.

carbon (up to C_5H_{10})/mole MoO_x was regained at 300°C. This suggests that polymerization of ethylene took place over the catalyst. A similar observation was made by Lombardo *et al.* (*12*) with 8% Mo on γ-Al_2O_3 catalyst reduced to an intermediate extent, and by Kin *et al.* (*13*) over 20% rhenium oxide on γ-Al_2O_3 catalyst reduced with hydrogen. By elution with nitrogen at 450°C an additional 0.1 mole of lower hydrocarbons/mole MoO_x was recovered and liquid hydrocarbon was condensed on the cooler wall of the reactor. The composition of liquid hydrocarbon was not determined while the composition of hydrocarbon gases desorbed at 300 and 450°C is shown in Table 2.

Transformation of Ethylene over Reduced Catalyst Evacuated at 40°C

The ratio of components in the gas phase was quite different from that formed over the SC (Fig. 2). In the first sample the amount of propylene was nearly the same as in the case of SC, but later propylene formation was slower. The amount of propylene formed during 1 hr was found to be one order of magnitude lower than that formed over the SC, while the amount of butenes, especially 2-butenes, greatly exceeded the amount of propylene.

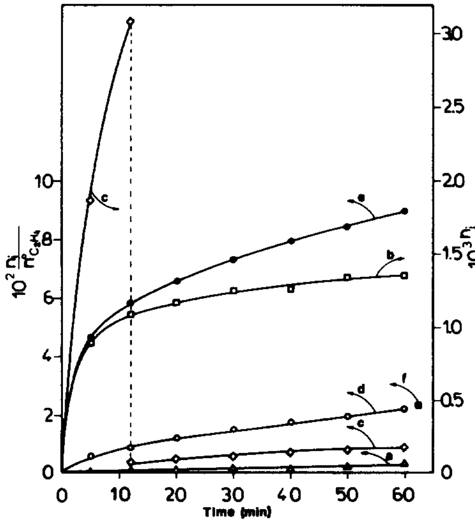


FIG. 2. Transformation of ethylene at 40°C over a reduced catalyst evacuated at 40°C. For symbols see Fig. 1.

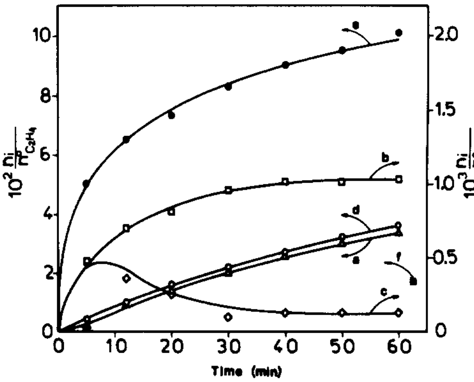


FIG. 3. Transformation of ethylene at 40°C over a reduced catalyst evacuated at 550°C and treated again with hydrogen at 40°C. For symbols see Fig. 1.

At first ethylene uptake was more rapid than over the SC but later slowed down and the total uptake was only 1.9 mole ethylene/mole MoO_x. The same amount of hydrocarbon was recovered at 300°C as from the standard catalyst. Traces of propane and *n*-butane were observed in the gas phase desorbed at 300°C.

Transformation of Ethylene over Reduced Catalyst Treated with Hydrogen at 40°C

Product distribution was similar (Fig. 3) to that obtained over the SC, while the rate of propylene formation was higher, and the amount of butenes was somewhat lower. The maximum observed in the amount of 2-butenes became more pronounced than over the SC. Ethylene uptake was slightly higher and the amount of hydrocarbon recovered at 300°C was less than in the case of the SC. Traces of propane were identified in the mixture desorbed.

Transformation of 85% Ethylene and 15% Hydrogen over the SC

As the rate of propylene formation increased upon the second hydrogen treatment of the catalyst, the transformation of ethylene containing hydrogen was examined. Hydrogen consumption was fast; no hydrogen was detected in the first sample after 5 min. First the rate of propylene formation was higher than in the case of the catalyst treated with hydrogen at 40°C (Fig. 4), but decreased with the disappearance of hydrogen; the amount of propylene developed in 1 hr was equivalent to that formed over the SC without hydrogen. First the rate of 2-butene formation was approximately 50% lower than the rate of propylene formation, then, when hydrogen disappeared, the amount of 2-butenes decreased. The extent of ethylene hydrogenation was much less than could be predicted on the basis of experiments carried out by Lombardo *et al.* (*12*). The amount of saturated hydrocarbons reached a constant level in the first few minutes. The ratio of ethane, propane, and butane produced was 1 :3.84 :22.20. First the amount of ethylene uptake was the same as obtained over the SC without hydrogen, but later on, when hydrogen completely disappeared, a faster decrease could be observed in the rate of uptake.

Transformation of Ethylene over Reduced Catalyst Oxidized with Water Vapor

In addition to ethylene only traces of propylene could be first observed in the gas phase (Fig. 5), and 1-butene could be traced only after 30 min. The amount of propylene continuously increased and in 1 hr twice as much propylene formed as over the reduced catalyst evacuated at 40°C. In contrast to the former only a slight amount of 1-butene was formed, and no 2-butene could be observed. Ethylene uptake over the catalyst oxidized with vapor was the highest, while the amount of hydrocarbons recovered at 300°C was the lowest in each case.

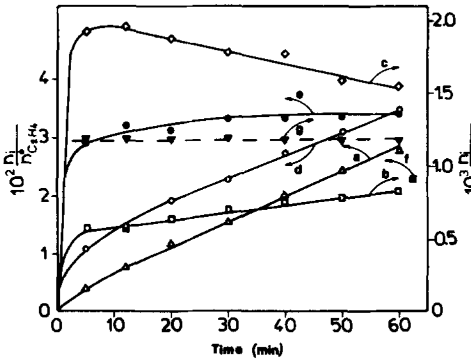


FIG. 4. Transformation of 85% ethylene, 15% hydrogen at 40°C over a reduced catalyst evacuated at 550°C. For symbols see Fig. 1. The amount of propane and butane was considered as propene and butene in the calculation of the degree of dimerization and polymerization: (g) amount of ethane, propane, and butane formed.

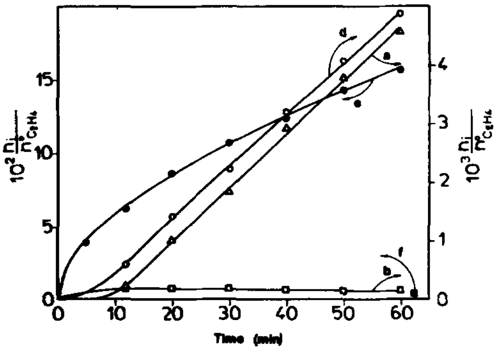


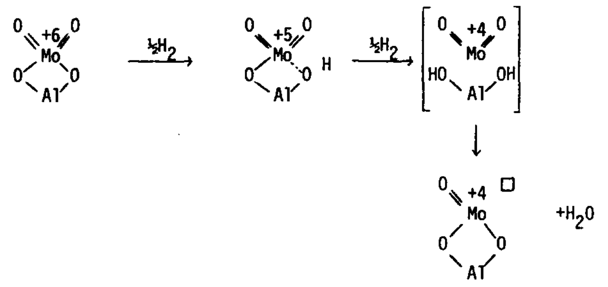
FIG. 5. Transformation of ethylene at 40°C over a reduced catalyst reoxidized with water vapor. For symbols see Fig. 1.

Transformation of Ethylene over Catalyst Activated with Oxygen

Only a trace amount of propylene was formed over the catalyst activated with oxygen as was described under "Catalyst pretreatment" (Fig. 6). Ethylene uptake was slight compared to the amounts bound by the reduced catalysts. Initially adsorption of 0.2 mole ethylene/mole MoO_x was observed which desorbed quantitatively in the form of ethylene at 300°C. With the elapse of time, a small increase in ethylene uptake was observed but this excess was not desorbed at 300°C.

DISCUSSION

The surface chemistry of the reduction of the molybdena–alumina catalyst was described by Hall *et al.* (*8, 11, 14*). According to their results, only part of the hydrogen consumed during reduction of the catalyst is released as water at the reduction temperature. A considerable part of the hydrogen is irreversibly retained by the catalyst, and another part of it is adsorbed reversibly and is removable at the reduction temperature by evacuation. According to these authors the changes in the valence state of molybdenum oxide attached to the surface of aluminum oxide may be described by the following reactions:



On the basis of the above reaction scheme (*14b*) the amount of water released can be correlated with coordinatively unsaturated molybdenum sites. This theory is consistent with the observation that molybdenum ions are difficult to reduce below Mo^{4+} when supported on alumina.

The amount of water released (0.735 mole H_2O/mole MoO_3) and the amount of hydrogen retained irreversibly (0.253 mole H_2/mole MoO_3) by our catalyst evacuated at 550°C led us to suppose that a part of the molybdenum ions are in a valence state lower than 4.

Most of the hydrogen removable with evacuation at 550°C is not removed from the catalyst evacuated at 40°C after reduction. In this case the hydrogen is bound to sites different from those where hydrogen is adsorbed at 40°C after evacuation at 550°C, as was verified by TPD (*7*). After the reduced catalyst evacuated at 550°C was treated with hydrogen at 0–120°C, hydrogen desorption was observed in peaks with maximum desorption rates at 75 and 115°C (α- and β-phases). However, if the second treatment with hydrogen was carried out above 300°C, or the catalyst was not evacuated at higher temperatures after reduction, the desorption of hydrogen was observed in peaks with maximum values at 340°C and above 560°C (γ- and δ-phases). Accordingly, the catalyst evacuated at 40°C retains hydrogen adsorbed in the γ- and δ-phase, while the catalyst treated again with hydrogen at 40°C holds hydrogen adsorbed in the α- and β-phase.

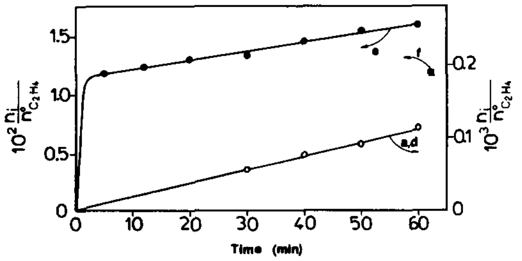


FIG. 6. Transformation of ethylene at 40°C over a catalyst activated with oxygen. For symbols see Fig. 1.

As pointed out by Massoth (*11*) and also in our previous publication (*9*) the reduced catalyst can be partially reoxidized with water vapor. By treatment of the catalyst with water vapor at 550°C the surface concentration of the coordinatively unsaturated molybdenum sites decreases.

Transformation of ethylene into propylene was determined by O'Neill *et al.* (*15*) over a molybdenum hexacarbonyl/alumina catalyst, by Otremba *et al.* (*16*) over reduced $MoO_3/\gamma\text{-}Al_2O_3$ at 300–400°C, and by Lombardo *et al.* (*12*) over the same catalyst in the course of ethylene hydrogenation. The mechanism of propylene formation has been interpreted by different assumptions. O'Neill *et al.* suggested the splitting of ethylene into methylenes, addition of the latter to another ethylene followed by rearrangement of the resulting trimethylene as a pathway for direct transformation. Otremba *et al.* concluded that propylene was not produced by secondary metathesis of ethylene and 2-butene but by the addition of alkyl groups and species poorer in hydrogen originating from the fragmentation of adsorbed ethylene. Lombardo *et al.* regarded the formation of propylene as an additional proof of the fact that metathesis proceeds through the metal carbon intermediate as presumed by Grubbs (*17*) and Katz *et al.* (*18*) for homogeneous catalytic systems and by Laverty *et al.* (*19*) for heterogeneous catalysts.

In Figs. 1 and 3 the shape of curves a and c, representing the formation of propylene and 2-butenes, indicates that in our case propylene was not formed by the direct transformation of ethylene but by the cometathesis of ethylene and 2-butenes:

$$C_2H_4 + 2 - C_4H_8 \rightleftarrows 2\,C_3H_6 \qquad (1)$$

This assumption is supported by the results obtained over the catalyst evacuated at 40°C (Fig. 2). Metathesis was found to be suppressed by hydrogen adsorbed on the catalyst at higher temperatures (*6*, *7*). It seems rather probable that the larger amount of 2-butenes and the small amount of propylene formed from ethylene over the catalyst retaining hydrogen adsorbed at 550°C is due to the suppressed metathesis.

In all cases studied the concentration of 2-butenes in butenes formed from ethylene was found to be lower than that in thermodynamic equilibrium (*20*). This may be explained by the subsequent metathesis of 2-butenes and ethylene. If, however, in the calculation of 2-butene concentration the propylene obtained from 2-butenes is also taken into account we obtain:

$$x_{2-C_4H_8} = \frac{(n_{2-C_4H_8} + 1/2\,n_{C_3H_6})}{n_{1-C_4H_8} + (n_{2-C_4H_8} + 1/2\,n_{C_3H_6})}. \qquad (2)$$

These values are similarly below the value obtained for thermodynamic equilibrium (Fig. 7). It can be seen from the figure that the corrected values of 2-butene concentration are lower than thermodynamic equilibrium even at the beginning of the reaction when propylene formation is relatively slow. It follows from this that the primary product of ethylene dimerization is 1-butene, and 2-butenes are formed by isomerization.

The extent of dimerization was characterized by the amount of ethylene converted to butenes, taking into account the amount of propylene formed in secondary metathesis (curves d in Figs. 1–6):

$$n_D = 2(n_{1-C_4H_8} + n_{2-C_4H_8}) + n_{C_3H_6}. \qquad (3)$$

Calculation of the extent of polymerization (curves e in Figs 1–6) was based on the decrease in the number of moles (Δn) calculated from pressure drop. This values was corrected by the amount of ethylene converted to butenes and propylene:

$$n_P = \Delta n - 2n_{\Sigma C_4H_8} - 3/2\,n_{C_3H_6}. \qquad (4)$$

Close correlation between dimerization and polymerization cannot be established on the basis of curves representing the two reactions.

From the change in reaction rates due to different treatment of the catalyst, it cannot be unambiguously determined whether po-

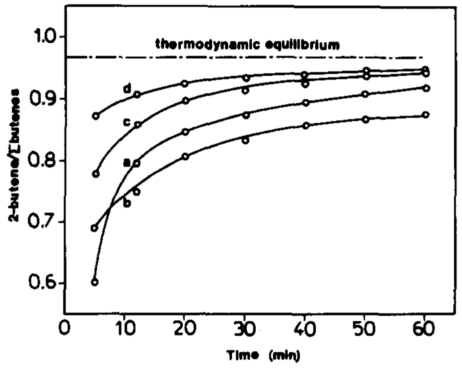


FIG. 7. Corrected concentration of 2-butene in the mixture of butenes formed. The catalyst: (a) evacuated at 550°C; (b) evacuated at 40°C; (c) evacuated at 550°C and treated again with hydrogen at 40°C; (d) evacuated at 550°C, 85% ethylene and 15% hydrogen.

lymerization, dimerization, and metathesis proceed on the same surface sites. The changes in reaction rate related to the results obtained over the SC are summarized in Table 3. In each reaction initial rate increased upon hydrogen adsorbed at 40°C. In the case of ethylene diluted with hydrogen, however, only the initial rate of dimerization and metathesis increased; the rate of polymerization decreased. The probable reason for this decrease is partial hydrogenation of the polymer formed over the catalyst. As hydrogen was consumed rapidly, and only small amounts of ethane, propane, and butane were observed, hydrogen consumption presumably can be attributed to the polymer. (Hydrogen consumption by the catalyst alone could not be observed.) A similar decrease in the rate of polymerization was observed over the catalyst evacuated at 40°C. Based on the previous assumption, this phenomenon can be explained by hydrogenation of the polymer with the hydrogen adsorbed on the catalyst at 550°C. Therefore, in this case the decrease in polymerization rate is not due to the change in surface sites caused by hydrogen adsorption, but to the shorter polymer chains formed.

The initial rate of dimerization increased, but later, as in the case of polymerization, it decreased upon hydrogen adsorption at 550°C. The rate of metathesis, however, showed considerable decrease as observed also in the case of propylene metathesis (*6, 7*). The rate of propylene metathesis was decreased also by the effect of catalyst oxidation with water vapor, to the level obtained over the catalyst activated with oxygen (*21*). The rate of dimerization substantially decreased, but the rate of polymerization increased over the catalyst oxidized with water vapor. By oxidation with water the surface concentration of Mo^{4+} species decreased and that of Mo^{5+} species increased. This points to the relationship between the rate of polymerization and the concentration of Mo^{5+}, as well as the rates of dimerization and metathesis and the concentration of Mo^{4+} species in the catalyst. The relationship between ethylene polymerization and Mo^{5+} species was described by Hashimoto *et al.* (*22*). They concluded that the activity of a MoO_3–Al_2O_3 in ethylene polymerization should be attributed to Mo^{5+} in the state of molybdenum oxide soluble in water. Over the catalyst activated with oxygen, i.e., containing mostly Mo^{6+} species, the rates of all three reactions are substantially lower than those observed over catalysts reduced previously.

TABLE 3

Effect of the Treatments of Reduced Catalyst on the Rate of Reactions[a]

Reaction	Hydrogen adsorbed at 550°C	Hydrogen adsorbed at 40°C	Hydrogen in ethylene	Oxidation with water vapor
Polymerization	( ) −	+ ( )	− −	( ) +
Dimerization	+ −	+ ( )	+ ( )	− −
Metathesis	− −	+ ( )	+ ( )	[b]

[a] The first symbols in the columns show initial reaction rates, the second symbols indicate reaction rates after 1 hr reaction period compared with the results obtained over the standard catalyst (SC). ( ), identical rates; +, higher rates and −, lower rates of reaction over treated catalyst compared with values obtained over the SC.

[b] Over the catalyst oxidized with water vapor only trace amounts of butenes were formed, therefore the rate of metathesis was not determinable.

Since contrary to the rate of dimerization and polymerization, the rate of metathesis decreases upon the effect of hydrogen adsorption at 550°C, and contrary to that of metathesis and dimerization the rate of polymerization increases over the catalyst oxidized with water vapor, it may be presumed that the three reactions proceed on different surface sites. For a deeper insight into the interactions of olefin hydrocarbons and hydrogen adsorbed in different states over a reduced molybdena–alumina catalyst more detailed investigations are required.

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