JOURNAL OF CATALYSIS **116**, 285–290 (1989)

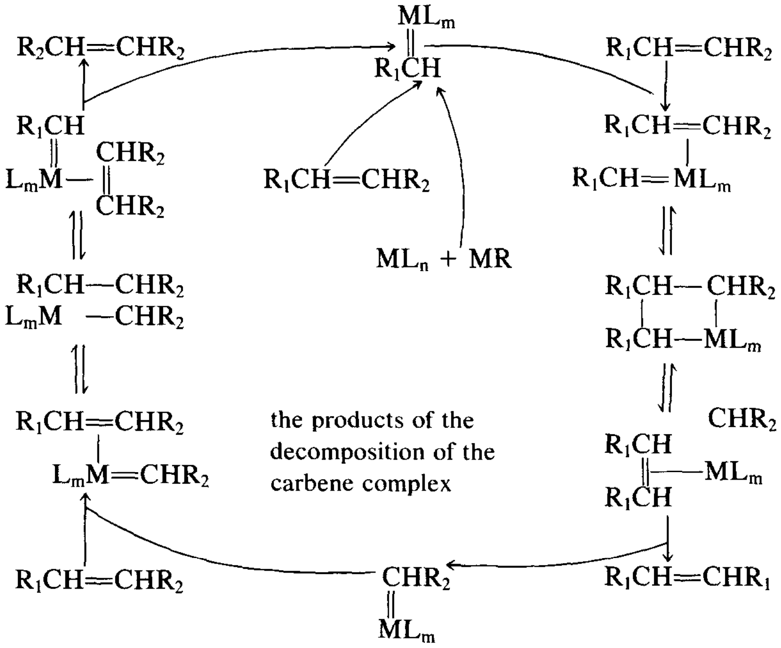
Activation of Tungsten Oxide Catalyst on SiO_2 Surface by Low-Temperature Plasma

INTRODUCTION

The disproportionation of alkenes, in particular propene, promotes an improvement in the balance of crude oil processing and is one of the possibilities of gaining a new raw-material source for petrochemical syntheses. The disproportionation processes comprising conversion of alkenes into the two qualitatively new ones proceed only in the presence of the catalysts. As the catalyst, tungsten oxide which is applicable on the silica gel carrier may be used.

It was a practical effort which led us to study the plasma interaction with the WO_3/SiO_2 catalyst to accelerate and achieve the more effective preparation of the catalyst needed for heterogeneous catalysis of propene, and thus to positively influence the catalyst quality. This means, especially, the shortening of activation time, the reduction of required energy, and the enhancement of catalyst activation, selectivity, and lifetime, respectively.

Disproportionation is assumed to be a chain reaction in which carbenes and/or carbines coordinated to the transient metal are the carriers of the kinetic chain. The bond of carbenes in the coordination sphere of the transient metal is responsible for their sufficient stability and leads to the required selectivity of the reaction (*1*).



0021-9517/89 $3.00

The formation of active centers capable of catalyzing the disproportionation is achieved by heating to a working temperature in the N_2 for 30 min as well as by subsequent washing with alkene for 100 min until the activity is stabilized.

In this period the active centers are formed. During their formation, the catalyst is likely to be reduced by alkene, which gives rise to the tungsten oxide mixtures of the fifth and sixth oxidation degrees, for example to $W_{20}O_{58}$ (*2*). The first preparation stage is designed to remove the catalyst poisons (water, oxygen compounds, etc.) and stabilize thermal conditions in the disproportionation reactor. The second stage in treatment involving the preparation by catalyst, i.e., the proper activation, can be accounted for by interaction of the unsaturated π-orbits of ligands and d-orbits of metal, which leads to the reduction of d-orbits.

From the kinetics point of view, the Langmuir–Hinshelwood model, according to which the reaction proceeds between two chemisorbed molecules on the catalyst surface, was taken into account,

$$\mathrm{P} + a \rightleftarrows \mathrm{P}a$$

$$2\mathrm{P}a \rightleftarrows \mathrm{E}a + \mathrm{B}a$$

$$\mathrm{E}a \rightleftarrows \mathrm{E} + a$$

$$\mathrm{B}a \rightleftarrows \mathrm{B} + a,$$

where P, B, and E are propene, 2-butene, and ethylene, and a represents the active center.

The rate of propene decomposition r_0 is described by the equation

$$r_0 = \frac{kC_\mathrm{p}^2}{[1 + K_\mathrm{p}C_\mathrm{p}]^2}, \qquad (1)$$

where k is the rate constant, K_p is the equilibrium constant for propene, and C_p is the propene concentration. From the straight line dependence,

$$\frac{C_\mathrm{p}}{r_0^{1/2}} = \frac{1}{k^{1/2}} + \frac{K_\mathrm{p}}{k^{1/2}} C_\mathrm{p}, \qquad (2)$$

the parameters k and K_p may be calculated. From the Arrhenius kinetics the dependences for k and K_p may be derived as

$$k = k_0 \exp\left[\frac{-\Delta E}{RT}\right]$$

$$K_\mathrm{p} = K_{\mathrm{p}_0} \exp\left[\frac{-\Delta H}{RT}\right],$$

where ΔE and ΔH represent the activation and adsorption energies for propene.

EXPERIMENTAL

Surface changes in the WO_3/SiO_2 system caused by the low-temperature plasma effect were evaluated by investigating the initial rates of reaction proceeding in the differential reactor as well as by studying the propene conversion dependent on the $W/\dot{F}$ variable (W means the amount of catalyst and $\dot{F}$ represents the amount of reaction mixture being processed within the unit of time) and on the space-time measured in the integral reactor.

The WO_3/SiO_2 catalyst was prepared from the carrier Silipor 300, and the tungsten oxide was deposited from ammonium wolframate, the content of WO_3 being 5%. In view of the fact that we were manipulating with powdered material demanding equal treatment, we decided to apply—for plasma activation—the fluidized bed reactor giving a guarantee of perfect mixing, the maximum contact area of the catalyst with plasma, and the low-temperature and concentration gradients in the fluidization layer. The scheme of the experimental apparatus is shown in Fig. 1. The whole system was evacuated under the pressure of 1.2 Pa. The convenient fluidization was reached with the N_2 flow corresponding to 3.2×10^{-4} m^3/s. The threshold fluidization rate was $w_\mathrm{p} = 0.225$ m/s. The fluidization rate was approximately four times higher than w_p. After the fluidization conditions had been stabilized, a high-frequency discharge in the reactor was generated. The generator performance was between 200

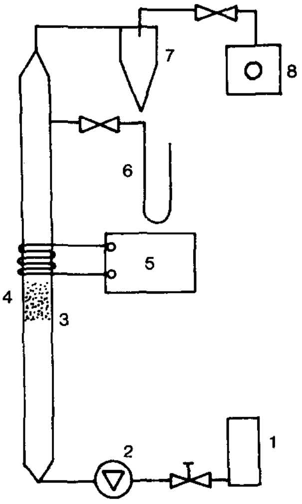


FIG. 1. The fluidization reactor for the catalyst pretreatment. (1) N_2 chamber, (2) flow meter, (3) porous grid, (4) catalyst, (5) hf generator, (6) vacuum gauge, (7) cyclone, and (8) vacuum pump.

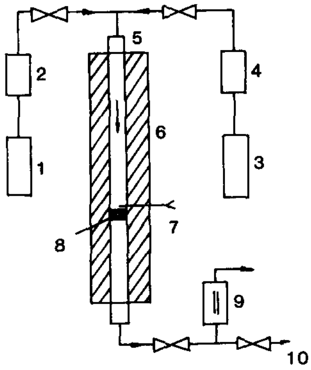


FIG. 2. The disproportionation reactor scheme. (1) N_2 chamber, (2) drying, (3) propene chamber, (4) drying, (5) stainless-steel pipe (ϕ 14 mm), (6) heater, (7) temperature regulation, (8) WO_3/SiO_2 fixed bed, (9) flow meter, and (10) products output.

and 800 W, and the discharge frequency was 10 MHz.

The neutral gas temperature in discharge varied from 75 to 150°C and was measured by a gas thermometer. The exposure time ranged from 0 to 15 min.

The disproportionation of propene was investigated in the tubular fixed-bed flow reactor. The scheme is outlined in Fig. 2.

In this arrangement the disproportionation temperature, propene flow, and character of reaction (differential and integral reactor) could be controlled. The mixture ratio was analyzed on the Becker–Packard 417 gas chromatograph equipped with the integrator Autolab 6300. The differential reactor arrangement permits the elimination of transfer phenomena. The degree of conversion X should not exceed in it 5% (*3*, *4*). For this reason the initial rates of reaction could be measured. From the experimental dependence $X = f(W/\dot{F})$ for different disproportionation temperatures it was possible to determine the values r_0 and ΔE or the values K_{p_0} and ΔH. On the contrary, the integral reactor was working under stable conditions (*5*). It allowed the dependences of conversion X upon the $W/\dot{F}$ variable to be defined for all of the reaction products.

RESULTS AND DISCUSSION

The propene conversion dependence upon the space-time, measured in the disproportionation reactor for the classically activated catalyst (without plasmochemical pretreatment), is illustrated in Fig. 3.

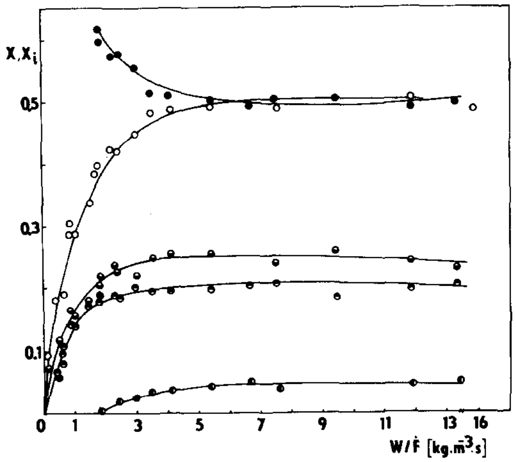


FIG. 3. The dependence of both the propene conversion X and the product distribution X_i upon the space-time at the temperature of 400°C. X_i represents the molar component fractions. The catalyst is without pretreatment in plasma. ○, $X = 1 - X_p$; ◒, X_E; ●, X_p; ◓, X_B; ◐, X_{PE}.

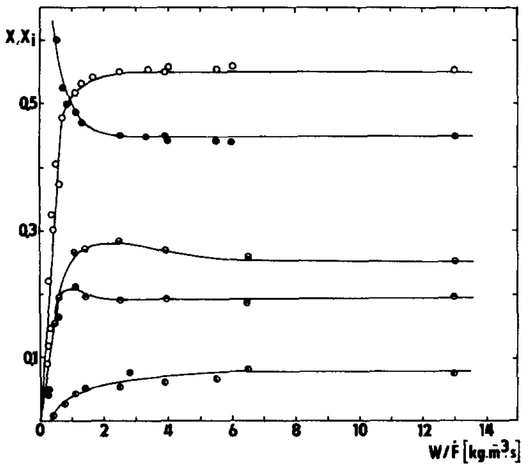


FIG. 4. The space-time dependence of propene conversion X and the products distribution X_i at the temperature of 400°C. ○, $X = 1 - X_p$; ⊖, X_E; ●, X_p; ⊖, X_B; ◐, X_{PE}. The catalyst is exposed in the N_2 plasma—800 W, 30 s.

The same dependence for the plasma-pretreated catalyst is shown in Fig. 4. This figure depicts a course of disproportionation in the integral reactor provided that the catalyst was pretreated in the N_2 plasma. The exposure time was 30 s and the generator performance was 800 W.

From the comparison of both dependences it is obvious that in applying the plasmochemically pretreated catalyst the equilibrium degree of conversion is attained at the lower $W/\dot{F}$ values. When the $W/\dot{F}$ value is equal to 1, the conversion is the same as in the case of the nonexposed catalyst at $W/\dot{F} = 5$. This fact is highly important since it allows the equipment efficiency to be essentially increased. The equilibrium shift to higher values occurs due to side reactions—penthenes. A change in the distribution of products is favorable. The C_2 content increases, which from the efficiency point of view is also favorable.

A significant shortening of the activation period for the plasma-pretreated catalysts is worth mentioning. While the activation time in the flow of propene, i.e., the time until activity stabilization, is 100 min for a nontreated catalyst, it is only 30 min for a plasma-exposed catalyst. This, naturally, leads to the shortening of the reactor's preparation time and to the improvement of the energy balance of the whole disproportionation process.

For the differential reactor the dependences $X = f(W/\dot{F})$ for different exposure times of the catalyst were measured. Figure 5 illustrates the above-mentioned dependences for the catalyst treated in the N_2 plasma with the generator performance of 460 W and different exposure times of the catalyst.

From the dependences indicated before it is evident that the conversion for the catalyst exposed for 30 s sharply rises. The exposures above 5 min in duration reduce X under the value of the nonirradiated catalyst. The experimental investigations show that the long-term exposures result in the profound tungsten content reduction in the catalyst. Due to the plasma effect a certain part of tungsten is removed from the SiO_2 surface, settling down on the walls of a discharge tube, closely above a discharge zone. In such a way a number of active centers in the catalyst will decrease.

From the viewpoint of the rate of disproportionation the ratio of k_0 to $-\Delta E$ is significant. The values k_0, $-\Delta E$, K_{p_0}, and $-\Delta H$ for varying exposure times of the catalyst in the N_2 plasma at 460 W are listed in Table 1.

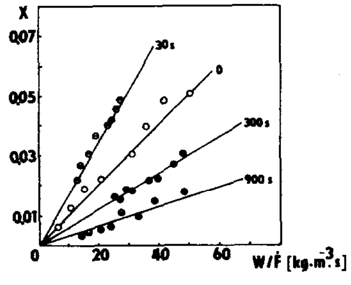


FIG. 5. The dependence $X = f(W/\dot{F})$ for different exposure times in the N_2 plasma at 460 W and at the disproportionation temperature of 400°C in the differential reactor.

TABLE 1

The Values r_0, $-\Delta E$, K_p, and $-\Delta H$ for Different Exposure Times of the Catalyst in the N_2 Plasma

τ(s)	0	30	60	120	300	900
k_0(m^6 kg^{-1} $kmol^{-1}$ s^{-1})	8×10^7	3×10^8	2×10^5	1×10^6	7×10^7	1×10^8
$-\Delta E$(J mol^{-1})	118	123	88	102	122	125
K_{p_0}(m^3 $kmol^{-1}$)	1×10^3	8×10^2	3×10^2	1.5×10^2	6×10^4	1×10^2
$-\Delta H$(J mol^{-1})	21.5	19	9	9	30	8

Note. The hf generator performed at 460 W. The disproportionation temperature was 400°C.

By consideration of adsorption proceeding on the catalyst surface the most favorable exposure time is 60 s (Table 1) since the $-\Delta H$, as an indicator of the energetic chemisorption demand, is minimal. However, Table 1 clearly shows that such an exposure time is disadvantageous for the chemical reaction process. Under these conditions, the most favorable time is 30 s as the rate of reaction is more susceptible to the value k_0 than to K_p, which results from the equations' defining the reaction rate of the surface reaction (5).

Several potential plasma influences on the catalyst, primarily an existence of tungsten oxide reduction, may be considered. Moreover, there is a possibility of influencing the surface structure of silica gel by the action of plasma. The silica gel surface is usually covered by the OH group layer and by the physically adsorbed water. In addition to these, the siloxane bonds affecting sorption of alkene molecules are also present. The presence of these groups has an influence on the sorption of alkene molecules. However, the study of water sorption on the catalyst surface showed only minor changes. Evidently, some profound changes caused by plasma in the WO_3 distribution occurred partly on the surface and partly in the pores of the catalyst. Note that all of these influences, although from a quantitative viewpoint very slight ones, can affect the catalyst properties during the disproportionation process.

CONCLUSION

In this paper some of the results obtained from the study of the WO_3/SiO_2 catalysts treated by the low-temperature plasma have been discussed. On the basis of investigation carried out on the catalyst's activity, selectivity, and lifetime—in relation to propene disproportionation—it may be stated that:

—the equilibrium degree of conversion is attainable with lower $W/\dot{F}$ values,

—the composition of disproportionation products is shifted more to the ethylene formation,

—the lifetime of the catalyst remains unchanged, and

—for both dimerization and cracking no active centers are formed.

APPENDIX: NOMENCLATURE

C_p	concentration of propene
ΔE	activation energy of the reaction
ΔH	adsorption energy
$\dot{F}$	feed rate
k	reaction velocity constant
K_p	adsorption equilibrium constant of propene
r_0	rate of propene decomposition at initial conversion
R	gas constant
T	temperature
W	mass of catalyst
X	degree of conversion

X_B molar fraction of 2-butene
X_P molar fraction of propene
X_{PE} molar fraction of ethylene

REFERENCES

1. Balcar, H., *Chem. Pap.* **78,** 35 (1984).
2. Hughes, W. B., *J. Amer. Chem. Soc.* **92,** 532 (1970).
3. Mol, J. C., and Moulijn, J. A., *Adv. Catal.* **24,** 131 (1975).
4. Kraus, M., Schneider, P., and Beránek, L., *in* "Chemická kinetika pro inženýry, SNTL, Prague," 1978.
5. Lodes, A., and Dudáš, J., *in* "Proceedings on Catalysis and Catalytic Processes, CHTF, Bratislava," 1983.

J. Blecha
J. Dudáš
A. Lodes
J. Derco

Faculty of Chemical Technology
Slovak Technical University
812 37 Bratislava, Czechoslovakia

Received March 10, 1987; revised September 16, 1988