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Ethylene hydrogenation mechanism on Ag/SiO_2 catalysts elucidated by isotope kinetics

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On a highly dispersed Ag/SiO_2 catalyst the reaction of ethylene with hydrogen was studied by means of isotopic exchange. Although hydrogenation does not proceed below 550 K, a latent but intensive interaction between ethylene and hydrogen could be observed already at 480 K. On the investigated catalyst the mechanism of the ethylene hydrogenation is similar to that known for nickel, the catalytic behaviour, however, being distinctly different.

Keywords: Hydrogenation; isotopic exchange

1. Introduction

When used as catalysts for the methanol-to-hydrocarbon conversion, silver salts of heteropoly acids show a change of their behaviour, if hydrogen is present [1,2]: the activity rises to a high and very stable level, while olefin selectivity does not change. In the presence of hydrogen, copper and palladium salts show also high and stable activities. Simultaneously their olefin selectivities decrease nearly to zero [2]. As deactivation is caused by coking, it can be assumed that the stabilising effect of hydrogen is due to the hydrogenation of coke precursors. Differing from copper and palladium, silver, however, is not known as a hydrogenation catalyst.

To characterize the interaction of hydrogen with the catalyst–olefin system we investigated the H–D homoexchange (tracer transfer between the molecules of one chemical species) and the heteroexchange reactions (tracer transfer between different chemical species) on a reduced $Ag_4SiW_{12}O_{40}$ catalyst. In the presence of hydrogen an acceleration of the homoexchange rate was found [2]. Unfortunately, on the strong acid Brønsted groups of the reduced HPA-silver salts the homoexchange of ethylene is occurring very fast. To study the silver effect in detail, we had to use a non-acid silver catalyst with the same high dispersion of the metal as in the case of the reduced $Ag_4SiW_{12}O_{40}$. Thus, further investigation was based on a special Ag/SiO_2 [3,4].

2. Experimental

The catalyst was prepared by a method described in ref. [4]. Aerosil 200 was used as the support, the silver content amounts to 2.3 wt%, silver being highly dispersed (diameter of Ag-clusters: 1–10 nm, metal surface: 3.7 m^2/g catalyst). Exchange experiments were carried out in a static apparatus with internal gas circulation, equipped with a microreactor. The experimental device, the pretreatment of the catalyst and the measurement procedure are described in detail in ref. [3].

3. Isotopic kinetics

Isotopic kinetics is very detailed described in earlier work [5] with ethane homoexchange used as an example. Here we can only briefly present it.

In analogy to methane, ethylene contains four equal hydrogen atoms. D-labelling results in five isotopic molecules, which differ only in their deuterium content (the steric isomers of the $C_2H_2D_2$-molecule are not taken into account). With the general amount of ethylene molecules N and with X_i being the relative concentration of an i-times labelled ethylene,

$$X_i = N_i/N, \quad i = 0, 1, 2, 3, 4$$

we get a system of five components. Thus, to describe the isotopic molecules distribution of D-labelled ethylene we need a system of five independent determinental equations. Two of them describe the balance of ethylene molecules and of the tracer:

$$\sum N_i = N, \quad \sum iX_i = 4\alpha\,.$$

Chemical conversion in the system (for instance hydrogenation of ethylene) is described by the time dependence of N. Usually, but not necessary, for exchange experiments it is assumed to be constant. This is realized under chemical equilibrium conditions. The heteroexchange experiments are dealing with the time dependence of α. Investigation of the homoexchange requires constant values of α during the experiments.

We yet need three parameters to determine the isotopic molecule distribution and its time dependence. If we select the relative concentrations of isotopic molecules (for instance X_2, X_3 and X_4), this will result in a very complicated system of differential equations even for our easy four-atomic molecule. In detail this system is described for the methane homoexchange in ref. [5].

For more comprehensive equations it is necessary to transform the variables. The new parameters Z_2, Z_3 and Z_4 we got by such transformation are easy combinations of the X_i and α. We define them as follows:

$$Z_2 = -\alpha^2 + \tfrac{1}{6}X_2 + \tfrac{1}{2}X_3 + X_4,$$

$$Z_3 = 2\alpha^3 - \tfrac{1}{2}\alpha X_2 + \tfrac{1}{4}(1 - 6\alpha)X_3 + (1 - 3\alpha)X_4,$$

$$Z_4 = -3\alpha^4 + \alpha^2 X_2 - (1 - 3\alpha)X_3 + (1 - 4\alpha + 6\alpha^2)X_4.$$

This way, we obtain a simple system of differential equations:

$$(N/K)\frac{\mathrm{d}Z_2}{\mathrm{d}t} = -A_2 Z_2,$$

$$(N/K)\frac{\mathrm{d}Z_3}{\mathrm{d}t} = -A_3 Z_3,$$

$$(N/K)\frac{\mathrm{d}Z_4}{\mathrm{d}t} = -A_4 Z_4 + A_{22} Z_2^2,$$

where K is the rate constant and N the amount of the component. A-parameters depend only on the exchange mechanism. The kind of this dependence is demonstrated in table 1.

As shown in ref. [5] only four types of mechanism can occur. They differ with the number of hydrogen atoms exchanged during one act of hydrogen transfer between the gas and the H-containing partner. Any real mechanism of exchange can be described as a linear combination of these four types.

4. Results and discussion

Under our experimental conditions no hydrogen exchange occurred on Aerosil 200 (support of the investigated silver catalyst) and on silver powder ($S_{\mathrm{BET}} = 10\ \mathrm{m}^2/\mathrm{g}$). We assume that the activity of our catalyst is caused by the high degree of the metal dispersion.

Table 1
Types of the mechanism for a four-atomic molecule

Type	Dissociation variants	A_2	A_3	A_4	A_{22}
1	(4H)	1	1	1	0
2	(2H + H_2)	5/6	1	1	0
3	(H + H_3)	1/2	3/4	1	0
4	($2H_2$)	2/3	1	1	1

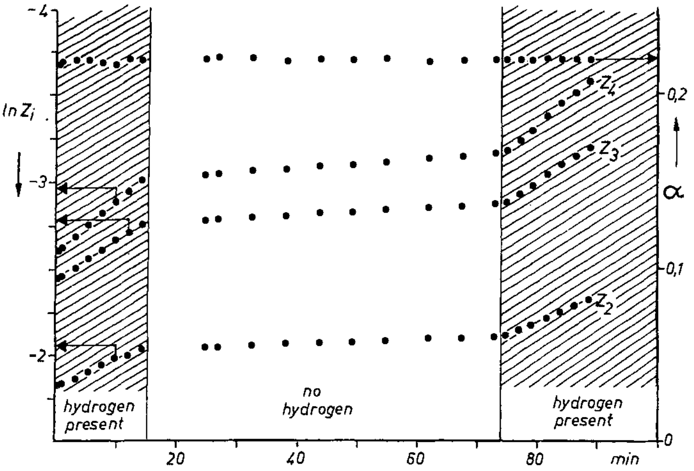


Fig. 1. Hydrogen effect on ethylene homoexchange at 480 K.

Fig. 1 shows the accelerating effect of hydrogen on the ethylene homoexchange rate at 480 K. During the first 15 min the gas phase consists of ethylene plus hydrogen. Then hydrogen is pumped off and added again after 75 min. The exchange rates found in this experiment are given in table 2.

The homoexchange rate is of first order with respect to ethylene and of 0.5th order with respect to hydrogen (table 3),

$$K = K_0 p^{1}_{C_2H_5} p^{0.5}_{H_2} \, .$$

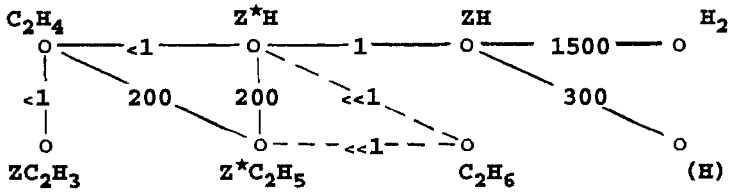
The hydrogenation of ethylene becomes remarkable only at higher temperatures ($T > 550$ K).

A-parameters show clearly, that the homoexchange occurs via the third type of mechanism (table 1). In this case A_2/A_4 and A_3/A_4 must be equal to 0.5 and 0.75 respectively. Our experimental data are in good agreement with this assumption.

The results obtained by following the H–D exchange in the triple system

$$C_2H_4\text{–}Ag/SiO_2\text{–}H_2$$

are depicted in the following graph. The unit of the hydrogen transfer rate in this graph equals 10^{10} hydrogen atoms per second and cm^2 Ag. The reaction temperature was 480 K, hydrogen and ethylene pressure amounting to 800 and 400 Pa respectively.



This graph corresponds to the following reaction scheme:

Reaction	Relative rate	Evidence from	
$H_2 + 2Z \rightleftharpoons 2ZH$	1500	*Homoexchange* of H_2	(1)
$ZH + (\ ) \rightleftharpoons Z + (H)$	300	*Heteroexchange* between H_2 and catalyst's–OH	(2)
$ZH + Z^* \rightleftharpoons Z^*H + Z$	1	*Heteroexchange* between H_2 and C_2H_4	(3)
$C_2H_4 + Z^*H \rightleftharpoons Z^*C_2H_5$	200	*Homoexchange* of C_2H_4 in presence of H_2	(4)
$Z^*C_2H_5 + Z^*H \rightleftharpoons C_2H_6 + 2Z^*$	$\ll 1$	*Ethane production*	(5)
$C_2H_4 + Z + Z^* \rightleftharpoons ZC_2H_3 + Z^*H$	< 1	*Homoexchange* of C_2H_4 in absence of H_2	(6)

The reactions (1)–(3) describe the hydrogen activation, the reactions (4) and (5) correspond to the hydrogen–ethylene interaction. The last reaction pays regard to the homoexchange in the absence of "outside" hydrogen.

Evidently, the hydrogen transfer graph and the reaction scheme proposed by us correspond to the classic ethylene hydrogenation mechanism of Polanyi and Horiuti [6,7] established for nickel catalysts:

Table 2
Exchange rates corresponding to fig. 1

Time (min)	Pressure (Pa)		Exchange rate (10^{12} molecules/s cm^2Ag)
	H_2	C_2H_4	
0–15	130	1330	1.3
15–75	0	1330	0.11
75–90	130	1330	1.2

Table 3
Pressure dependence of the homoexchange of ethylene at 480 K

Ethylene (Pa)	Hydrogen (Pa)	Rate (10^{12} molecules/s cm^{2}Ag)	A_2/A_4	A_3/A_4
1330	400	2.4	0.49	0.77
1330	130	1.4	0.48	0.76
1330	40	0.85	0.48	0.79
1330	130	1.3	0.49	0.75
1330	0	0.11	0.51	0.74
2000	130	1.6	0.50	0.76
670	130	0.57	0.51	0.76
670	0	0.055	0.59	0.72

$$H_2 \rightarrow 2H^* \tag{a}$$

$$C_2H_4 + H^* \rightleftharpoons C_2H_5 \tag{b}$$

$$C_2H_5 + H^* \rightarrow C_2H_6 . \tag{c}$$

If reaction (3) (hydrogen activation) is fast, then the surface concentration of the active hydrogen species is high enough to enable not only reaction (4) (resulting in the "half-hydrogenated state") but also reaction (5), by which ethane is produced. Low rates of reaction (3) are the reason for very low concentrations of active hydrogen in the presence of ethylene. After ethylene reacting with the first H*, the probability of a C_2H_5-species to dissociate into ethylene and active hydrogen is much higher than the possibility to interact with a second active H*. In this case the ethane production must be very slow. Ethylene homoexchange, however, is expected to be rather fast and to depend strongly on the hydrogen pressure in the system, as was shown for our catalyst.

Hence, active surface hydrogen is acting as a catalyst for the ethylene homoexchange and thus becomes detectable even at very low concentrations.

The main difference between our proposals and the Horiuti–Polanyi mechanism is the existence of different one-atomic hydrogen species on the catalyst. There is no doubt that dissociative adsorption of hydrogen occurs: The homoexchange of the molecular hydrogen is the fastest reaction in our system. The surface species (ZH) taking part in that reaction and also in the heteroexchange between surface OH-groups and molecular hydrogen, however, cannot be identical with the active hydrogen in the ethylene homoexchange. Otherwise, a high speed of hydrogenation and a low rate of ethylene homoexchange should occur. Thus for a complete interpretation of our experimental results we suggest introducing a second kind of surface hydrogen (Z*H). As ethylene homoexchange proceeds also in the absence of molecular hydrogen, an additional dissociative adsorption of ethylene is assumed.

5. Conclusions

(1) Silver is able to catalyze hydrogenation. To be active, it must be highly dispersed.

(2) Surface hydrogen species, active in the hydrogenation, can act as a catalyst in the ethylene homoexchange of hydrogen.

(3) Therefore, the ethylene homoexchange of hydrogen can be used as a very sensitive indicator to prove the presence of any active hydrogen.

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