Kinetics and Catalysis, Vol. 45, No. 3, 2004, pp. 391–393. Translated from Kinetika i Kataliz, Vol. 45, No. 3, 2004, pp. 417–419.

Estimates of the Catalytic Efficiency of a Heterogeneous Catalyst for Acetylene Hydrochlorination on the Surface of Mechanically Activated K_2PtCl_6 Salt

S. A. Mitchenko*, E. V. Khomutov*, A. A. Shubin, and I. P. Beletskaya*****

** Litvinenko Institute of Physicoorganic and Coal Chemistry, National Academy of Sciences of Ukraine, Donetsk, 83114 Ukraine*

*** Donetsk State University of Commerce and Trade, Donetsk, 83050 Ukraine*

**** Department of Chemistry, Moscow State University, Vorob'evy gory, Moscow, 119899 Russia*

Received November 4, 2002

Abstract—Acetylene hydrochlorination by gaseous HCl on the surface of the mechanically activated salt K_2PtCl_6 is shown to occur as a catalytic reaction. Using a modified kinetic distribution method, the specific catalytic activity of the mechanically activated catalyst was found to be equal to ~0.2 (mol C_2H_2) (mol Pt)$^{-1}$ s^{-1}.

INTRODUCTION

The effect of mechanical activation on the catalytic and stoichiometric conversion of various hydrocarbons has been extensively studied (see, for instance, [1–4]). It is known that Pt(II) chloride complexes catalyze acetylene hydrochlorination in aqueous solutions, whereas Pt(IV) complexes do not show noticeable catalytic activity [5].

However, earlier we found [6] an unusual fact of acetylene hydrochlorination by gaseous HCl in the absence of a solvent on the surface of mechanically treated K_2PtCl_6

$$C_2H_2 + HCl_{gas} \xrightarrow[\text{mechanically activated } K_2PtCl_6 \text{ salt}]{} H_2C{=}CHCl. \quad \text{(I)}$$

It remained unclear if reaction (I) is catalytic. The goal of this work was to prove that reaction (I) is catalytic and to estimate the specific catalytic activity of the catalyst.

EXPERIMENTAL

Reactions were carried out at room temperature in a closed glass vibration reactor containing glass grinding bodies. An MMVE-0.005 vibration mill was used, which was able to maintain a specific power rating of 15 W/kg. The kinetics of acetylene consumption was controlled by GLC using an LKhM-8-MD chromatograph with a flame-ionization detector and a Multichrome system for data accumulation from Ampersand. Samples of the gas phase were taken via a syringe through a rubber sealing. The relative concentration (φ) of acetylene (RH) and vinyl chloride (RCl) was determined as the ratio of the chromatographic peaks of acetylene, vinyl chloride, and methane. The latter was used as an internal standard. To obtain an active catalyst, the freshly crystallized K_2PtCl_6 salt was obtained using a standard method. The salt (0.3 g) was preliminarily ground in an acetylene atmosphere at a pressure of 1 atm for 1 h, a time period sufficient to obtain the maximum surface area. Then, the reactor was purged with dry air or argon and acetylene, the internal standard (methane), and HCl, were added through a rubber sealing. The BET specific surface area of the salt determined from argon desorption was 3.1 m^2/g.

Deuterium chloride was obtained from calcined NaCl and D_2SO_4. The resulting gas passed through an IR cell with side NaCl windows and then through a reactor. After purging the reactor, the cell was sealed, acetylene was added to the reactor together with the internal standard, and the kinetics of acetylene hydrochlorination was studied. The IR spectrum of the gaseous mixture was recorded using a FTIR Perkin Elmer Spectrum BX instrument, with software for integration.

RESULTS AND DISCUSSION

Acetylene consumption from the gas phase in a closed reactor in the hydrochlorination reaction in an atmosphere of HCl (without continuous mechanical load is described by first-order kinetics (Fig. 1). The yield of vinyl chloride based on the consumed acetylene η_{RCl} is close to the quantitative one (see table). After eight catalytic cycles based on bulk platinum or 1700 cycles based on complex platinum anions on the catalyst surface, no noticeable decrease in the catalytic activity was observed.

The values of the apparent rate constant of acetylene hydrochlorination (acetylene consumption from the gas phase of the closed reactor) in an HCl atmosphere

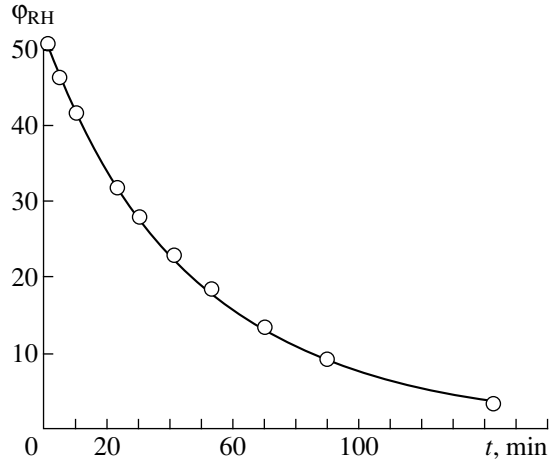

Fig. 1. Dependence of acetylene concentration in the gas phase of the closed reactor on time. Dots refer to the experimental values, and the curve corresponds to calculation according to the first-order rate law at $k_{app} = (3.4 \pm 0.2) \times 10^{-4}$ s^{-1}. The catalyst weight was 0.3 g.

$k_{app} = -\frac{d(\ln \varphi_{RH})}{dt}$ are the same within the experimental error in two cases: 20-fold and 3-fold excess of HCl over acetylene (see table). This may be due to the fact that an HCl molecule does not participate in the rate-limiting step of the reaction or due to the fact that a change in the concentration of HCl on the catalyst surface can be neglected. The latter is possible, for instance, in the case of a limiting Langmuirian or multilayer coverage of the surface by HCl molecules. As shown below, the second situation is our case.

Indeed, the participation of an HCl molecule in the rate-limiting step should result in the appearance of the kinetic isotope effect if HCl is replaced by DCl. We found that, when the reaction is carried out in the medium of HCl/DCl, the reaction rate noticeably decreases. The values of the apparent rate constants in HCl and in the HCl/DCl mixture are $k_{app}^{HCl} = (3.4 \pm 0.2) \times 10^{-4}$ and $k_{app}^{DCl/HCl} = (2.5 \pm 0.2) \times 10^{-4}$ s^{-1}, respectively. According to IR spectroscopic data, the fraction of DCl in the mixture used for kinetic isotope effect measurements was 58 mol %. Therefore, the value k_{app}^{DCl} in an atmosphere of pure DCl determined from the equation $k_{app}^{DCl} = \frac{k_{app}^{DCl/HCl} - k_{app}^{HCl}\chi}{1-\chi}$ [8] (where χ is the molar fraction of HCl in the mixture HCl/DCl) is 1.8×10^{-4} s^{-1}. Therefore, the value of the kinetic isotope effect $\frac{k_{app}^{HCl}}{k_{app}^{DCl}}$ is 1.9. The presence of a noticeable isotope effect proves the participation of HCl in the rate-limiting step.

Characteristics of acetylene hydrochlorination reaction and the yield of vinyl chloride based on reacted acetylene on the ratio $\nu_{HCl}/\nu_{C_2H_2}$

$\nu_{HCl} : \nu_{RH}$	$k_{app} \times 10^{-4}$, s^{-1}	η_{RCl}, %
3	3.0 ± 0.2	86 ± 15
6	3.4 ± 0.2	89 ± 14
10	3.9 ± 0.2	100 ± 8
15	3.5 ± 0.1	98 ± 9
20	3.1 ± 0.1	94 ± 9

The first-order rate law of acetylene consumption in the heterogeneous catalytic reaction (I) probably means that acetylene is adsorbed according to the Henry law:

$$[RH]_{ads} = KP_{RH}, \quad (1)$$

where $[RH]_{ads}$ is the surface concentration of acetylene, K is the rate constant of adsorption equilibrium and P_{RH} is the partial pressure of acetylene. Indeed, in this case, the total amount of acetylene in the reactor is determined by the equation

$$\nu_{RH} = \frac{V_g P_{RH}}{RT} + S_{sp} m K P_{RH}, \quad (2)$$

where V_g is the volume of the gas phase, R is the universal gas constant, T is temperature, and S_{sp} and m are the specific surface area and the weight of the catalyst, respectively. Differentiation of Eq. (2) with respect to time gives

$$\frac{d\nu_{RH}}{dt} = \frac{V_g dP_{RH}}{RT dt}\left(1 + \frac{1}{\alpha\lambda}\right), \quad (3)$$

where $\alpha = (RTK)^{-1}$ and $\lambda = V_g/(S_{sp}m)$. A change in ν_{RH} with time is due to the occurrence of the reaction; that is,

$$\frac{d\nu_{RH}}{dt} = -kS_{sp}m[RH]_{ads}, \quad (4)$$

where k is the rate constant of reaction (I). Using Eqs. (3), (4), and (1) we obtain the first-order rate law of acetylene consumption in the gas phase in the reactor:

$$\frac{dP_{RH}}{dt} = -\frac{k}{1+\alpha\lambda}P_{RH}. \quad (5)$$

It follows from Eq. (5) that the experimental value of k_{app} is related to the intrinsic rate constant k:

$$k_{app} = \frac{k}{1+\alpha\lambda}. \quad (6)$$

Equation (6) agrees with the experimental dependence of k_{app} on the catalyst weight at $k = (4.4 \pm 1.5) \times 10^{-4}$ s^{-1} and $K = (1.2 \pm 0.6) \times 10^{-8}$ mol m^{-2} Pa^{-1} (Fig. 2).

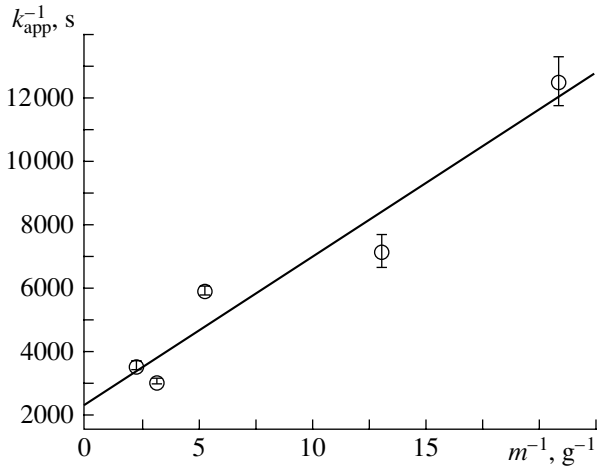

Fig. 2. Dependence of the value k_{app} on the catalyst weight. Linearization of Eq. (6).

Note that a similar relation between the true and apparent rate constants was first obtained for reactions in solutions under conditions of equilibrium distribution of a substrate between the gas and liquid phases [9], and α is equal to the ratio between these phases, and λ is equal to the volume of the cited phases.

Using the above values of the intrinsic rate constant of the reaction k and the constant of adsorption equilibrium K for acetylene, we can estimate the catalytic activity. The amount of platinum on 1 m^2 of the catalyst surface ν_{Pt} can be estimated using the lattice constant $a = 9.78 \times 10^{-10}$ m [10]:

$$\nu_{Pt} = \frac{2a^{-2}}{N_A} \approx 3.5 \times 10^{-6} \text{ mol/m}^2. \quad (7)$$

Here N_A is Avogadro's number, the multiplier 2 takes into account the fact that one unit cell includes two palladium atoms. Then, the value of the specific catalytic activity of the catalyst at a limiting surface coverage by HCl (see above) and a partial pressure of acetylene of 1 atm is ~0.2 mol C_2H_2 (mol Pt)$^{-1}$ s^{-1}.

The study of the mechanism of catalytic reaction (I) will be continued in our laboratories.

REFERENCES

1. Krylov, O.V., Firsova, A.A., Bobyshev, A.A., *et al.*, *Catal. Today*, 1992, vol. 13, p. 381.
2. Dolgoplosk, E.A., Yakovlev, V.A., Tinyakova, E.I., *et al.*, *Izv. Akad. Nauk, Ser. Khim.*, 1996, no. 6, p. 1386.
3. Lin, G.I., Samokhin, P.V., Kaloshkin, S.D., *et al.*, *Kinet. Katal.*, 1998, vol. 39, no. 4, p. 624.
4. Subbotina, I.R., Shelimov, B.N., and Kazanskii, V.B., *Kinet. Katal.*, 1998, vol. 39, no. 1, p. 87.
5. Sil'chenko, L.A., Panova, S.A., Shestakov, G.K., and Temkin, O.N., *Kinet. Katal.*, 1997, vol. 38, no. 6, p. 861.
6. Mitchenko, S.A., *Kinet. Katal.*, 1998, vol. 39, no. 6, p. 936.
7. *Sintez kompleksnykh soedinenii metallov platinovoi gruppy: Spravochnik* (Synthesis of the Complex Compounds of Platinum Group Metals: A Handbook), Chernyaev, I.I., Ed., Moscow: Nauka, 1964.
8. Melander, L. and Saunders, W., *Reaction Rates of Isotopic Molecules*, New York: Wiley, 1980.
9. *Reaktsii alkanov s okislitelyami, metallokompleksami i radikalami v rastvorakh* (Reactions of Alkanes with Oxidants, Metal Complexes, and Radicals in Solutions), Rudakova, E.S., Ed., Kiev: Naukova Dumka, 1985.
10. Kukina, G.A., *Zh. Strukt. Khim.*, 1962, vol. 3, no. 1, p. 108.