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OLEFINS POLYMERIZATION ON TITANIA AND TITANIA-SUPPORTED RHODIUM

M.J. HOLGADO and V. RIVES *

Dpto. de Química Inorgánica, Universidad de Salamanca, Facultad de Farmacia, Av. Campo Charro, s/n, 37007-Salamanca, Spain

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The adsorption of ethene and propene on titania and titania-supported rhodium has been studied, observing a continuous adsorption even after 24 h. The samples have been reduced at 623 or 773 K, but no difference was observed, whichever the reduction temperature or the presence of rhodium, on the amount of gas adsorbed per unit of surface area of the solid. A study of the polymerization has been done following the "equal reactivity hypothesis", and it has been concluded that the role played by the rhodium particles is to facilitate adsorption of the gaseous molecule, that is then transfered to the surface of the support, where it polymerizes.

1. Introduction

Although formation of Ti^{3+} species has been claimed as one of the factors involved in developing of Strong Metal-Support Interactions (SMSI) when noble metals are supported on titania [1], very little attention has been paid to polymerization processes that may compete with hydrogenation of unsaturated hydrocarbons on these materials. We have recently reported [2] that upon adsorption at room temperature of ethene or propene on a Rh/TiO_2 catalyst, its reaction depends on the simultaneous presence of hydrogen: in the presence of hydrogen total hydrogenation to ethane or propane, respectively, takes place, while in the absence of this gas a polymerization reaction takes place. Such a polymerization process is here studied assuming a Flory mechanism.

2. Experimental

Preparation of the catalyst has been described elsewhere [3]. Briefly, it consists of Rh supported (2.5% w/w) on titania (P-25, from Degussa, ca. 50 m^2/g) and reduced in hydrogen (30 mL/min) at 473 K for 4 h and further reduced at 773 K for 2 h. Two samples were obtained by oxidation at 773 K for 2 h and further reduction in H_2 at 623 or 773 K (samples Rh-623 and Rh-773, respectively), in order to increase the developing of such SMSI. The metal dispersion values of the samples, as determined by hydrogen chemisorption, were 26% (sample Rh-623) and 13% (sample Rh-773), although these values may be affected by the presence of SMSI. A portion of the pure support was treated in the same conditions (TiO_2-623 and TiO_2-773, respectively). All gases were supplied by S.C.O. and had a nominal purity better than 99.95% and were used without any further purification. The adsorption measurements were carried out in a conventional high vacuum system, using a Baratron MKS pressure transducer to determine pressure changes, connected to a recorder from Konik, after reducing and outgassing the samples in situ at the same temperature used to prepare them (623 or 773 K). In order to avoid the adsorption of water vapour formed along the reduction process, a cold trap (77 K) was kept by the sample in order to condensate water, and was removed, after isolating the sample, before performing the adsorption experiments.

3. Results and discussion

When contacting the gas (ethene or propene) with the pretreated catalysts, a decrease in the gas pressure was observed, without reaching a constant value even after 24 hours, while in a sample reduced at 473 K instead of 623 or 773 K (where such SMSI seem to be absent) the equilibrium was reached after 20 min. As an example, fig. 1 shows the adsorption isotherms (room temperature) of ethene and propene on sample Rh-623. A similar behaviour was observed on all other samples, with a first, fast adsorption, followed by a second, slower process. It should be noted that when plotting this figure the corrections due to gas expansion at $t = 0$ have been already taken into account. The amount of gas adsorbed after 115 min are included in table 1 for all four samples (columns A). This contacting time has been taken arbitrary, but well after starting the experiment and when a steady slope has been reached. As shown in this table, the amount of gas adsorbed depends on the nature of the gas and the nature of the solid, but not on the reduction temperature. On the other hand, the amount adsorbed on a rhodium-containing samples is lower than on the unloaded support. However, if the amount of gas adsorbed is referred to a surface unit instead to a weight unit, i.e., molec/nm^2 instead of μmol/g (columns B in table 1), it is found that the amount of gas adsorbed is constant whichever the solid (unloaded titania or Rh/TiO_2) and the reduction temperature (673 or 773 K), depending only on the nature of the gas, and corresponds to 0.58 ± 0.04 molec C_2H_4/nm^2 and 1.20 ± 0.1 molec C_3H_6/nm^2. Moreover, the value for propene is roughly twice that for ethene. This difference may be related to the well known

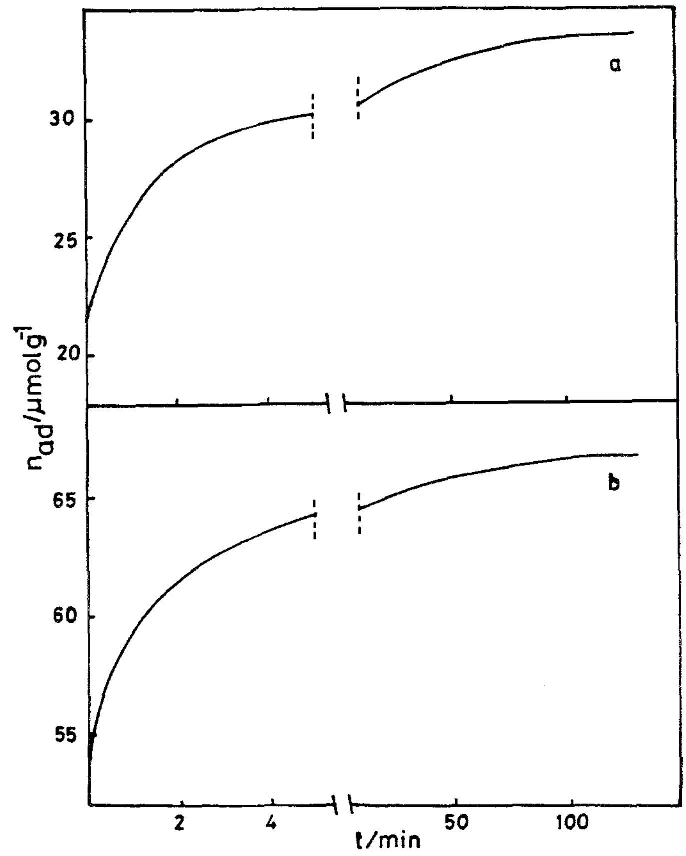

Fig. 1. Adsorption of ethene (a) and propene (b) on sample Rh-623.

larger reactivity of the secondary carbon atom in propene than that of primary carbon atoms in ethene.

Previous studies of the adsorption of ethene on these same samples [2] have shown that polymeric species are formed, and so the results above mentioned

Table 1
Specific surface area (BET) and data of adsorption of C_2H_4 and C_3H_6 on TiO_2 and Rh/TiO_2 samples

Sample	S_{BET} [a]	C_2H_4		C_3H_6		$B_{C_3H_6}/B_{C_2H_4}$
		A*	B**	A*	B**	
TiO_2-623	46.5	45	0.59	95	1.25	2.12
TiO_2-773	46.5	48	0.62	102	1.31	2.11
Rh-623	36.4	34	0.56	67	1.10	1.96
Rh-773	34.3	32	0.56	66	1.15	2.05
average	–	–	0.58	–	1.20	2.06

[a] m^2/g; * μmol/(g catalyst); ** molec/nm^2.

may be related to polymerization of ethene and propene on our catalysts. The study has been performed following the equal reactivity hypothesis by Flory [4], assuming that all radical species have the same reactivity, whichever the length of the chain.

If the monomer is designated by M and a radical by M*, the starting reaction

$$2\mathrm{M} \xrightarrow{k_i} 2\mathrm{M}^*$$

would be followed by a propagation reaction

$$\mathrm{M}^* + \mathrm{M} \xrightarrow{k_p} \mathrm{M}^*$$

ending with a termination reaction

$$\mathrm{M}^* + \mathrm{M}^* \xrightarrow{k_t} M_{xy}$$

the reaction rates for each one of these processes can be calculated as:

$$r_i = \mathrm{d}[\mathrm{M}^*]/\mathrm{d}t = k_i[\mathrm{M}]^2 \tag{1}$$

$$r_p = -\mathrm{d}[\mathrm{M}]/\mathrm{d}t = k_p[\mathrm{M}^*][\mathrm{M}] \tag{2}$$

$$r_t = -\mathrm{d}[\mathrm{M}^*]/\mathrm{d}t = k_t[\mathrm{M}^*]^2 \tag{3}$$

From eq. (1) and (3):

$$k_i[\mathrm{M}]^2 = k_t[\mathrm{M}^*]^2$$

i.e.,

$$[\mathrm{M}^*] = (k_i/k_t)^{1/2}[\mathrm{M}]$$

and by substitution in eq. (2):

$$r_p = k_p[\mathrm{M}^*][\mathrm{M}] = k_p(k_i/k_t)^{1/2}[\mathrm{M}]^2. \tag{4}$$

Following Flory, if the starting reactions are very less numerous than the propagation reactions, it can be assumed that the overall reaction rate equals the propagation rate:

$$r \approx r_p = k_p(k_i/k_t)^{1/2}[\mathrm{M}]^2 \tag{4}$$

that is,

$$r \approx K[\mathrm{M}]^2 \tag{6}$$

where

$$K = k_p(k_i/k_t)^{1/2}. \tag{7}$$

From eqs. (2), (5) and (6):

$$r = K[\mathrm{M}]^2 = -\mathrm{d}[\mathrm{M}]/\mathrm{d}t$$

$$-\mathrm{d}[\mathrm{M}]/[\mathrm{M}]^2 = K\,\mathrm{d}t \tag{8}$$

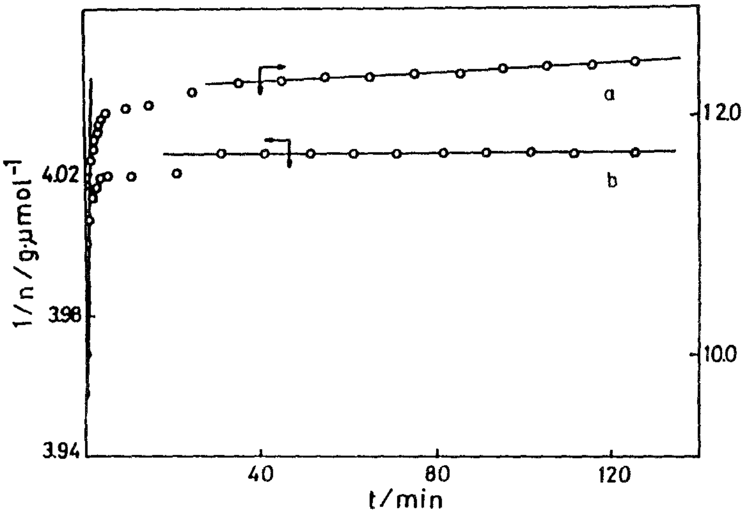

Fig. 2. Analysis of the adsorption of propene on samples Rh-623 (a) and TiO_2-623 (b).

and now integrating with [M] = [Mo] when $t = 0$ and [M] = [M] when $t = t$:

$$[M]^{-1} = Kt + [Mo]^{-1} \tag{9}$$

In our case, the fraction of unreacted monomer [M] can be taken as the mass of unadsorbed gas per unit (gram or square meter) of catalyst, a value easily calculated from the pressure and the volume of the adsorption chamber and the weight of catalyst. By plotting the reciprocal of this value against time, a straight line should be obtained, which slope will correspond to the overall polymerization constant, as defined by eq. (7) above.

Such a plot is included in fig. 2 for adsorption of propene on samples Rh-623 and TiO_2-623; similar plots were obtained for the other samples and gases. The experimental data can be fitted to two straight lines, one below $t \approx 1$–2 min (with rate constant $K1$), and the other between 20 and 115 min (rate constant $K2$). The values for the polymerization constants thereof calculated have been included in table 2. As it is obviously a surface process, the units for these constants are $(\text{molec})^{-1}$ $(\text{s})^{-1}$ nm^2.

Table 2
Polymerization constants for adsorption of C_2H_4 and C_3H_6 on TiO_2 and Rh/TiO_2 samples

Sample	C_2H_4		C_3H_6	
	$K1$ *	$K2$ *	$K1$ *	$K2$ *
TiO_2-623	$6.6 \cdot 10^{-5}$	$5.7 \cdot 10^{-7}$	$8.4 \cdot 10^{-5}$	$4.5 \cdot 10^{-11}$
TiO_2-773	$3.4 \cdot 10^{-5}$	$9.2 \cdot 10^{-7}$	$6.3 \cdot 10^{-5}$	$5.9 \cdot 10^{-11}$
Rh-623	$2.5 \cdot 10^{-4}$	$1.5 \cdot 10^{-6}$	$5.7 \cdot 10^{-4}$	$2.0 \cdot 10^{-6}$
Rh-773	$2.0 \cdot 10^{-4}$	$1.4 \cdot 10^{-6}$	$2.8 \cdot 10^{-4}$	$1.3 \cdot 10^{-6}$

* $(\text{molec})^{-1}$ $(\text{s})^{-1}$ $(\text{nm})^2$.

It can be observed that the $K1$ and $K2$ values for those samples containing rhodium are very close ($K1 \approx 10^{-4}$, $K2 \approx 10^{-6}$), whichever the reduction temperature, and $K1$ is two orders larger than $K2$. For unloaded titania, there exists nearly no difference between those data corresponding to samples reduced at 623 or 773 K, with $K1 \approx 10^{-5}$ and $K2 \approx 10^{-7}$ (for ethene) and 10^{-11} (for propene).

As the results obtained with the TiO_2 samples and those containing rhodium are so similar, and even coincident, at least according to the data included in table 1, this behavior should be related to the nature of the support, and not to the nature of the metal. It is well known that Ti^{3+} species are readily formed in titania upon outgassing at ≈ 600 K and above, and this effect is even more marked upon reduction with hydrogen [5], and these sites can be responsible for this polymerization. These Ti^{3+} sites are also formed on M/TiO_2 systems (M = Ru, Rh, Pd, Pt) [5], but it has been claimed that they are preferentially formed in the close vicinity of the rhodium particles [6], being, in some sort of way, the precursors of the "reduced support" migrating over the surface of the metal particles to develop the SMSI state. In such a case, despite the polymerization should take place on the reduced surface of the support, the role played by the rhodium particle would be to easy the adsorption of the gaseous molecule, that when would be "transfered" to the titania surface, where it would become polymerized. This effect seems to be more marked for propene adsorption, where $K2$ is four orders larger for samples containing rhodium than for unloaded titania. On the other hand, although the number of Ti^{3+} sites increases with the reduction temperature, the fact that the behaviour shown by these samples is the same, whichever the reduction temperature, indicates that the polymerization takes place on a very few number of sites, already existing after reduction at 623 K.

We have previously reported that these samples are active for ethene and propene hydrogenation even at room temperature [2]. This "bifunctional" behaviour (hydrogenation vs. polymerization) could be related to the presence of water vapour: if water vapour is present, the titanium ions could retain an octahedral coordination despite elimination of oxide ions from the lattice, thus making unneccesary the developing of shear planes; however, in the absence of water vapour, the formation of such distorted structure would be favoured to accomplish the octahedral coordination [7]. In order to pretreat the samples in conditions as similar as possible to those existing in our reaction system, a special care was taken to avoid the presence of water vapour during pretreatment of our samples. In addition, a portion of catalyst was pretreated in the adsorption chamber in the same conditions used to prepare it for ethene adsorption, but in this case a 1 : 1 mixture of ethene and hydrogen was admitted, and no pressure change was observed after two hours at room temperature, while in the absence of hydrogen, as mentioned above, a pressure decrease is immediately observed This result indicates that the final state of the catalyst in the reaction chamber and in the adsorption chamber is the same, if care is taken to eliminate water vapour, and thus the different behaviour observed, polymerization (pressure decrease) or hydrogenation (an ethene : hydrogen 1 : 1 mixture should not show any pressure change upon hydrogenation) depends only on the absence or presence of hydrogen.

Acknowledgments

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