Review Paper

Mechanism and kinetics of the selective hydrogenation of ethyne and ethene

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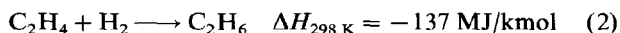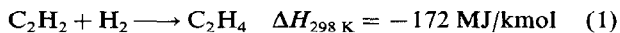
Abstract

A review of the kinetics and mechanism for the selective hydrogenation of ethyne and ethene on palladium catalysts is presented. The progress made in the last fifteen years is mainly discussed. It has become clear that the classical view, where the selectivity of the reaction was believed to be due to the thermodynamic factor is an over-simplification. Currently, it is generally assumed that at least two different sites are active during the selective hydrogenation, one of these might possibly involve the support. Ethene hydrogenation also occurs in the presence of high ethyne concentrations, which cannot be explained by the classical theory. Besides the two main hydrogenation reactions and the oligomerisation, there exists a direct route from ethyne to ethane, which, however, is only of minor importance. Possibly due to the rather complex nature of the system, there have been relatively few kinetic studies presenting practical rate expressions.

Introduction

In the manufacturing of polymer grade ethene, the removal of ethyne from the hydrocarbon mixtures obtained in cracking plants, is an important step. Typically, ethyne is present as approximately 1% in either complex gas mixtures containing 10–20% of hydrogen (front-end mixtures) or in essentially ethene and ethane only (tail-end mixtures).

An elegant and widely used method is the catalytic hydrogenation of ethyene. With regard to the ethyne hydrogenation, the process must be highly selective since the ethyne content has to be reduced to less than 5 ppm, while higher ethene losses are economically intolerable. Palladium based catalysts have proven to be capable of meeting these demands. The main reactions involved are:

$$C_2H_2 + H_2 \longrightarrow C_2H_4 \quad \Delta H_{298\,K} = -172 \text{ MJ/kmol} \quad (1)$$

$$C_2H_4 + H_2 \longrightarrow C_2H_6 \quad \Delta H_{298\,K} = -137 \text{ MJ/kmol} \quad (2)$$

Recent studies [1] have revealed that the direct hydrogenation of ethyne to ethane can also take place:

$$C_2H_2 + 2H_2 \longrightarrow C_2H_6 \quad \Delta H_{298\,K} = -309 \text{ MJ/kmol} \quad (3)$$

Besides these main reactions oligomerisation also occurs, yielding a complex mixture of C_4^+ compounds, commmonly named 'green oil'. In order to obtain a good selectivity and to reduce or prevent a net loss of ethene, small amounts of carbon monoxide are added to the feed gas.

Industrially this hydrogenation is usually carried out in adiabatic packed bed reactors. This reaction is accompanied by several chemical reaction engineering problems, in particular the phenomenon of thermal runaway, which is known to occur rather often in industrial practice. Here we present a brief literature review on the kinetics and catalytic aspects of the selective hydrogenation of ethyne/ethene on palladium based catalysts, that is Pd/Al$_2$O$_3$. First, we shall discuss the properties of palladium catalysts with respect to adsorption of hydrogen, ethyne and ethene on the metal surface. After a brief discussion on the oligomerisation, the literature on the mechanisms and kinetics of the hydrogenation reactions will be reviewed.

Properties of Pd/Al$_2$O$_3$ catalysts

For the selective hydrogenation of ethyne/ethene, low surface area alumina supports are mostly used, while the palladium content typically amounts to only 0.01–0.1% by weight. Industrially, for the selective hydrogenation

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reaction, egg shell type catalysts are often used to avoid the mass transfer resistances becoming important.

Adsorption/absorption of H_2 on Pd catalysts

It is generally accepted that hydrogen adsorbs dissociatively on palladium. Adsorption enthalpies have been reported in the range of 24–110 kJ/mol, dependent on many factors such as type of support, impurities, pre-treatment, see for example, refs. 2–4. Besides adsorption, absorption of hydrogen can also take place, in particular for unsupported palladium. Two different phases of palladium hydride can be formed: a hydrogen poor α-phase and a hydrogen rich β-phase. The role of the hydride formation in the hydrogenation has been discussed by a number of authors, but it is not clear whether it is important for industrially applied supported palladium catalysts, which usually have a very low Pd content, see for example refs. 5 and 6.

If formed, the β-phase has been shown to be more active, but less selective than the more common α-phase, see for example, ref. 7. The formation of the β-phase is suppressed by a high metal dispersion. The influence of the metal dispersion has recently been subject to some discussion and controversy, see for example, refs. 8–12. Although for certain catalysts and conditions the degree of metal dispersion has been found to be of crucial importance for the activity and selectivity, the results of both Sarkany *et al.* [8] and Aduriz *et al.* [10] seem to indicate only a limited influence of the metal dispersion for the conditions as found in industrial applications.

Adsorption of C_2H_2 and C_2H_4 on Pd catalysts

For the adsorption of ethene on Pd catalysts different types of adsorbed species have been proposed and both associative and dissociative adsorption can occur. A part of the adsorption was shown to be irreversible [13]. Dissociative adsorption of ethene might be responsible for a self hydrogenation of ethene: hydrogen atoms from dissociatively adsorbed ethene can react with associatively adsorbed ethene to form ethane. Figure 1 shows different forms of adsorbed ethene that have been shown to exist on Pd catalysts by means of spectroscopic techniques, see for example, refs. 11, 13 and 14. For ethyne also different forms of adsorbed species have been reported, see for example, refs. 11, 13 and 14 and these are shown in Fig. 2. Both associative
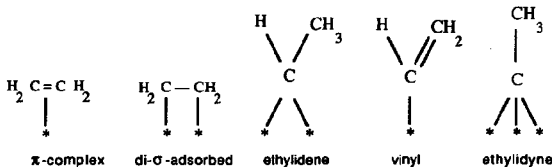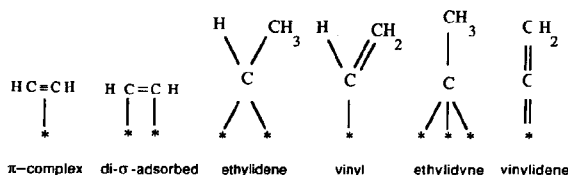

Fig. 2. Adsorption forms of ethyne on Pd.

and dissociative ethyne adsorption can occur. Most authors agree that a dissociative adsorption of ethyne is responsible for the oligomerisation.

Al-Ammar and Webb [15] reported having found an adsorbed species with an average composition C_2H_x for different types of catalysts, for example, $C_2H_{1.4}$ for palladium. They suggested an important role for this C_2H_x species in the hydrogenation reaction: it could act as a medium for hydrogen transfer between associatively adsorbed ethyne and a dissociatively adsorbed species. Evidence has been given that the adsorption of ethyne and ethene takes place in two stages; in the first stage an irreversible dissociative adsorption occurs, while in the second stage ethyne and ethene adsorb on this primary layer. Thus, the species that participate in the hydrogenation reaction might not be adsorbed directly on the metal, but on a carbonaceous overlayer, see for example, refs. 15–18.

It has been generally accepted that the adsorption of ethyne on Pd is much stronger than that of ethene, while ethane is adsorbed very weakly. This had led to the classical explanation for the selectivity of the ethyne/ethene hydrogenation, while in the absence of ethyne, ethene is hydrogenated readily on Pd. In this classical explanation, the selectivity was thought to be a consequence of the thermodynamic factor, see for example ref. 14, which says that due to the higher adsorption enthalpy of ethyne, the ratio of surface coverages of ethyne and ethene remains very high until ethyne is virtually no longer present. This could also explain the influence of CO, which is known to increase the overall selectivity: like ethyne, CO adsorbs stronger than ethene and also at low ethyne pressures the surface coverage of ethene remains low. Consequently, addition of CO improves the overall selectivity, because it prevents hydrogenation of ethene at low ethyne partial pressures. However, as will be discussed below, in the last few years it has become clear that these classical interpretations do not lead to a satisfactory explanation of all the phenomena.

Oligomerisation

During the hydrogenation of ethyne in ethene, oligomers and polymers are also formed, which is a

Fig. 1. Adsorption forms of ethene on Pd.

serious problem in industrial practice. These oligomers and polymers are commonly referred to as C_4^+ and the liquid part of C_4^+ is usually named 'green oil'. In the absence of ethyne no oligomers are formed. Further it is generally assumed that the C_4^+ fraction formed during the selective hydrogenation of ethyne in ethene originates solely from ethyne, see for example, refs. 18 and 19.

Sarkany et al. [8] investigated the formation of green-oil and they have determined by means of gas chromatography that most of the volatile part of the C_4^+ formed consisted of C_4 hydrocarbons, like butenes and iso-butene. The formation of the liquid compounds, which remained on the catalyst surface, corresponded in their experiments to at most 2% of the consumed C_2H_2. The presence of these heavy polymers on the catalyst surface was examined by means of thermographic analysis, TG, and differential scanning calorimetry. From the TG experiments it was concluded that the amounts of 'heavies' was 6–36 g per kg of catalyst.

Yayun et al. [20] reported on experiments performed in an industrial hydrogenation plant. They have studied the formation of polymers during hydrogenation with four types of Pd/Al_2O_3 catalysts, among others Girdler G58-B. Their results are summarized below.

— It has been demonstrated clearly that during ethyne hydrogenation the following are formed: a) gaseous light oligomers like C_4–C_6 olefines and, to a minor extent, di-olefines and paraffins, and b) liquid heavy polymers, with a mean composition $C_nH_{1.9n}$ where $n = 14$–17 and the olefine/paraffin ratio being 0.1–0.4. The olefines are mainly mono-olefines with internal double bonds, some di-olefines and no aromatics.

— Although at higher temperatures more C_4^+ are formed, the temperature is only of secondary importance for the oligomerisation.

— The formation of polymers is mainly controlled by the ratio H_2/C_2. In the range studied by them, $H_2/C_2 = 1.5$–4, increasing the ratio content inhibits the polymer formation.

With respect to this latter result, at H_2/C_2 ratios in the range of 3–7, other authors [21] have found no effect of this ratio on the formation of polymers. This has led Yayun et al. to the conclusion that in the lower ranges there must be another, still unknown effect, for no polymers are formed when hydrogen is absent. Therefore, dependent on the ratio H_2/C_2, the role of hydrogen may be either initiating or inhibiting.

Further, according to Yayun et al. [20], their experiments have shown that the oligomerisation of ethene cannot be ignored and they suggested that oligomerisation of ethene might be explained by assuming similar mechanisms for the hydrogenation of ethyne as that of ethene. However, their view constrasts with that of most other authors, who assume that oligomerisation occurs solely from ethyne, see for example, refs. 18 and 19.

Mechanisms

Recently, Nakatsuji et al. [22] presented a theoretical study and from their ab initio quantum-chemical calculations it followed that a Langmuir–Hinshelwood type mechanism is much more likely than an Eley–Rideal mechanism. They suggested a two-step mechanism with a vinyl radical as intermediate. They explained why C_2H_2 is selectively hydrogenated to C_2H_4 and not further to C_2H_6: according to them the ethene formed on the surface by ethyne hydrogenation is coplanar with the active sites, which favours the desorption and thus prevents further hydrogenation.

McGown et al. [5] studied the selective hydrogenation on Pd/Al_2O_3 at atmospheric pressure in a spinning basket reactor. CO was also present in their reaction mixtures, in concentrations in the order of 1000–5000 ppm. Some of their experiments were found to be influenced by pore diffusion limitations. In the absence of ethene in the feed gas and at low levels of ethyne concentration, the formation of ethane increased with increasing ethyne concentration. At higher levels of ethyne concentration, the formation of ethane became independent of both ethyne and ethene concentrations. A first order dependence on the hydrogen pressure was found. Mechanistically they suggested two types of active sites. The X type sites are mainly occupied by ethyne because on these sites the adsorption enthalpy of ethyne is much higher than that of ethene. On the Y type sites ethene is hydrogenated even in the presence of high ethyne gas phase concentrations. The influence of carbon monoxide on the selectivity towards the ethene formation was attributed to the competition of CO with ethene on the Y type sites. They also found that oligomerisation – according to them essentially the production of butenes from C_2H_2 – decreased at increasing concentration of CO, presumably caused by a decreasing availability of adsorbed H_2.

Around the same time, Al-Ammar and Webb published a series of papers [15–17], mainly involving silica supported Pd. On the basis of direct surface monitoring and ^{14}C labelling experiments, they proposed that three distinct sites are involved in the hydrogenation of ethyne/ethene. Ethene does not adsorb on the ethyne hydrogenation sites and, similar to the results of McGown et al. [5], ethene hydrogenation occurs even at high ethyne pressures. At low ethyne partial pressure the ethene hydrogenation rate increases, which – ac-

cording to Al-Ammar and Webb – is not due to higher ethene surface concentrations, but instead because of a higher availability of hydrogen. The influence of CO is also interpreted in terms of the competition of CO with hydrogen rather than with ethene.

Margitfalvi et al. [1] showed by means of ^{14}C labelling the existence of an additional, separate route from ethyne to ethane, acting parallel to the hydrogenation of ethyne to ethene. This so-called direct hydrogenation is thought to occur via the formation of a strongly adsorbed surface species, for example, ethylidyne. The formation of this species – and therefore also the direct hydrogenation – is thought to be favoured by low ethyne pressures and higher hydrogen pressures. This may explain the fall in selectivity towards ethene at low ethyne contents. The influence of carbon monoxide is then explained by assuming that CO chemisorption decreases the number of sites available for ethylidyne. It should be recalled that ethylidyne requires three neighbouring active sites. Thus, the addition of CO decreases the formation of ethane via the direct hydrogenation route and consequenty improves the selectivity towards ethene.

LeViness et al. [19] using supported Pd catalysts, some of them containing Cu, showed by ^{14}C labelling that the direct hydrogenation route does exist, and also that the intrinsic selectivity for ethyne hydrogenation to ethene is higher than 90%. Thus, ethane is formed mainly due to ethene co-hydrogenation.

Ethene hydrogenation always occurs, even at high ethyne concentrations. LeViness et al. suggested that at high ethyne partial pressures, ethene hydrogenation proceeds on the surface of the carrier material of catalyst, which is assumed to be covered almost exclusively by ethene. They proposed a kind of spill-over effect and hydrogen is thought to migrate to the carrier material through a surface polymer, present on both the metal and the carrier. At lower surface polymer concentration this migration is suppressed, so all factors that lower this polymer concentration consequently improve the selectivity. Two such factors are the insertion of Cu into the Pd matrix and the addition of CO to the reaction mixture, both of which decrease the surface polymer concentration by decreasing the dissociative adsorption of ethyne. Nevertheless, LeViness et al. assume that the influence of CO is mainly due to hydrogen displacement from the metal by CO; at lower hydrogen surface concentration, less hydrogen can migrate to the carrier and thus the rate of ethene hydrogenation is diminished. In effect, this explanation is quite similar to the two sites mechanism of for exmaple, McGown et al. [5], who assumed two types of sites. One of these types might thus involve the carrier.

Sarkany et al. [8] also showed the direct hydrogenation route to contribute only a few percent to the total ethyne hydrogenation and that the ethane formed is mainly the result of ethene hydrogenation. They give further evidence for the role of the metal polymer-support system in the co-hydrogenation of ethene, which can be suppressed by adding CO. As discussed the addition of CO reduces the coverage of H_2.

Battiston et al. [23] studied the selective hydrogenation of ethyne under industrial tail-end conditions. They mainly focussed on the aging phenomena, but also found considerable differences in activity and selectivity between different Pd catalysts. Their results seemed to indicate that the activation energies also differ significantly. This is in constrast with the work of Gigola et al. [9] who studied different Pd catalysts – and in particular particle size effects – and found apparent activation energies in the order of 65 kJ/mol for all catalysts, assuming first order H_2 and zeroth order hydrocarbon dependences. Battiston et al. concluded that the optimum operating conditions like for example, the CO level, the H_2/C_2H_2 ratio and the reaction temperature depend on the type of catalyst. As a general rule, they found that at higher temperatures ethyne conversion rates as a function of the CO content exhibited a maximum, while at lower temperatures they decreased with increasing CO content. Conform to all other studies, they also found the overall selectivity to increase with increasing CO concentration.

Mechanistic schemes incorporating different hydrogenation and oligomerisation routes have been proposed by Guczi et al. [24] and Margitfalvi et al. [1]. These schemes consist of: (1) the direct hydrogenation of ethyne to ethane via a strongly adsorbed species, e.g. ethylidyne, (2) the hydrogenation of ethyne to ethene via associatively adsorbed ethyne and (3) oligomerisation via a dissociatively adsorbed ethyne. In Fig. 3 the mechanism given in Margitfalvi et al. [1] is shown.
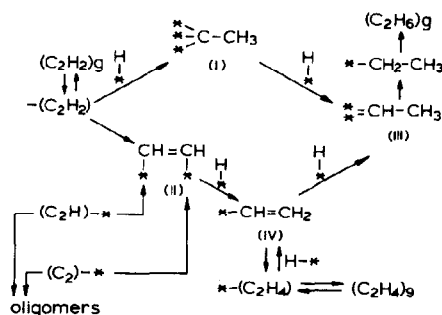

Fig. 3. Mechanism according to Margitfalvi et al. [1].

Kinetics

There have been only a few kinetic studies of the selective hydrogenation of ethyne/ethene that actually present kinetic expressions. The rather complex mechanisms discussed above, which are still partly speculative, are difficult to translate into practical rate expressions. Usually, authors report dependences on the hydrogen and hydrocarbon pressures in terms of simple nth orders. Mostly the first, and also the 0.5th and the 1.5th orders in hydrogen, zeroth orders in ethene and orders around zero or slightly negative for ethyne have been given. At low ethyne concentrations, first order behaviour in C_2H_2 has been found. Rate expressions with their corresponding parameter values have scarcely been presented.

Men'shchikov et al. [25] have performed a kinetic study of the hydrogenation of ethyne in the presence of ethene under industrially relevant conditions, using a 0.005 wt.% Pd/Al_2O_3 catalyst. They have found experimentally that – in contrast to what previous authors had reported – the rate of ethene hydrogenation is not influenced by the partial pressure of ethyne. They have considered two sets of equations, but only the two rate expressions given in Table 1, for reactions (1) and (2) respectively, could describe their experimental data quite well over the whole experimental range of $P = 2$ MPa, 0.8–0.0002% ethyne, 8–0.003% hydrogen, 0.02–1% ethane, 140 ppm carbon monoxide, the balance being ethene, and the temperature 353–433 K. To explain the absence of an influence of the ethyne pressure on the rate of ethene hydrogenation, they put forward that ethyne and ethene might adsorb on different types of actives sites – thus in agreement with the later work of McGown et al. [5] – and that the ethyne partial pressures applied were too low. We would like to point out that the presence of CO in their experiments might be of major importance, because if the adsorption of CO on certain type of sites is larger than that of ethyne, practically no effect of ethyne adsorption will be found. If these same sites are
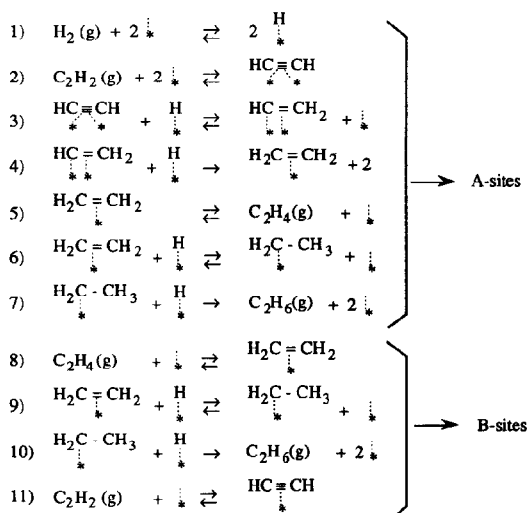

Fig. 4. Mechanism of Gva and Kho [26].

involved in the hydrogenation of ethene, the ethyne pressure will not influence ethene hydrogenation. Unfortunately Men'shchikov et al. [25] did not vary the CO content.

Gva and Kho [26] performed kinetic experiments in a recycle reactor at atmospheric pressure, temperatures between 30 and 70 °C and in the absence of carbon monoxide. They found the acetylene hydrogenation rate to be of first order in the hydrogen partial pressure over the whole temperature range. No such simple dependence for the net conversion rate to ethene and the rate of ethane formation was found. They assumed the simplified two-site mechanism shown in Fig. 4. Similar to the work of McGown et al. [5], in their proposed mechanism, ethyne adsorption on the A-type sites is much stronger than that of ethene, thus favouring the hydrogenation of ethyne to ethene. On the B-type sites ethene is hydrogenated even in the presence of ethyne. They estimated that the free energy of adsorption of ethyne and ethene on these B-type sites differ by only 4 kJ/mol, enabling competitive adsorption of ethyne and ethene on these sites. Note that the mechanism shown in Fig. 4 does not account for the direct hydrogenation of ethyne. After a number of assumptions they derived the following rate equations:

$$r_4 = k_4 \frac{K_1 K_2 K_3 P_{H_2} P_{C_2 H_2}}{K_2 P_{C_2 H_2} + K_5 P_{C_2 H_4}} \qquad r_7 = k_7 \frac{K_1 K_5 K_6 P_{H_2} P_{C_2 H_4}}{K_2 P_{C_2 H_2} + K_5 P_{C_2 H_4}}$$

$$r_{10} = k_{10} \frac{K_1 K_8 K_9 P_{H_2} P_{C_2 H_4}}{(K_8 P_{C_2 H_4} + K_{11} P_{C_2 H_2})^3}$$

$$R_{C_2 H_2} = r_4 \qquad -R_{C_2 H_4} = r_4 - (r_7 + r_{10})$$

$$-R_{C_2 H_6} = r_7 + r_{10}$$

TABLE 1. Kinetic rate expressions given by Men'shchikov et al. [25]

$$R_{C_2 H_2} = \frac{k_1 K_2 K_H P_{C_2 H_2} P_{H_2}}{(1 + K_2 P_{C_2 H_2})(1 + K_H P_{H_2})}$$

$$R_{C_2 H_6} = \frac{k_2 K_4 K_H P_{C_2 H_4} P_{H_2}}{(1 + K_4 P_{C_2 H_4})(1 + K_H P_{H_2})}$$

$k_1 = 0.29 \times 10^9 \exp(-7045/T)$ (kmol/s m³ catalyst)
$k_2 = 20.5 \times 10^9 \exp(-8050/T)$ (kmol/s m³ catalyst)
$K_2 = 0.2 \exp(1510/T)$ (kPa⁻¹)
$K_H = 0.13 \times 10^{-3} \exp(1860/T)$ (kPa⁻¹)
$K_4 = 0.54 \times 10^{-3} \exp(1810/T)$ (kPa⁻¹)

R_i being the net rate of conversion of component i and r_i the rate of a reaction step according to the mechanism proposed by Gva and Kho, shown in Fig. 4. K_i refers to the equilibrium of the ith step of this mechanism. Under special conditions, that is, for high enough ethyne partial pressures, $R_{C_2H_2}$ can be further simplified to yield simple first order dependences on hydrogen and zeroth order on hydrocarbon partial pressure. They fitted the above equations to their kinetic data with satisfactory results, but did not present the parameter values.

Conclusion

Considerable progress has been made in the last years, in particular about the nature of the adsorbed species and the main reaction routes. These results have been obtained by modern spectroscopic techniques and labelling methods. The classical view, explaining the selectivity in terms of the thermodynamic factor, has been replaced by mechanistic explanations involving more than one site and several intermediate surface species. The influence of carbon monoxide, on which little quantitative information is known, is now usually explained in terms of competitive adsorption with hydrogen, rather than ethene in the classical view. Comprehensive mechanistic schemes have been proposed, although many details of the reaction mechanisms are still speculative. Possibly due to the rather high complexity of even the very simple mechanistic schemes, only a few practical kinetic rate expressions have been presented. Indeed, it seems to be optimistic to expect that simple – but still appropriate over a wide range of operating conditions – explicit rate expressions can be derived from the more recently proposed mechanisms for the selective hydrogenation. We doubt that such expressions are able to reflect with high accuracy the complex processes that have been shown to occur on the catalyst surface during the selective hydrogenation on Pd catalysts.

Acknowledgements

Nomenclature

ΔH reaction enthalpy, kJ/kmol
K_i kinetic parameter, kPa^{-1}
k kinetic rate constant, kmol/s m^3 cat.
P pressure, kPa
P_i partial pressure of component i, kPa^{-1}
R_i rate of conversion of component i, kmol/s m^3 cat.
r_i rate of reaction step i, kmol/s m^3 cat.
T temperature, K

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