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Low temperature oxidative dehydrogenation of ethane over Ni-based catalysts

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In contrast to supported palladium, nickel-based catalysts give interesting results in the oxidative dehydrogenation of ethane. Unsupported nickel catalysts are active at temperatures as low as 490 K. Reduced nickel particles are present during the reaction.

Keywords: Nickel; palladium; oxidative dehydrogenation; ethane; ethylene

1. Introduction

Ethylene is produced mainly by means of gas-phase reactions, such as the steam cracking of naphtha and the cracking of ethane. This latter reaction is highly endothermic and has to be carried out at high temperature in order to obtain an acceptable conversion (typically 60% per pass at 1100 K). Research into reactions aimed at transforming ethane into ethylene at low temperature with high selectivity is desirable: in this respect, the design of low temperature catalysts selective towards ethylene in the oxidative dehydrogenation of ethane (ODHE) is of special interest.

Another interest of the low temperature ODHE is related to the oxidative coupling of methane (OCM), which produces primarily ethane. Ethane is subsequently converted into ethylene, the desired product. The OCM reaction occurs generally at high temperatures, in conditions where gas-phases reactions play an important role and where selectivities are much less controllable than in a purely catalytic regime. Attempts at carrying out this reaction at lower temperatures have been made, and some significant results were obtained with palladium-based catalysts [1–3] at 600 K. Yields, however, never exceeded 0.35%. Furthermore, ethane was almost exclusively formed, raising the question of its possible transformation into ethylene at low temperature.

In this work we examine to what extent the palladium- and nickel-based catalysts, studied elsewhere in OCM reaction [3], are capable of catalysing the ODHE reaction at low temperatures.

2. Experimental

Catalyst preparation is partly described elsewhere [2]. Pd/SiO_2 (1.5 wt%) is obtained by reacting SiO_2 (Degussa) with a solution of $Pd(NH_3)_4(OH)_2$. Pd/MgO (2 wt%) is prepared by reacting MgO (Aldrich) with a solution of acetylacetonate of palladium in toluene. After centrifugation and washing, these precursors are dried and calcined at 673 K. NaCl is added to Pd/SiO_2 by impregnation and evaporation; the Pd/Na mole ratio is equal to unity. All Pd-based catalysts are pretreated under an oxygen flow at 773 K. Ni/SiO_2 (4.27 wt%) is obtained by reacting SiO_2 (Degussa) with a solution of nickel hexammine nitrate as described elsewhere [4]. K–Ni/SiO_2 (4.08 wt% Ni and 2.05 wt% K) is obtained by impregnating the Ni/SiO_2 precursor with a KNO_3 solution and K/SiO_2 (1.48 wt%) using the same procedure starting from pure SiO_2. Supported catalysts are pretreated under a helium flow at 700 K. Unsupported $Ni(OH)_2$ catalysts are prepared by removing ammonia at 300 K from a solution of nickel nitrate hexammine [5]. The initial BET surface area is 180 m^2/g. Unsupported nickel catalysts are pretreated under a helium flow at 573 K. Reactors consist of quartz tubes, Di = 4 mm; catalyst powders (0.1 g, unless otherwise stated) are held by quartz wool. The partial pressures in the reacting mixture (total gas flow 3.6 h^{-1}) are 8, 3.1 and 90.2 kPa for ethane, oxygen and helium, respectively. Blank experiments in an empty clean reactor have shown that the gas phase reaction starts at 950 K (conversion 0.3%). The temperature of the catalytic system is raised linearly to the desired temperature at 1 K min^{-1} heating rate. Then, catalytic measurements are performed and the system heated again. In some cases, aging experiments are carried out for a few hours to check the stability of the solid.

3. Results and discussion

Over palladium-based catalysts, CO_2 is the main reaction product. Some CO is observed at temperatures above ca. 700 K. The selectivity towards CH_4 does not exceed 0.1%. Addition of NaCl, a flame retardant which has been shown to inhibit the gas phase oxidation of ethylene into carbon oxides [6], does not result in a significant improvement of catalytic performance (table 1). The nature of catalyst pretreatment does not change to a large extent catalytic behaviour.

The ethylene yield obtained in the ODHE is of the same order of magnitude as that obtained for ethane in the OCM over Pd-based catalysts (table 1). Surprisingly, Ni/SiO_2 solids, which are less selective towards C_2 hydrocarbons than Pd/SiO_2 in the OCM reaction are very selective in the ODHE: selectivities towards

Table 1
Catalytic properties of catalysts in oxidative dehydrogenation of ethane

Catalyst	Temperature of reaction (K)	Conversion (%)	Selectivity toward ethylene (%)
Pd/SiO_2	573	7.2	5
	723	7.1	12
Pd/MgO	573	7.4	1
	723	13	2.5
$NaCl-Pd/SiO_2$	573	0.64	22
	673	11	3.5
	673[a]	13.6	2.8
	673[b]	13.5	3.7
Ni/SiO_2	673	1.3	82
	723	4	80

[a] Catalyst prereduced with ethane.
[b] No pretreatment.

ethylene as high as 80% are obtained at 723 K. It decreases somewhat as temperature increases as shown in fig. 1; besides ethylene, CO_2, CH_4 and CO are also observed (selectivities vary from 20 to 14, 1 to 3 and 0 to 8%, respectively, when T increases from 700 to 900 K). Small amounts of C_3 hydrocarbons are also detected (0.3%). The influence of potassium addition to Ni/SiO_2 catalysts was put to the test. Fig. 2 shows that for $K-Ni/SiO_2$ catalysts the selectivity towards ethylene is

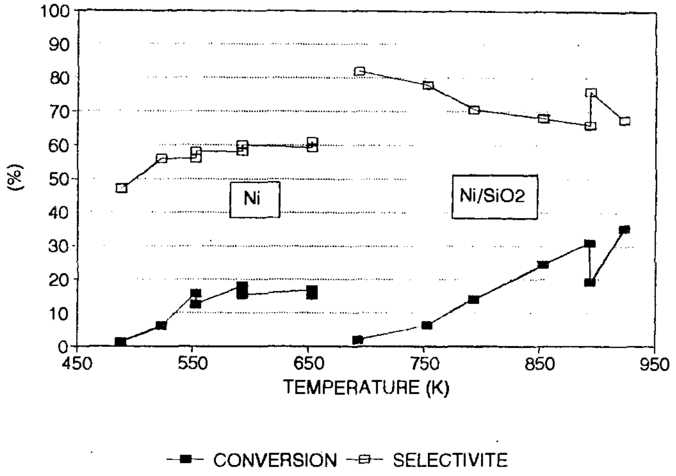

Fig. 1. Conversion (black squares) and selectivity towards ethylene (open squares) over (0.1 g of unsupported and silica-supported nickel. Points at 550, 590 and 895 K correspond to 3, 1 and 5 h aging, respectively.

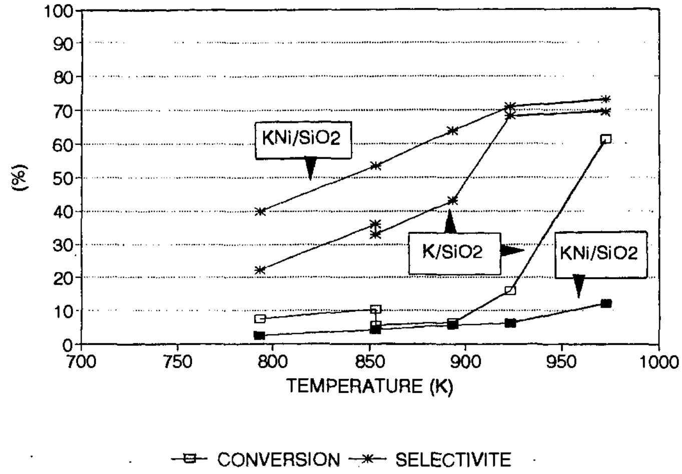

Fig. 2. Conversion (squares) and selectivity (stars) towards ethylene over 0.1 g of K–Ni/SiO_2 and Ni/SiO_2 as a function of reaction temperature; the point at 850 K corresponds to a 1 h aging.

small at 773 K, while it increases at increasing temperatures. This behaviour is in contrast to that achieved by Ni/SiO_2 catalyst where the reverse situation occurs, and is reminiscent of that of Li/MgO catalysts [7,8]. K/SiO_2 catalysts yield the same behaviour as K–Ni/SiO_2, suggesting that in the latter catalyst, Ni does not participate to a large extent in the reaction; it can be inferred from this observation that the potassium-containing phase in K–Ni/SiO_2 decorates more or less completely the nickel surface, preventing contact with the gas phase. This hypothesis is consistent with conclusions drawn from a study of gas chemisorption over similar catalysts [9]. It is worth noting that K–Ni/SiO_2 and K/SiO_2 in contrast to Ni/SiO_2 do not produce any CO at $T < 900$ K. This could result from an inhibition by potassium compounds [6] of the gas-phase oxidation of hydrocarbons which leads to CO [9]. Furthermore, methane which is observed on Ni/SiO_2 and K/SiO_2 (a few percents) is not detected over K–Ni/SiO_2, for still unclear reasons.

The particular behaviour demonstrated by Ni/SiO_2 led us to assess the specific role of nickel and to examine catalytic properties of unsupported nickel powders. The results are shown in fig. 1 where they can be compared with the results obtained with supported nickel. As can be seen, both catalysts show similar features: the selectivity towards ethylene is relatively large at low temperature and is almost unchanged at increasing temperature. At temperature in excess of 550 K, aging occurs for unsupported catalysts. At lower temperature, however, the stability is sufficient to estimate approximately the apparent activation energy, $E_a = 75$ kJ mol^{-1}. This value is comparable to that calculated for Ni/SiO_2, 86 kJ mol^{-1} suggesting as a first step similar active sites and reaction mechanism. Reaction starts over unsupported catalysts at low temperature, 490 K, and a 10% conversion is achieved at 540 K, making unsupported nickel one of the most active low temperature ODHE catalysts (comparable temperatures are reported for Nb-promoted Mo–V–O catalysts [10,11]).

The question of the chemical state of unsupported nickel during reaction was addressed, and some magnetic measurements aimed at detecting ferromagnetic nickel were carried out. After reaction at 600 K and cooling at room temperature in the reacting mixture, the powder was transferred in a sample holder in air. The extent of reduction into metallic nickel is found to be equal to 19%, indicating that in reaction conditions metal particles of nickel are present. Further experiments are under way from which more information on the nature of active sites is expected.

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