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Preparation of bifunctional catalysts by solid-state ion exchange in zeolites

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Bifunctional catalysts containing an acidic as well as a hydrogenation/dehydrogenation function were prepared by solid-state ion exchange. Preparation and properties of Pd-loaded H-ZSM-5 are described in detail. The catalytic behavior of the reduced catalysts was investigated using hydrogenation and hydroisomerisation of ethylbenzene as a test reaction. The catalytic performance of the catalysts could be significantly improved by concomitant incorporation of Ca^{2+}. This was advantageously achieved in a two-step procedure, where first a solid-state ion exchange with $CaCl_2$ and subsequently a second solid-state ion exchange with $PdCl_2$ was carried out. A Ca, H-ZSM-5 with 1.5 wt-% Pd obtained via this two-step procedure and subsequent reduction in H_2 exhibited high activity, long life-time and good selectivity with respect to hydrogenation and hydroisomerisation of ethylbenzene to ethylcyclohexane and dimethylcyclohexanes, respectively. Electron micrographs of the reduced catalyst showed finely dispersed palladium with maximum size of about 2.0 nm.

Keywords: Catalysis; zeolites; palladium; ion exchange; solid-state; hydrogenation; hydroisomerisation; ethylbenzene

1. Introduction

Zeolites loaded with noble-metals play an important role in catalysis of hydrogenation, hydrocracking and hydroisomerisation reactions [1–3]. The metal component can be introduced in many ways, for instance during the synthesis of the zeolite or by decomposition of volatile metal compounds such as carbonyls on the (internal and external) zeolite surface. The most frequently used procedures of introducing the noble metal into the zeolite structure, however, are the conventional ion exchange (IE) in a solution of the in-going noble-metal ion (see e.g. ref. [4]) or the technique of incipient wetness impregnation (IWI) [5,6]. Zero-valent noble-metal particles may be obtained by subsequent reduction in,

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for instance, a stream of hydrogen at elevated temperatures. This, however, simultaneously generates bridging acidic OH groups, so-called Brønsted acid sites [7]. Therefore, a bifunctional catalyst with a hydrogenation/dehydrogenation as well as an acidic function is obtained even in those cases where the original zeolite, e.g. NaY, did not contain any protonic centers [3]. Location, sizes and size distribution of the noble-metal particles formed via this route significantly depend on (i) the zeolite structure and chemistry [3] and (ii) the treatment prior to and during reduction [8]. A number of studies have shown that cations may be introduced into zeolites also via solid-state ion exchange (SSIE) [9–13]. Moreover, it has been demonstrated that SSIE is a promising way to prepare acidic zeolite catalysts [14–16] or, with transition metals, redox zeolite catalysts [17]. The aim of the present paper is to investigate whether or not SSIE is also a possible route to zeolite-based, noble-metal-containing hydrogenation/dehydrogenation and bifunctional catalysts and their modification.

2. Experimental section

The starting zeolite, H-ZSM-5, was provided by Degussa, Wolfgang, FRG under the label CAZ 36. Its (idealized) composition was $H_{2.43}Na_{0.12}Fe_{0.11}Al_{2.77}Si_{93.23}O_{192}$. A detailed description of the properties of this material was given elsewhere [18]. All the other chemicals used ($PdCl_2$, $CaCl_2$, NH_4Cl, ethylbenzene) were analytical grade and purchased from Merck, Darmstadt, FRG. Solid-state ion exchange was carried out by intimately grinding the dried zeolite powder and the respective salts, followed by heating ($5\ K \cdot min^{-1}$) to 675 K and treatment at this temperature for 2 h in high vacuum (10^{-5} Pa). In order to check the crystallinity of the zeolite samples after SSIE, five-times-repeated conventional ion exchange was carried out in a solution of 1 N NH_4Cl at 335 K. The degree of NH_4^+ re-exchange was determined through titration of the NH_3 evolved upon heating in a stream of N_2 using the method of Kjeldahl. In several cases, the integrity of the crystal lattice was also scrutinized by XRD.

IR spectra were obtained with Perkin Elmer grating spectrometers (Models 225 or 325); cells and procedures have been described previously [19,20]. Electron micrographs (TEM) were obtained by a Siemens EM 102 electron microscope. Conversion of ethylbenzene was used as a convenient test reaction as described in earlier publications [14,21].

3. Results and discussion

After careful mixing and heat-treatment of the $PdCl_2$/H-ZSM-5 mixture ($Pd/Al = 0.5$) in high vacuum the in situ IR spectrum of the sample proved that

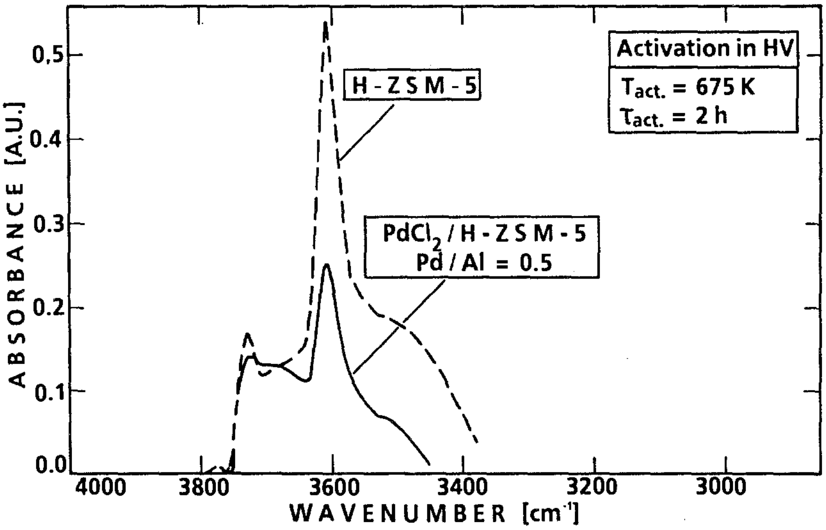

Fig. 1. IR spectra of H-ZSM-5 and a mixture of $PdCl_2$/H-ZSM-5 after solid-state ion exchange (2 h) in high vacuum at 675 K.

55% of the original content of acidic OH groups were consumed by solid-state reaction (see fig. 1). Evolution of HCl was monitored by MS. In a separate experiment, the heat treatment of the zeolite/salt mixture was carried out in a flow of dry N_2 and the evolved HCl trapped in a 0.1 N solution of NaOH. Back-titration showed that the equivalent amount of acidic OH groups had reacted.

Catalytic tests with ethylbenzene were carried out with a mixture of $PdCl_2$ and H-ZSM-5 after in situ heat-pretreatment ($5\ K \cdot min^{-1}$, 675 K, 2 h, high vacuum) and reduction (575 K, H_2 stream, $60\ ml \cdot min^{-1}$) in a micro flow reactor [21]. Results are shown in fig. 2. One recognizes that the activity of the catalyst rapidly decreased. Moreover, the main products were light paraffins, benzene (B) and diethylbenzenes (DEB). Only minor fractions of ethylcyclohexane (ECH*x*) and dimethylcyclohexanes (DMCH*x*) were detected.

These results seem to indicate that (i) the acidic and hydrogenation functions were not properly balanced and (ii) larger palladium particles had formed. The strong acidity caused partial dealkylation of ethylbenzene with subsequent polymerisation and coke formation; the large particles of palladium preferentially catalysed hydrogenolysis of the hydrocarbons, yielding C_1-C_5 paraffins. Therefore, efforts were made to improve the balance between the acidic and hydrogenation function of the catalyst. In a previous study it has been shown that the solid-state reaction between hydrogen mordenite and alkaline earth halides reduced the acidity of the zeolite [12]. Therefore, in a first stage, SSIE between $CaCl_2$ and H-ZSM-5 was carried out. The amounts of $CaCl_2$ employed corresponded to 30, 60 and 90% of the OH groups of the starting zeolite. The

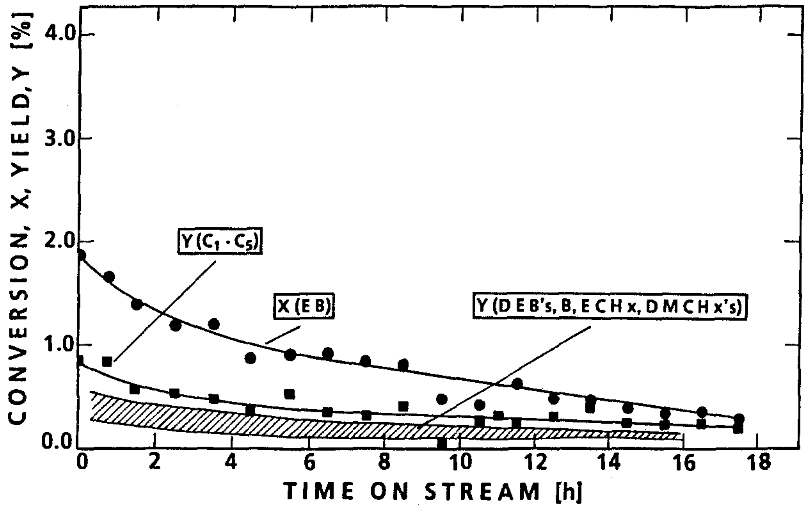

Fig. 2. Conversion of ethylbenzene at 475 K over a Pd/H-ZSM-5 (0.5 wt% Pd) catalyst obtained via solid-state ion exchange (2 h) between $PdCl_2$ and H-ZSM-5 at 675 K in high vacuum and subsequent reduction (3 h) in H_2 (60 ml·min^{-1}); m_{cat}: 0.25 g feed: EB (1.5 vol%), H_2 (30 vol%) in He, 30 ml·min^{-1}.

number of the acid sites of the exchange product was characterised by IR, NH_3 adsorption measurements, as well as by the selective conversion of ethylbenzene to benzene and diethylbenzene (compare refs. [21,22]), whereas the strength of the acidic sites was determined via TPD of ammonia [23] and microcalorimetry [24]. From the results in table 1 it can be derived that the solid-state ion exchange with $CaCl_2$ indeed reduced the amount but essentially left unaffected

Table 1
Acidic properties of H-ZSM-5 and $CaCl_2$/H-ZSM-5 after solid-state ion exchange

Sample *	(a) A(OH) [a.u.]	(b) X(EB) [%]	(c) $Q_{diff.}$ [kJ·mol^{-1}]	(d) NH_3 (ads.) [molec./u.c.]	(e) T_{max} [K]
H-ZSM-5	0.4	4.00	150.1	1.7	585
H-ZSM-5 +30% $CaCl_2$	0.3	2.70	150.1	1.3	610
H-ZSM-5 +60% $CaCl_2$	0.3	2.60	149.0	1.3	600
H-ZSM-5 +90% $CaCl_2$	0.3	2.55	149.0	1.3	600

* The percentage of $CaCl_2$ admixed refers to the maximum amount of OH groups which could be exchanged by solid-state reaction.
(a) Absorbance of the 3605 cm^{-1} band.
(b) Selective steady-state conversion of ethylbenzene to B and DEBs (1:1) at 495 K.
(c) differential heat of adsorption of NH_3 measured with a Calvet calorimeter [24].
(d) NH_3 molecules per u.c. adsorbed on strong Brønsted sites (with $Q_{diff} > 100$ kJ·mol^{-1}).
(e) Temperature of the TPD peak corresponding to NH_3 desorbing from strong Brønsted sites.

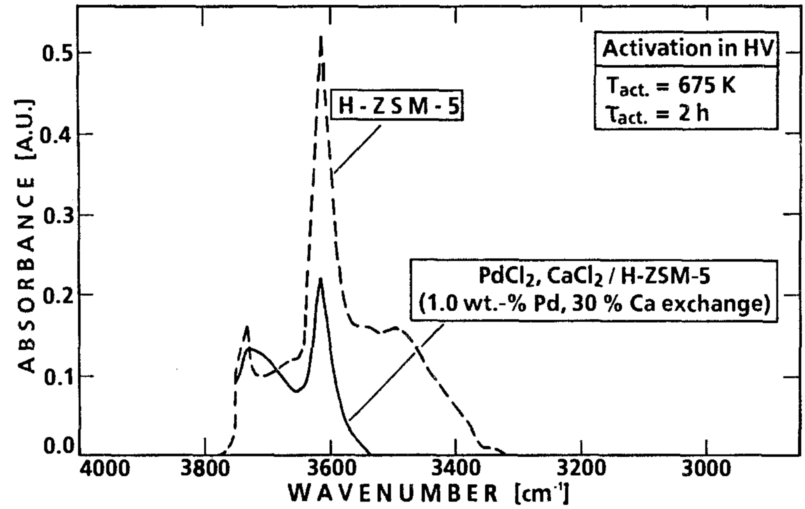

Fig. 3. IR spectra of H-ZSM-5 and a mixture of $CaCl_2$ and $PdCl_2$ with H-ZSM-5 after solid-state ion exchange (2 h) at 675 K in high vacuum.

the strength of the zeolite acidity. According to TPD, the strength was only slightly increased by SSIE with $CaCl_2$. The reduction of the number of strong Brønsted sites is significant with the 30% $CaCl_2$/H-ZSM-5 with respect to the parent sample. Further addition of $CaCl_2$ did not bring about another marked change. Obviously, solid-state ion exchange of $CaCl_2$ with the highly siliceous H-ZSM-5 was limited by the geometric difficulties in balancing fairly distant lattice charges by a bivalent cation [25]. Furthermore, the product of the solid-state ion exchange between $CaCl_2$ and H-ZSM-5 was investigated by XRD and conventional back-exchange with NH_4Cl solution. Both methods confirmed that the crystallinity of the zeolite has not been affected by the solid-state reaction releasing HCl. The exchange capacity of the solid-state ion-exchanged sample was exactly the same as that of the parent zeolite (0.36 mmol NH_4^+ per gram).

Since the reaction with $CaCl_2$ in fact reduced the acidity of H-ZSM-5, experiments with *simultaneous* solid-state incorporation of both Ca^{2+} and Pd^{2+} ions into H-ZSM-5 were undertaken, in order to prepare, via subsequent reduction with H_2, improved bifunctional catalysts.

The decrease in the density of acid sites upon simultaneous incorporation of Ca^{2+} and Pd^{2+} into the H-ZSM-5 structure is demonstrated by fig. 3. If necessary, e.g. for preparation of monofunctional hydrogenation/dehydrogenation zeolite catalysts, the remaining acidity as well as the acidity newly generated during reduction of the noble (or transition) metal could be eliminated by a further solid-state reaction with, for instance, alkaline compounds.

Indeed, Pd/Ca, H-ZSM-5 catalysts with 1.0 wt-% Pd prepared via simultaneous SSIE with $CaCl_2$ and $PdCl_2$ exhibited significantly higher activity, lower

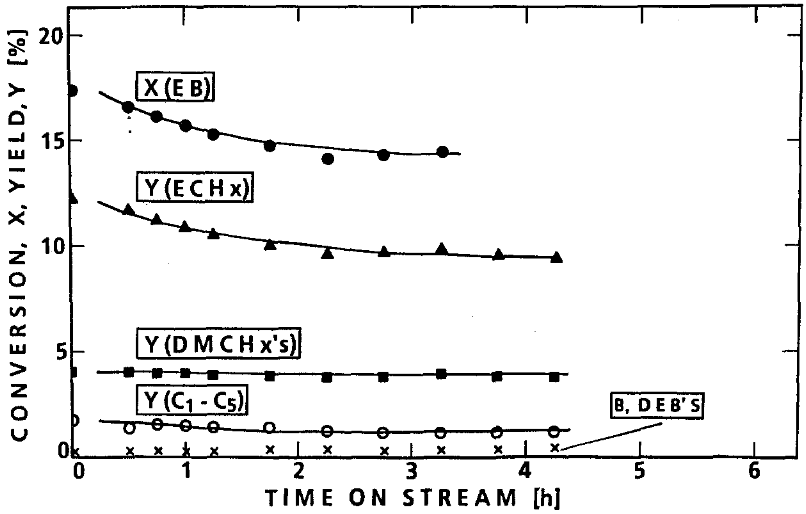

Fig. 4. Conversion of ethylbenzene at 475 K over a Pd/Ca, H-ZSM-5 (1.5 wt% Pd) catalyst obtained via solid-state ion exchange (2 h) of $CaCl_2$ (introduced in the first step) and $PdCl_2$ (second step) with H-ZSM-5 at 675 K in high vacuum and subsequent reduction (3 h) in H_2 (60 $ml \cdot min^{-1}$); admixed $CaCl_2$ was equivalent to 30% of the acidic OH groups of the parent zeolite; m_{cat}: 025 g; feed: EB (1.5 vol%); H_2 (30 vol%) in He, 30 $ml \cdot min^{-1}$.

propensity to deactivation (coke formation) and enhanced selectivity to products of hydrogenation (ECH*x*) and hydroisomerisation (DMCH*x*). However, it turned out that the catalytic behavior of the Pd/Ca, H-ZSM-5 catalysts was further improved if they were prepared via a two-step procedure, i.e. by incorporation of Ca^{2+} in a first and Pd^{2+} in a subsequent solid-state reaction. An example of catalytic performance of Pd (1.5 wt%)/Ca (30%), H-ZSM-5 in ethylbenzene conversion in the presence of hydrogen is shown in fig. 4. The overall activity is remarkably high and the main products are ECH*x* and DMCH*x*, whereas the hydrogenolysis is low and disproportionation of ethylbenzene almost completely suppressed (compare with fig. 2). It is assumed that the introduction of Ca^{2+} preceding the solid-state ion exchange with $PdCl_2$ not only affected the acidity but also facilitated the generation of a more homogeneous distribution of small palladium aggregates upon subsequent reduction by H_2. Indeed, electron micrographs seem to indicate well dispersed relatively small Pd particles (fig. 5). In fact, the size of the larger particles (1.4 nm) shown in the micrograph exceeds the diameter of the channel intersections of ZSM-5 (about 9 Å). Therefore, further investigations are required to more precisely localize the metal aggregates. However, as has been shown in many studies by Jaeger and Schulz-Ekloff (see, e.g., ref. [26]), it is very likely that metal particles bigger than intracrystalline zeolite cavities may form inside the zeolite matrix.

Results similar to those reported here on the solid-state ion exchange between $PdCl_2$ and H-ZSM-5 were obtained with PdO/H-ZSM-5, $PdCl_2/NH_4$-Y, $Pd(NO_3)_2/NH_4$-Y, $PtCl_2/NH_4$-Y and $PtCl_4/NH_4$-Y.

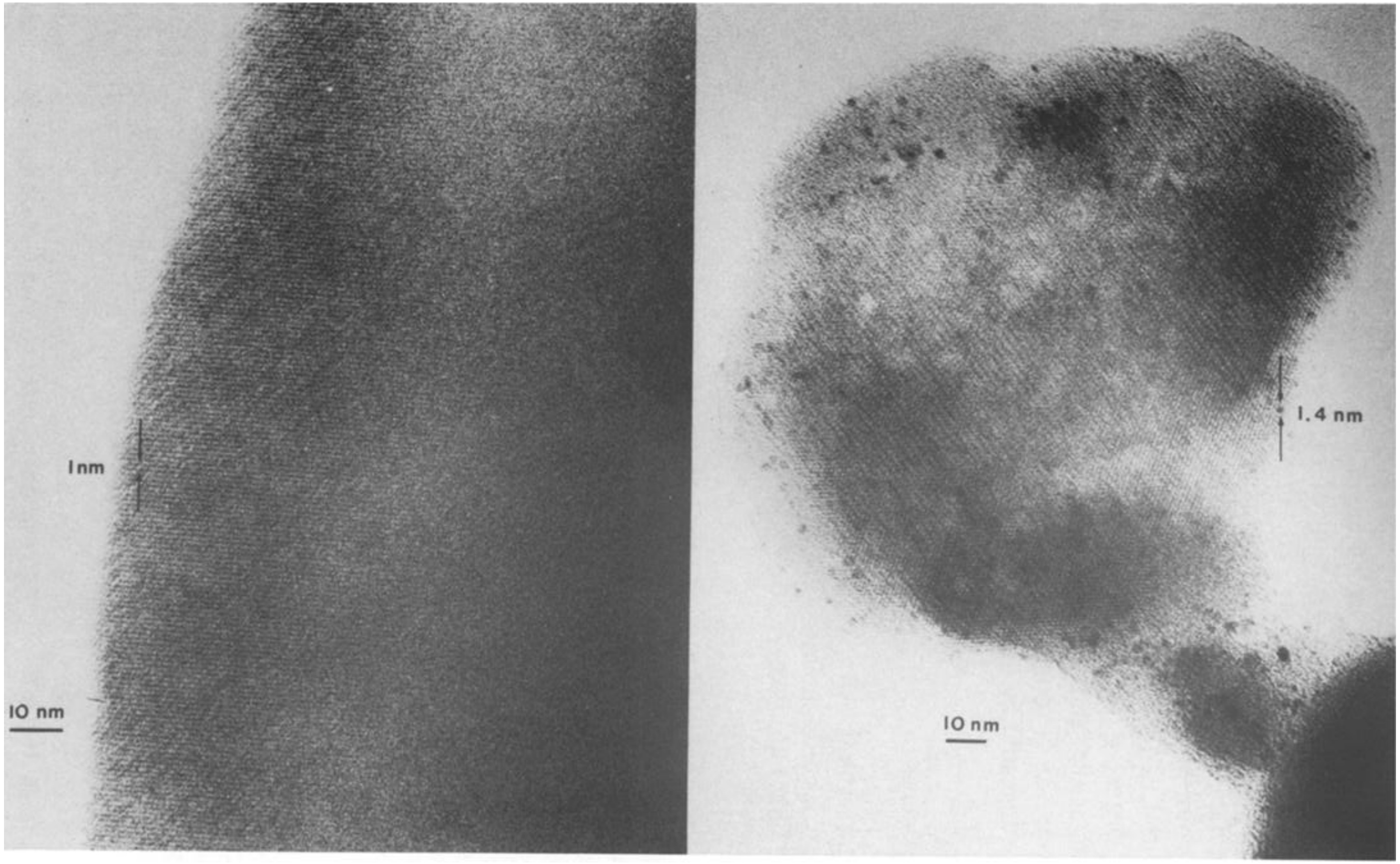

Fig. 5. Electronmicrograph of H-ZSM-5 (left) and a reduced Pd/Ca, H-ZSM-5 (1.5 wt% Pd) catalyst (right) as employed for the experiment of fig. 4; total magnification, left part: 715000: 1, right part: 520000: 1

4. Conclusions

Noble-metal cations, e.g. Pd^{2+}, can be introduced into zeolites such as H-ZSM-5 via solid-state ion exchange where, by contrast to the conventional procedure (ion exchange in solution or by the incipient wetness method), no water is present. Reduction by H_2 of the metal-loaded zeolites, which are obtained via solid-state reaction, yields active bifunctional catalysts. Their catalytic properties, i.e. activity, life-time and selectivity can be significantly improved by simultaneous or, more advantageously, by preceding solid-state ion exchange with $CaCl_2$. This affects the density but essentially not the strength of the strong Brønsted sites. Incorporation of Ca^{2+} provides a better balance between the acidic and the hydrogenation/dehydrogenation function of the catalyst. Moreover, it most likely improves also the dispersion of the palladium particles as suggested by electron micrographs.

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