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Palladium–Copper-exchanged Y Type Zeolites: A True Heterogeneous Wacker Catalyst

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Evidence is presented that faujasite-type zeolites with specific Si : Al framework ratios exchanged with $Pd(NH_3)_4^{2+}$ and Cu^{2+}, catalyse the oxidation of ethylene into acetaldehyde, in exactly the same way as the homogeneous Wacker system [Pd^{II} and Cu^{II} in concentrated chloride solution]; the active centre is found to be a partially ammoniated Pd^{II} ion, most probably $Pd^{II}(NH_3)_2$, which itself belongs to an electron transfer chain consisting of the alkene reagent, the faujasite encaged Pd^{II}/Pd^0 and Cu^{II}/Cu^I redox couples and dioxygen.

The industrial direct catalytic oxidation of ethylene with dioxygen towards acetaldehyde was first reported by Smidt.[1] This reaction, actually known as Wacker or Wacker–Hoechst process, consists of three distinct steps, as shown in eqns. (1)–(3).

$$C_2H_4 + PdCl_4^{2-} + H_2O \rightarrow MeCHO + Pd + 2\,H^+ + 4\,Cl^- \quad (1)$$

$$Pd + 2\,Cu^{2+} + 8\,Cl^- \rightarrow PdCl_4^{2-} + 2\,CuCl_2^- \quad (2)$$

$$2\,CuCl_2^- + 2\,H^+ + 1/2\,O_2 \rightarrow 2\,Cu^{2+} + H_2O + 4\,Cl^- \quad (3)$$

From the fundamental point of view it represents an electron transfer chain by which electrons are subsequentially transferred from ethylene over Pd and Cu ions to dioxygen. The use of very low pH, high chloride concentration and the formation of chlorinated byproducts represents serious technical and environmental drawbacks.

Zeolites have often been claimed to function as solid solvents, which are able to heterogenize soluble catalysts. Previous authors have reported the possibility to oxidize ethylene to acetaldehyde over Cu–Pd exchanged Y zeolites.[2–4] However, in no case was convincing evidence presented as to the specificity and mechanistic action of this catalyst. In this note we report that the preparation of an active, selective and stable catalyst is very specific and advance arguments indicating that the reaction mechanism is totally identical to that of the homogeneous case.

The catalysts were prepared by exchanging the parent Na-exchanged zeolites first for 24 h at room temperature with 0.01 mol dm^{-3} aqueous solutions of $Cu(NO_3)_2$, containing a ten-fold excess of Cu^{II} compared to the zeolite cation exchange capacity. Subsequently, such CuY zeolite was exchanged with the desired amount of $Pd(NH_3)_4^{2+}$, assuming that total exchange of Pd^{II} occurs. Standard catalytic tests were performed in a continuous fixed bed reactor at atmospheric pressure. The on-line analysis was performed by a 5880 HP gas chromatograph or a HP GC–MS. IR spectra were

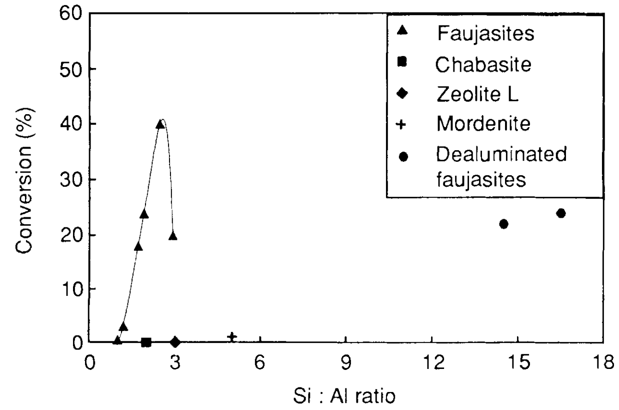


Fig. 1 Conversion of ethylene as a function of the Si : Al ratio of the zeolite framework of different zeolite structures at a constant Cu : Pd ratio of 2. *Conditions*: 0.2 g catalyst; total pressure 0.101 MPa; reaction temperature 363 K. Feed composition: 41.9% O_2, 41.9% helium, 14% water, 2.2% ethylene. WHSV = 0.59 kg/(kg h) (WHSV = weight hourly space velocity). Selectivity to acetaldehyde is in all cases higher than 90%.

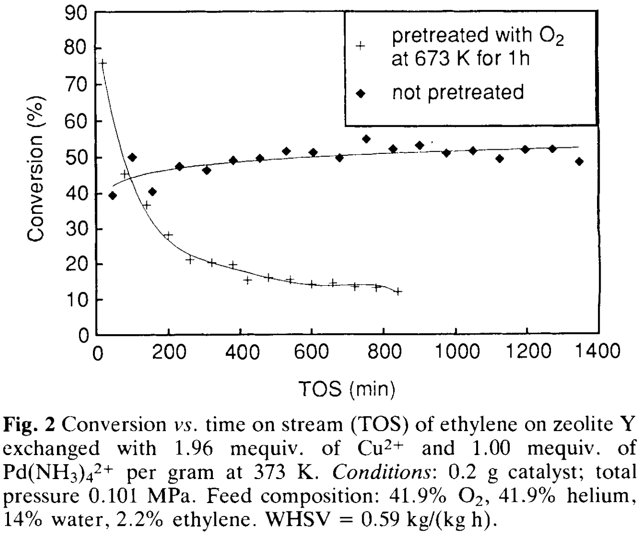


Fig. 2 Conversion *vs.* time on stream (TOS) of ethylene on zeolite Y exchanged with 1.96 mequiv. of Cu^{2+} and 1.00 mequiv. of $Pd(NH_3)_4^{2+}$ per gram at 373 K. *Conditions*: 0.2 g catalyst; total pressure 0.101 MPa. Feed composition: 41.9% O_2, 41.9% helium, 14% water, 2.2% ethylene. WHSV = 0.59 kg/(kg h).

taken on a Perkin-Elmer 580 B spectrometer and TPO (temperature programmed oxidation) measurements were performed on a homemade instrument.

Our main results can be summarized as follows. Out of a whole serious of zeolite structure types, only the faujasite structure seems an efficient 'solid solvent'. Moreover, the activity as well as the acetaldehyde yield depends in a critical way on the Si : Al ratio of this structure (Fig. 1), pointing to a pronounced maximum for zeolite Y. Furthermore, in the latter zeolite the activity is optimal for a Cu : Pd ratio of two. Therefore, in general terms it can be stated that cation environment and density are major activity determining parameters.

For the reaction mechanism in homogeneous conditions, much evidence is present for the existence of an electron transfer chain.[5,6] It consists of (*i*) the coordination of ethylene to Pd^{II}. This enables the nucleophilic attack by water to occur leading to the formation of an hydroxypalladate adduct. The formation of this complex is followed by (*ii*) an intramolecular hydrogen transfer, which after decomposition leads to the formation of acetaldehyde. The occurrence of the same mechanism using an optimized Cu–Pd–Y-zeolite could be established using labelled organic molecules. With $^{18}O_2$, no ^{18}O incorporation in acetaldehyde was found, implying that (*i*) water is the nucleophile and (*ii*) ethylene coordinates to Pd^{II} since an unactivated ethylene is inert towards water.[7] With $^{2}H_2O$ no ^{2}H incorporation was obtained, undoubtedly confirming an internal hydrogen rearrangement in ethylene towards acetaldehyde.

The nature of the active centre for this reaction over Cu–Pd-exchanged Y zeolites was assumed to be a hydrated palladium ion, thus replacing the chloroanion in the homogeneous phase with the anion of the zeolite.[2,3] However, in the latter case Pd^{II}-ions are exchanged in the zeolite using the tetramine complex and consequently residual ammonia ligands can be of crucial importance. Indeed, we only obtained a superactive and stable low temperature (363 K) catalyst (Fig. 2) when the zeolite was pretreated so as to yield on average two residual amine ligands per Pd^{II} ion. Total removal of NH_3 generates an initially active, but totally unstable catalyst. This allows us to conclude that the active centre in the heterogeneous Wacker catalyst is a partially ammoniated Pd^{II}. This was also confirmed by IR spectroscopy of an active catalyst after reaction, which still shows a band at 1310 cm^{-1}, assigned to the symmetric deformation mode of ammonia coordinated to Pd^{II}. The absence of this band is associated with an unstable catalyst. Residual ammonia will lower the redox potential of the Pd^{II}/Pd^{0} redox couple and prevent Pd^{0} from agglomeration.

The following indirect evidence is available for the existence of an electron transfer chain operating in the Cu–Pd zeolite catalyst. (*i*) As was already reported by Kubota *et al.*,[3] there is a synergism between Pd and Cu in the oxidation of ethylene. We found that Y zeolites containing only Pd^{II} have an initial activity which is at least five times lower than the same zeolite containing Cu^{II} and Pd^{II} in an atomic ratio of two. In addition, the former catalysts also deactivate rapidly. This synergism can be interpreted by the occurrence of the equilibrium reaction [see eqn. (4)]. (*ii*) The actual redox potential of the couples involved is determined by the structure type of the zeolite, the cation density (Fig. 1) and for the Pd^{II}/Pd^{0} couple the presence of two residual amine ligands (Fig. 2). (*iii*) The existence of a zeolite (structure and cation density) effect and the observation of a first-order reaction in ethylene and dioxygen indicates that this equilibration of valencies is slow. (*iv*) A similar equilibration is observed when CO is admitted at room temperature to a Cu–Pd Y zeolite (Fig. 3). Indeed on such a sample, CO indicates the simultaneous presence of Cu^{+}, Pd^{+} and Pd.

$$Pd + 2\,Cu^{2+} \rightleftharpoons 2\,Cu^{+} + Pd^{2+} \qquad (4)$$

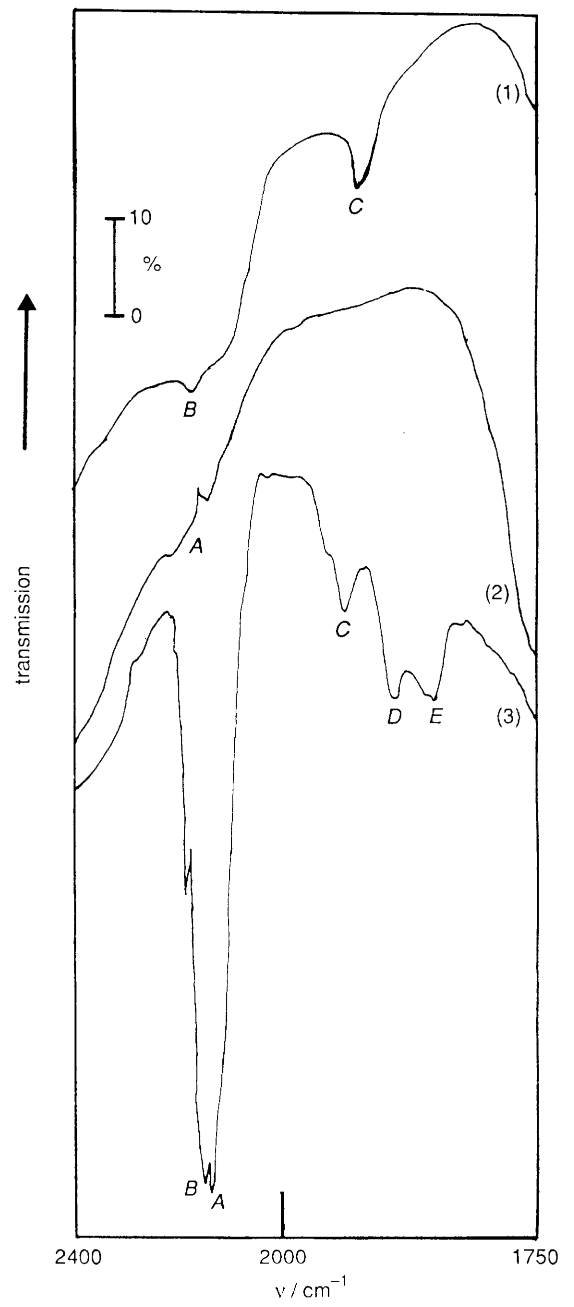
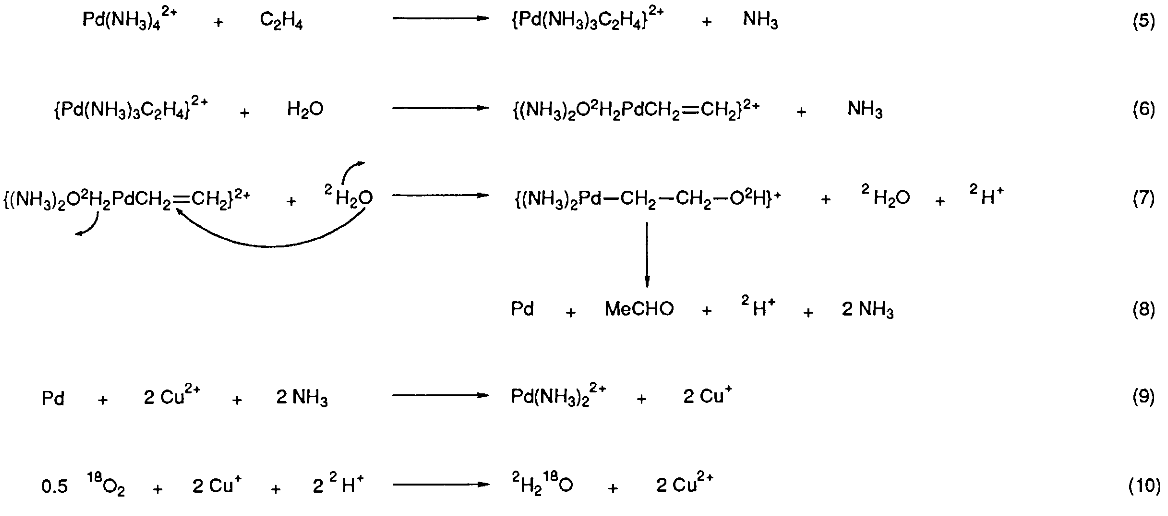


Fig. 3 Adsorption of CO at room temperature on zeolite Y exchanged (1) with 2 mequiv. of $Pd(NH_3)_4^{2+}$, (2) with 3 mequiv. of Cu^{2+} and (3) with 1.96 mequiv. of Cu^{2+} and 1 mequiv. of $Pd(NH_3)_4^{2+}$. Band *A* can be assigned to Cu^{+}–CO, band *B* to Pd^{+}–CO, bands *C*,*D* and *E* to CO adsorbed on metallic Pd.

In conclusion, the sequence of events in the heterogeneous Wacker oxidation of ethylene equals that of the homogeneous one and can be represented as in Scheme 1 (using labelled molecules). All cation charges are neutralized by the zeolite lattice. Its presence has been omitted for simplicity in the equations in Scheme 1. Eqn. (5) represents the displacement of an ammonia ligand by ethylene. Subsequently a second ammonia ligand in *trans* position to ethylene is displaced [as represented by eqn. (6)], caused by the enhanced substitution lability of that ligand due to the presence of ethylene. Eqn. (7) represents the nucleophilic attack of $^{2}H_2O$, leading to the formation of an oxypalladate adduct, which decomposes to acetaldehyde [eqn. (8)]. The reoxidation of Pd^{0} by Cu^{II} [eqn.



Scheme 1

(9)] is enhanced by the presence of ammonia. Finally Cu^{II} is regenerated by dioxygen [eqn. (10)]. All these elementary steps perfectly parallel the steps involved in the homogeneously catalysed reaction. In addition they appear to be strongly dependent on the nature and composition of the zeolite.

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