Platinum-Copper on Carbon Catalyst Synthesised by Reduction with Hydride Anion

INITIAL FINDINGS ON REACTIVITY AND DISPERSION CHARACTERISTICS

By Hany M. AbdelDayem

Chemistry Department, Faculty of Science, Ain Shams University, 11566-Abassia, Cairo, Egypt; E-mail: monamohus@yahoo.com

*With a view to improving the catalytic performance of supported bimetallic platinum-copper catalysts in hydrogen-assisted dechlorination of halogenated alkanes, a range of catalysts were prepared by reduction of oxide precursors by the hydride anion H⁻, using both sodium and calcium hydrides (NaH and CaH₂). The catalytic performance of the resulting catalyst samples in the hydrodechlorination (HDCl) of 1,2-dichloroethane at 220°C was investigated, to gain understanding of metal alloying phenomena governing the variation in ethene selectivity with time on stream (TOS). Metal dispersion was also investigated by O₂ chemisorption and transmission electron microscopy (TEM). PtCuCaH(**b**) catalyst, synthesised by reduction with CaH₂ at 450°C, showed a high selectivity towards ethene in comparison with that of catalysts synthesised by reduction with either NaH or hydrogen. In view of the chemisorption and TEM results, the significant high selectivity of this catalyst towards ethene was attributed to the fact that reduction by CaH₂ enhanced alloying of Pt and Cu. On the other hand, the ethene selectivity of PtCuCaH(**b**) catalyst did not show any variation with TOS, but reached a steady state at early TOS. This suggested that Pt and Cu alloying did not take place during the course of the reaction, but might have occurred during the reduction process.*

Bimetallic alloys are versatile catalysts for important industrial processes, including Fisher-Tropsch synthesis, fuel reforming, hydrogenation and dehydrogenation of alkanes, decomposition of methanoic acid, and hydrodechlorination of chloroorganic compounds (1). Selectivity may potentially be greatly improved through the rational design of bimetallic alloy catalysts from fundamental principles (2). However, the preparation of supported bimetallic alloy catalysts presents some problems as compared with model catalysts (3).

The production of alkenes from halogenated alkanes by hydrogen-assisted dechlorination over supported metal catalysts has received considerable attention in the past few years (4–7), especially the hydrodechlorination of 1,2-dichloroethane to ethene (7–10). Supported monometallic noble metal catalysts (from Group VIII) are very active for HDCl reactions (11, 12). Extensive research with monometallic catalysts (platinum, palladium, silver, copper, etc.) has shown that the dechlorinated C_2H_4 is immediately converted into the fully hydrogenat-

ed product, C_2H_6, which is much less industrially useful (7, 13). However, several authors have demonstrated that bimetallic catalysts, composed of alloys such as Pt-Cu, Pd-Cu and Pd-Ag, possess a high ability to convert chlorinated alkanes selectively into non-chlorinated alkenes (10, 14–16). In the case of supported Pt-Cu catalyst, earlier investigation suggested that the increase in ethene selectivity with TOS was due to an increase in the degree of alloying of Pt and Cu under reaction conditions (17). On the other hand, recent results indicate that alloying of Pt and Cu depends on the pretreatment reduction conditions of the catalyst (18).

The hydride anion is one of the most powerful reducing agents known; the reduction potential of the H^-/H_2 couple has been estimated at –2.25 V (19). $LiAlH_4$ and KBH_4 are used extensively as reducing reagents in solution chemistry (20). Recently, NaH and CaH_2 have been used as powerful reducing agents in solid-state topotactic reduction, at lower temperatures than would be required for a H_2 gas process (21–23).

The present work addresses the following questions:

– Can we discover a new route for enhancing the alloying of Pt and Cu in supported catalysts, based on the reduction of their metal oxide precursors in *solid-state reaction* using metal hydrides?

– Can this suggest a new way to master catalyst selectivity in HDCl reactions?

The bimetallic catalyst, Pt-Cu supported on carbon, was prepared by reduction of its oxide precursor, using different metal hydrides (CaH_2 and NaH) at different temperatures. Hydrogen was also used to prepare a reference sample. The reactivity of all catalysts studied was tested for the hydrodechlorination of 1,2-dichloroethane (DCE) as a model reaction, looking for a significant modification in catalytic performance. Oxygen chemisorption and TEM were used to investigate metal dispersion.

Experimental Work
Catalyst Preparation

0.5 wt.% Pt-0.5 wt.% Cu/C catalyst was prepared by co-impregnation of a carbon support (Aldrich, Darco® KB, SBET 1500 m^2 g^{-1} and pore volume 2 ml g^{-1}) with an aqueous solution containing the appropriate quantity of $H_2PtCl_6 \cdot 6H_2O$ (Aldrich, 99.9%) and $CuCl_2 \cdot 2H_2O$ (Aldrich, 99.9%) overnight. The material was allowed to dry at room temperature for 24 h, and then at 100°C for 2 h *in vacuo*. The produced solid was calcined at 200°C for 4 h to give an oxide precursor sample. This sample of PtO and CuO was mixed and ground with a twofold stoichiometric excess of the metal hydride (CaH_2, Aldrich, 99.9% or NaH, Aldrich, 95%) in a He-filled glove box, and then sealed in an evacuated Pyrex ampoule ($p < 2 \times 10^{-4}$ torr). The sealed reaction vessel was then heated for two periods of 4 days at 300°C with intermediate grinding. The byproduct (CaO or Na_2O) and any unreacted metal hydride from the reaction mixture were removed from the produced solid by washing with a solution of 1M NH_4Cl in CH_3OH, in a Schlenk filter under a nitrogen atmosphere. The product was then further washed with CH_3OH before being dried under vacuum ($p < 1 \times 10^{-1}$ torr). The complete removal of Ca and Na from the catalyst samples was confirmed by energy dispersive X-ray (EDX) analysis.

Another catalyst sample was prepared by reduction with CaH_2 at 450°C, following the same procedure as above. The catalyst prepared by reduction with NaH was denoted as PtCuNaH, and catalysts prepared by reduction with CaH_2 at 300 and 450°C were denoted as PtCuCaH(a) and PtCuCaH(b), respectively. A reference sample (denoted as $PtCuH_2$) was prepared by reduction with 10% H_2/He gas mixture at 300°C for 4 h. Monometallic catalysts, 0.5 wt.% Pt/C and 0.5 wt.% Cu/C, were also prepared by reduction with hydrogen.

Dispersion Study

Metal dispersion in the catalysts was determined from O_2 chemisorption at 350°C. The catalyst was charged into the adsorption cell in a He-filled glove box to avoid any oxidation of the catalyst. Before measurements were taken, the catalyst was heated *in vacuo* at room temperature for 4 h at 1.33×10^{-3} Pa. The net adsorption (μmol g^{-1}) on the supported metal catalyst was calculated by measuring adsorption on the nonmetallised support, and subtracting this value from total adsorption on the catalyst. The net adsorption was simply converted into the apparent degree of dispersion (D_{app} = [O]/[Pt + Cu]), which is regarded as a measure of the number of atoms of adsorbed oxygen per metal atom (24–26). The adsorption stoichiometry was assumed to equal 2.

Transmission electron micrographs were obtained using a JEOL 1200 EX II transmission electron microscope operated with an acceleration voltage of 50 kV.

Catalytic Tests

Hydrodechlorination of 1,2-dichloroethane (DCE) was carried out at 220°C in a flow reactor. Catalyst was charged into a quartz reactor (12 mm internal diameter) in the He-filled glove box to avoid any oxidation of catalyst. Then the reactor was connected directly to the catalytic system in a flow of H_2 (4 ml min^{-1})/He (28 ml min^{-1}) at 110°C. After 1 h, the gas stream was switched to a mixed

flow of 41 ml min^{-1}, consisting of DCE (7000 ppm), H_2 (35,000 ppm) and the remainder He. The feed and product streams were analysed using a Shimadzu GC-17A gas chromatograph equipped with a 27.5 mm Chrompack PoraPLOT capillary column and a flame ionisation detector. Note that the HCl detected was not quantified in this study. The weight of bimetallic catalyst was adjusted to maintain the conversion at approximately 2%.

Results and Discussion
Selectivity and Reactivity

Figures 1 to 4 represent the variation of ethane and ethene selectivities with time on stream. In the case of PtCuH$_2$ catalyst, both ethane and ethene selectivity changed by only 5% during the course of the reaction (Figure 1). However, the variations in selectivity were more pronounced for the PtCuNaH catalyst: before a steady state was achieved, the change observed was ~ 15% (Figure 2). As shown in Figure 3, in the case of PtCuCaH(a) there was an initial sharp rise in selectivity towards ethene, from 70 to 80% during the first 3 h TOS; after which it reached steady state (at 7.5 h), with selectivity to ethene ~ 82%. However, bimetallic PtCuCaH(b) (Figure 4) did not show significant variation in the selectivity towards products with TOS. On the other hand, none of the catalysts under investigation showed significant variation in the conversion of dichloroethane with TOS.

The activity results for the hydrodechlorination of 1,2-dichloroethane at steady state over the studied catalysts are summarised in Table I. It is clear that the PtCuCaH(b) catalyst exhibited the highest selectivity (100%) towards ethene, but with low activity. Ethene is also the major product detected with the PtCuCaH(a) catalyst, showing selectivity ~ 82%, with a higher activity than for the PtCuCaH(b) catalyst. Both PtCuH$_2$ and PtCuNaH catalysts were selective for the dechlorination of 1,2-dichloroethane to ethane; the major product
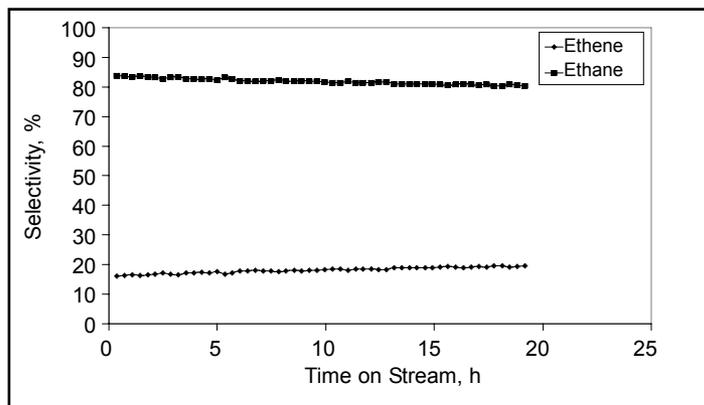

Fig. 1 Selectivities toward ethene and ethane vs. time on stream for hydrodechlorination of 1,2-dichloroethane over PtCuH$_2$ catalyst at 220°C
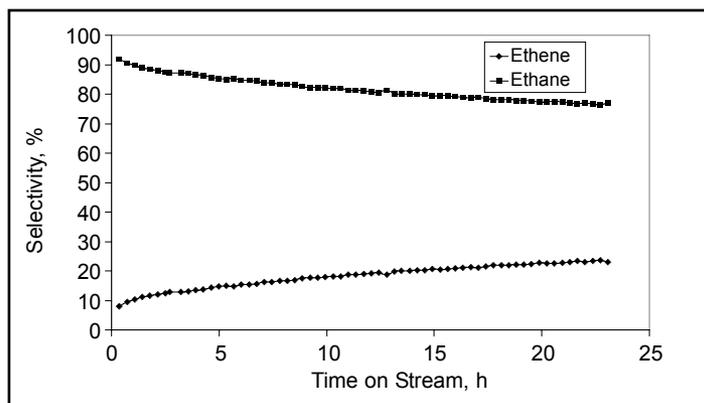

Fig. 2 Selectivities toward ethene and ethane vs. time on stream for hydrodechlorination of 1,2-dichloroethane over PtCuNaH catalyst at 220°C

Table I				
Steady-State Activity Parameters of Pt-Cu/C Catalysts for the Hydrodechlorination of 1,2-Dichloroethane				
Catalyst	Time on	Selectivity, mol%		Activity,
	stream, h	Ethene	Ethane	μmol min^{-1} g^{-1}
Pt/C	3	6	94	2.0
PtCuH$_2$	13	19	81	7.7
PtCuNaH	17	22	78	5.2
PtCuCaH(**a**)	8	82	18	6.7
PtCuCaH(**b**)	0.5	100	0	1.4
Cu/C	9	93	7	0.05

Table II		
Chemisorption Data of Oxygen on the Surface of Different Samples of Pt-Cu/C Catalysts		
Catalyst	Net adsorption, μmol g^{-1}	Degree of dispersion, D_{app} = [O]/[Pt + Cu]
Pt/C	11.8	0.92
PtCuH$_2$	14.2	0.74
PtCuNaH	15.4	0.80
PtCuCaH(**a**)	14.6	0.24
PtCuCaH(**b**)	2.0	0.10

was ethane, at ~ 81% and ~ 78 %, respectively. However, monometallic Pt/C is the most selective to ethane, at ~ 94%. Monometallic Cu/C catalyst has high ethene selectivity, ~ 93 %, but its activity is very low.

Dispersion Results

The chemisorption results are summarised in Table II. The net adsorption (micromoles oxygen per gram of sample) on the metal was taken as the difference between the total adsorption on the catalyst and the adsorption on the corresponding support. From this, it is evident that the values of the degree of dispersion of PtCuCaH catalysts are lower than for the other catalysts. A more detailed study is required before quantitative dispersion

*Fig. 3 Selectivities toward ethene and ethane vs. time on stream for hydrodechlorination of 1,2-dichloroethane over PtCuCaH(**a**) catalyst at 220ºC*
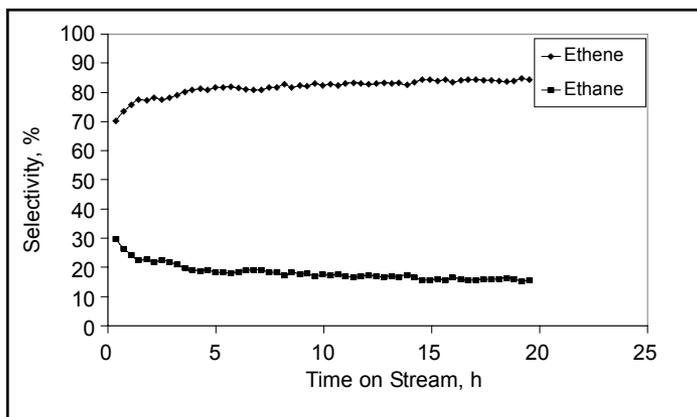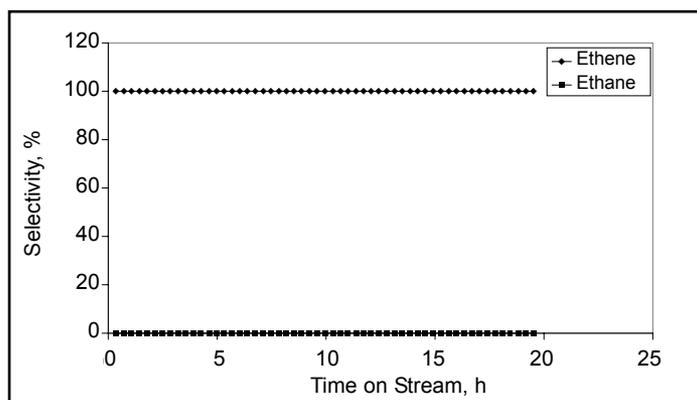

*Fig. 4 Selectivities toward ethene and ethane vs. time on stream for hydrodechlorination of 1,2-dichloroethane over PtCuCaH(**b**) catalyst at 220ºC*

changes are discussed, but the present results could give a qualitative account of the relative dispersion obtained.

TEM micrographs of the PtCuH$_2$, PtCuNaH and PtCuCaH(**b**) catalysts are shown in Figure 5. The micrographs of both PtCuH$_2$ and PtCuNaH
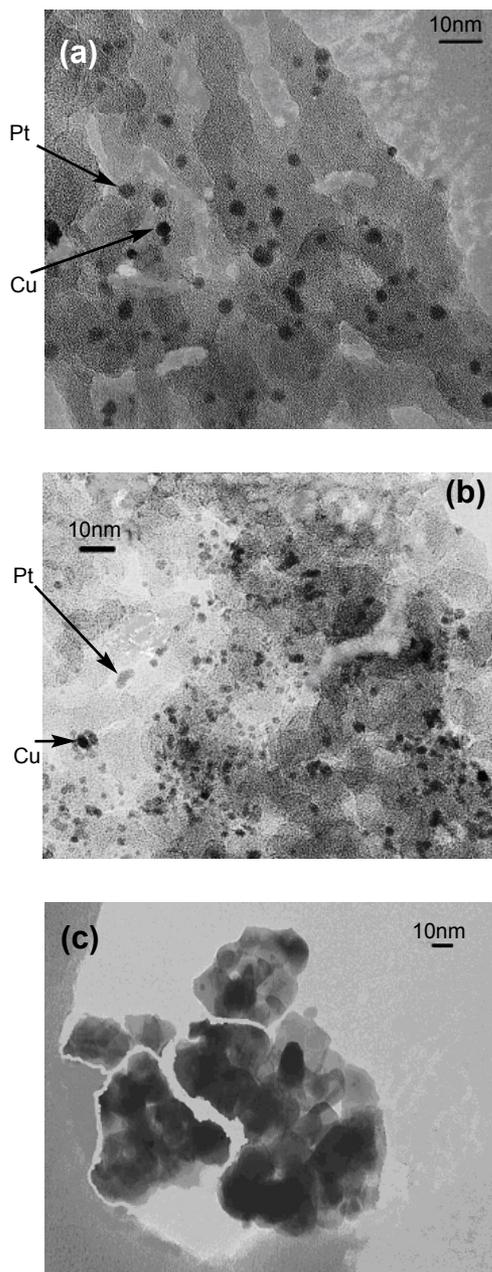

Fig. 5 TEM micrographs of the catalysts: (a) PtCuH$_2$; (b) PtCuNaH and (c) PtCuCaH(**b**)

(Figures 5(a) and 5(b)) show small Pt and Cu particles in a highly dispersed state, without significant aggregations. However, aggregated large particles of Pt and Cu are shown in the micrograph of the PtCuCaH(**b**) catalyst (Figure 5(c)).

Catalytic Activity

Recent studies on the HDCl of DCE over Pt-M (M = Cu, Ag) catalysts proposed that alloying of Pt and M atoms played an effective role in determining the selectivity of the catalyst towards ethene (4, 9). Recalling the present activity results, the observed difference in ethene selectivity between the catalysts studied may be due to the different capacities of various reducing agents to enhance the alloying of Cu and Pt. In the case of PtCuH$_2$ catalyst, the microcrystallites of Pt and Cu ions might be separated on the support surface after drying due to chromatographic effects (1). These effects are expected to be especially pronounced due to the high surface area and narrow pores of the activated carbon support used. Thus, if Pt and Cu chlorides in a dry catalyst are not in close proximity to one another, the standard reduction by hydrogen would not result in significant alloying (as shown in Figure 5(a)). This suggestion can also be verified from the high apparent degree of dispersion of Pt and Cu observed in PtCuH$_2$ (Table II).

We have shown that PtCuCaH catalysts have the highest ethene selectivity among the catalysts studied. According to the TEM and chemisorption results, reduction by CaH$_2$ may promote surface migration of Pt and Cu, which results in alloying of the two metals. It is important to note that the change in ethene selectivity of PtCuCaH(**b**) catalyst is independent of TOS; this result suggests that Pt and Cu alloying did not take place during the course of the reaction, but might have occurred during the reduction process. This phenomenon might be attributable to the different processes for the reduction of Pt-Cu catalyst by metal hydrides and by H$_2$. However, the observed low ethene selectivity of PtCuNaH, which was reduced following the same procedure as for PtCuCaH(a), excludes this possibility. Furthermore, PtCuNaH catalyst showed approximately the same ethene

selectivity as PtCuH$_2$ catalyst, independently of the different reduction procedures used. It is well known in the literature that many of the transition metal oxychlorides migrate more easily over the surface of a carbon support than do the pure metal atoms (27). Hayward *et al.* (22, 23) reported that reduction of metal oxides by CaH$_2$ (hydride anion) could produce metal oxide hydrides. Thus, we can envisage that during the reduction with CaH$_2$, Pt and/or Cu, oxy-hydride species might be formed as intermediates of high surface mobility. The formation of these intermediates could facilitate the aggregation of Pt and Cu, as shown from the micrographs and their enhanced alloying. To clarify this hypothesis further, specific characterisation studies are required; these are beyond the scope of this work.

As already observed, PtCuCaH(a) catalyst prepared by reduction with CaH$_2$ at 300°C has a higher ethene selectivity than does PtCuNaH reduced by NaH at the same temperature. This may be due to the difference in thermal stability between CaH$_2$ and NaH. CaH$_2$ has a high decomposition temperature (~ 885°C), therefore mainly H$^-$ may be present as reducing agent at the temperatures used (300 and 450°C) (26). However, NaH thermally decomposes at a lower temperature (~ 220°C) (26); in this case, hydrogen is present in thermal equilibrium with H$^-$ during reduction of the catalyst, and the probability of formation of Pt and Cu oxy-hydride intermediates is decreased. It seems that 450°C is an optimum temperature to reduce the Pt-Cu catalyst for the selective HDCl of DCE to ethene, but further investigations are necessary to determine precisely the most efficient temperature.

Finally, the catalytic performance of the PtCuCaH(b) catalyst might also be affected by the presence of trace amounts of calcium from the hydride precursor. As mentioned above, the complete removal of Ca from all catalysts was confirmed by EDX analysis, but one cannot exclude the possibility that highly dispersed Ca species may be present on a support of high surface area, such as the carbon used here. The Ca issue is outside the scope of this article; however, some conclusions can be drawn on the basis of lit-

erature results. It has been reported that calcium can improve the dispersion of both supported Cu and Pt (29, 30). This effect might lead to a change in the geometry of Pt sites responsible for hydrogenolysis of 1,2-dichloroethane to ethane. Nevertheless, at the same time, the greatest effect of Ca is to decrease the possibility of alloying Pt and Cu. The above interpretation suggests that Ca does not play a decisive role in determining the selectivity of PtCuCaH catalysts towards ethene.

Conclusions

The results discussed above demonstrate that supported Pt-Cu catalysts synthesised by reduction of oxide precursors with CaH$_2$ exhibit high ethene selectivity, because alloying of Pt and Cu was enhanced during the reduction process. CaH$_2$ apparently affords the hydride anion as a reducing species at the reduction temperatures used. The formation of intermediate Pt and/or Cu oxide hydride species of high surface mobility was proposed. To clarify this hypothesis, further specific characterisation studies are still required; these are beyond the scope of the present work. As a reagent, CaH$_2$ is easily to handle, readily available, and has a high decomposition temperature, allowing the reduction of various supported bimetallic catalysts over a wide temperature range.

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The Author

Hany AbdelDayem holds a B.Sc. degree in Chemistry and an M.Sc. in catalysis from Ain Shams University, Egypt, as well as a Ph.D. in Chemistry for research on chemical kinetics and catalysis from the Université catholique de Louvain, Belgium. He subsequently held a Fulbright postdoctoral award at the University of Pittsburgh, U.S.A. and a postdoctoral fellowship from the Agence universitaire de la Francophonie (AUF) at the Université catholique de Louvain. In 2001 he was appointed Assistant Professor in the Chemistry Department at Ain Shams University. He joined King Faisal University, Saudi Arabia, as Assistant Professor in 2005. His main focus is the development of heterogeneous catalytic processes, including oxidations/oxidative dehydrogenations and hydrodechlorination. He has particular interests in catalyst synthesis, and in *ex-* and *in situ* characterisation of catalysts and reaction kinetics.