

RESEARCH NOTE

Chemoselective Hydrogenation of Cinnamaldehyde to Cinnamyl Alcohol over Pt/K-10 Catalyst

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The preparation and application of a 5% Pt/K-10 catalyst is described. The catalyst was found to be highly selective in the hydrogenation of cinnamaldehyde with almost exclusive formation of cinnamyl alcohol. The unsaturated alcohol was formed with selectivities up to 99% during cinnamaldehyde hydrogenation under mild experimental conditions (25°C, 4 bar). The beneficial role of a significant support effect was interpreted to be due to the Lewis acid centers of the support, which provide suitable anchoring sites for C=O moieties. © 1998 Academic Press

Research in heterogeneous catalysis focuses increasingly on the chemo- and regioselective catalytic hydrogenation of α,β -unsaturated carbonyl compounds to produce fine chemicals (1, 2). Cinnamaldehyde, a member of this group of compounds, is of great practical importance; both the aldehyde and its semi-hydrogenated products find wide application in the perfume industry. In addition, cinnamyl alcohol is an important building block in organic synthesis (2). The selective synthesis of unsaturated alcohols, including cinnamyl alcohol, is however, difficult to achieve, despite the extensive efforts being made to develop suitable catalysts (3–15). Due to their potential importance, these hydrogenation reactions remain in the forefront of recent catalysis research (12–15) which includes the preparation of new catalysts or their modification by doping with metal salts. High selectivities were frequently obtained for the formation of cinnamyl alcohol. Catalyst preparation, is however, tedious, with various additives and special preparation conditions always being necessary.

Similar to zeolites, clays are often used as a catalyst support. It is surprising therefore, that clays are rarely applied in the preparation of metal catalysts (16, 17). Carbonyl compounds have been reduced to alcohols using Cu-bentonite or kaolinite catalysts (18), while clay-supported Ni was also found to be effective (19). In the hydrogenation of unsatu-

rated compounds, only MgO-containing bentonite was applied in the presence of hydrogen donors (20). Additional examples are the intercalation of clays with chiral metal complexes and their use in hydrogenation reactions (17, 21) or the application of clays as electrophilic catalysts after chiral modification (22).

As a follow-up to our recent studies of the hydrogenation of bifunctional compounds (23), here we report the preparation and characterization of a new 5% Pt/K-10 catalyst with excellent features for the selective hydrogenation of cinnamaldehyde. The crucial role of the K-10 montmorillonite support, as well as the effect of hydrogen pressure and temperature to find optimized conditions, will be presented.

Cinnamaldehyde (Fluka) of analytical grade was distilled before use (99% GC purity), while isopropyl alcohol, used as a solvent, had a minimum purity of 99.5% (Reanal) and was used as purchased. Hydrogen (99.995%) was purchased from Linde.

The 5% Pt/K-10 catalyst was prepared by impregnating a K-10 montmorillonite (Aldrich, $S_{\text{BET}} = 250 \text{ m}^2 \text{ g}^{-1}$) support (5 g) with 30 cm³ aqueous solution of 0.6902 g H₂[PtCl₆], followed by reduction carried out in refluxing ethanol for 4 h (24). The catalyst was characterized by transmission electron microscopy (TEM) using a Philips CM10 electron microscope at 90 kV at a magnification of 300,000. Samples were dispersed in toluene, mounted, and air-dried on a plastic film supported by a Formvar grid. The metal particle size distribution was determined, and the mean metal particle diameters were calculated as the average of individual diameters ($\sum n_i d_i / \sum n_i$, $n = 10^3$). The stability of the clay structure and the position of platinum were studied by X-ray diffractometry with a Phillips PW 1820 diffractometer (Cu K α , $\lambda = 0.154 \text{ nm}$, PW 1830 Phillips generator with options of 50 kV and 40 mA). The basal distances were calculated according to the Bragg equation, using the PW 1877 automated powder diffraction program with an accuracy of $\pm 0.01 \text{ nm}$.

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The hydrogenation reactions were performed in a stainless steel autoclave equipped with a thermostat, and a stirrer (800 rpm) under different hydrogen pressures. Before the reaction, the catalyst (20 mg) was activated in 10 cm³ isopropyl alcohol at 25°C under 15 bar hydrogen pressure. After the activation period 2.5 mmol (0.31 cm³) of cinnamaldehyde were introduced and hydrogenated under the desired hydrogen pressures and temperatures.

Product identification was carried out by mass spectrometry using a HP 5890 GC/HP 5970 MS system (50-m long HP-1 capillary column); the products were compared with authentic samples (semi-hydrogenated products from Aldrich, and 3-phenyl-1-propanol prepared by a NaBH₄ reduction of 3-phenylpropanal). Quantitative analysis was performed with a HP 5890 GC-FID gas chromatograph using a 30-m long Cyclodex-B (J&W Scientific) capillary column.

When using clay-supported catalysts, the question of structural stability always arises. The preparation method of K-10 used in the present study includes a high temperature treatment with mineral acids (26) resulting in ion-exchange, as well as dealumination, as expected. As our solid state ²⁹Si NMR studies demonstrated (22), the main constituent is a quartz-like material (−110 ppm) resulting from dealumination, in addition to kaolinite (−100 ppm) and montmorillonite (−91 ppm). The appearance of these signals is in agreement with a previous study by Cativiela *et al.* (25) using K-10 of SüdChemie origin, except that the latter sample contains much less quartz. It is likely that the Aldrich sample was treated under more severe conditions which resulted in extensive dealumination and a progressive destruction of the structure and the partial loss of crystallinity. The X-ray diffraction patterns of the parent K-10 and 5% Pt/K-10 catalyst are shown in Fig. 1.

The mean basal distance of the montmorillonite sheets was found to be ~10 Å. As it is also shown, the deposited platinum did not modify the basic structural characteristics of K-10. Two alterations, however, can be observed: two broad, small peaks in the 3°–6° 2θ range and a broad, relatively intense peak of Pt crystals at 40° of 2θ appeared. These changes indicated that platinum was deposited mainly on the outer surface, whereas a small part intercalated into the interlamellar space, as indicated by the increased basal distances (between 3° and 6° of 2θ). Taking into account the reduction method used (24), the formation of relatively small platinum particles was expected. The TEM results (Fig. 2) proved this to be the case; the mean metal particle diameter was found to be 3.8 nm. The metal particle size distribution is illustrated in Fig. 2.

Besides the structural position and size distribution of the metal, it is important to point out that the support is unusually acidic and, as such, is a widely used solid acid in electrophilic organic transformations (17). The acid strength of K-10 surpasses by far the acidity of the usual catalyst sup-

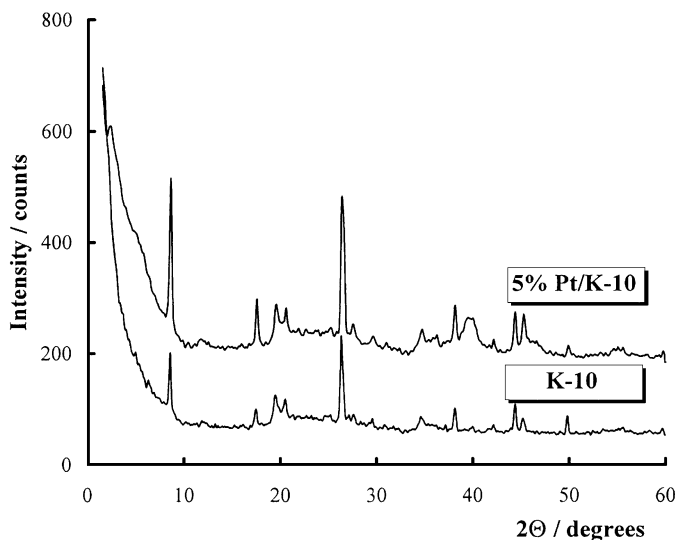


FIG. 1. X-ray diffraction patterns of the parent K-10 montmorillonite and the 5% Pt/K-10 catalyst.

ports (SiO₂, Al₂O₃, TiO₂, etc.). According to the literature, its Hammett acidity constant is $H_0 = -8$. For the sake of comparison, this value is as high as the acidity of concentrated nitric acid (16, 17). Even if we accept that this is not a valid comparison, since one acid is solid and the other liquid, it cannot be denied that K-10 is strongly acidic. The relative ratio of the Lewis and Brønsted acid sites was found to be 1.91 to 2.23, indicating its mixed acidic character (26).

According to literature data the major products of the hydrogenation reaction of cinnamaldehyde are dihydrocinnamaldehyde (1), cinnamyl alcohol (2), 3-phenyl-1-propanol (3), propylbenzene (4), and β-methylstyrene (5) (Scheme 1). When alcohols are applied as solvents, the formation of acetals occurs.

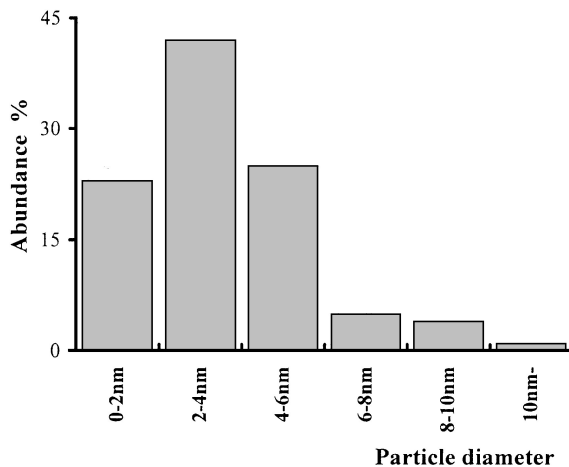
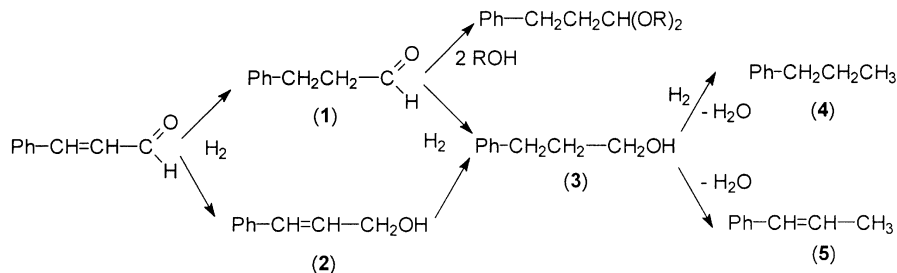


FIG. 2. Metal particle size distribution of the 5% Pt/K-10 catalyst determined by transmission electron microscopy.



SCHEME 1. Possible reaction pathways in the hydrogenation of cinnamaldehyde over platinum catalysts.

Using our newly prepared 5% Pt/K-10 catalyst under atmospheric hydrogen pressure at 60°C excellent selectivity of the formation of the cinnamyl alcohol (92.4%) was observed. As a result, the rate and selectivities were systematically studied as a function of the hydrogen pressure. Both the activity and selectivity data are plotted in Fig. 3a, while the complete set of results is summarized in Table 1.

As the data indicate, the catalyst produces cinnamyl alcohol in good yield and very high selectivity. The reaction rates increased monotonously as a function of the hydrogen pressure and excellent selectivities were observed. It is important to note that the formation of dihydrocinnamaldehyde was negligible at all hydrogen pressures. On the basis of this series of results 4 bar hydrogen pressure was selected for a temperature-dependence study (Fig. 3b), since the activity is satisfactory (70% conversion after 17 h) and the almost exclusive formation of cinnamyl alcohol (99%) is observed. As shown in Fig. 3b, the rates in this case also increase continuously with increasing temperature. The selectivity, however, passes through a maximum at 25°C. The formation of high molecular weight products tended to increase with increasing temperature.

In order to clarify the effect of support acidity on selectivity, additional experiments were carried out using a 5% Pt/K-10 catalyst treated with 5% aqueous NaOH and a 5% Pt/Nafion-H/silica-nanocomposite sample. The Nafion-H/silica-nanocomposite support contains very strong Brønsted acid sites ($H_0 = -12$) and only a very small number of Lewis acid sites (27), while the base-treated 5% Pt/K-10 catalyst has practically no acid sites. As a result, both catalysts performed very poorly: low activities and low selectivities of the formation of cinnamyl alcohol were observed (Table 1).

The generally accepted mechanism of the hydrogenation of cinnamaldehyde, published by Gallezot *et al.* (3, 6), stated the dominant role of steric constraints. However, using metal chlorides as additives a different mechanism was proposed (4, 5). In the case of $FeCl_2$ or $GeCl_4$ the authors suggested the deposition of electron deficient centers on the platinum surface. These electron acceptor sites tend to adsorb C=O groups through the unshared electron pairs of carbonyl oxygen. This selective adsorption increased the selectivity of the C=O hydrogenation up to 94% (4).

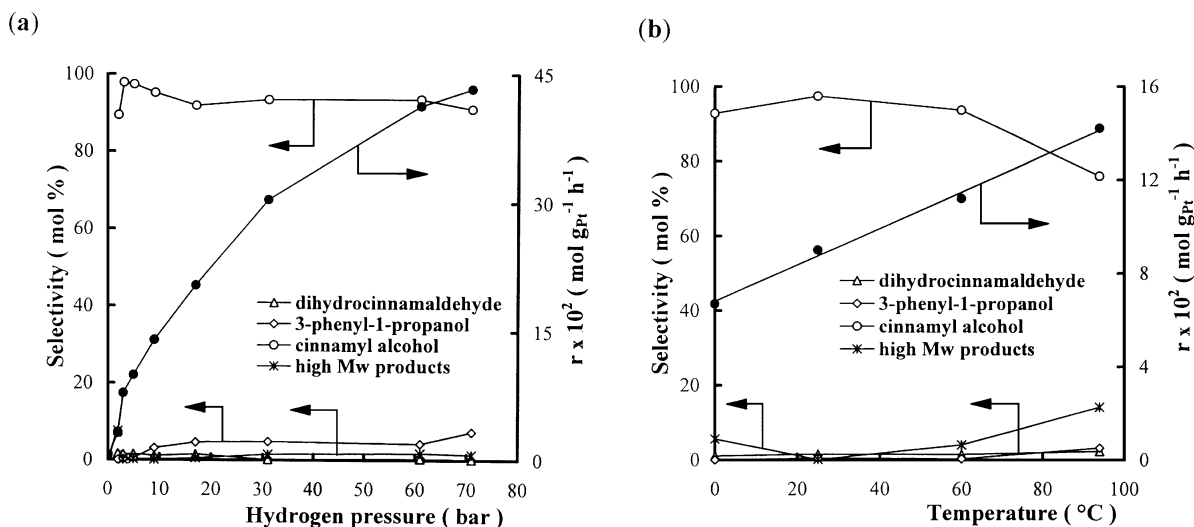


FIG. 3. Activity and selectivity vs hydrogen pressure (25°C) (a) and temperature (4 bar) (b) functions of the hydrogenation of cinnamaldehyde over a 5% Pt/K-10 catalyst (20 mg catalyst, 2.5 mmol cinnamaldehyde, 10 cm³ iPrOH).

TABLE 1
Activity and Selectivity Data of the Hydrogenation of Cinnamaldehyde over a Pt/K-10 Catalyst
(20 mg catalyst, 2.5 mmol cinnamaldehyde, 10 cm³ iPrOH)

Entry	Time/h	P _{H₂} /bar	Temperature/°C	Conversion/%	Selectivity (mol%)			
					(1)	(2)	(3)	Unidentified
1	17	1	25	22.1	1.7	91.3	-	7.0
2	17	2	25	53.2	1.5	97.8	0.1	-
3	17	4	25	67.5	1.0	98.9	0.1	-
4	17	8	25	95.5	1.0	95.9	3.1	-
5	11	16	25	94.1	1.5	93.4	4.6	0.5
6	7	30	25	95.2	0.2	93.5	4.8	1.5
7	5	60	25	94.8	0.3	93.7	4.2	1.8
8	4.5	70	25	95.3	0.2	91.1	7.3	1.4
9	17	4	0	45.5	1.0	92.8	-	6.2
10	17	4	60	91.5	1.5	93.6	0.3	4.6
11	15	4	94	90.3	2.3	75.8	3.2	18.7
12 ^a	21	4	25	39.9	11.4	33.5	15.6	39.5
13 ^b	17	4	25	8.0	21.6	70.5	0.6	7.3

Note. **1** = dihydrocinnamaldehyde; **2** = cinnamyl alcohol; **3** = phenylpropanol; unidentified = cracking products and oligomers.

^a The original Pt/K-10 catalysts were pretreated with a 2.5% aqueous NaOH solution.

^b A 5%Pt/Nafion-H/silica-nanocomposite catalyst was used.

Although, the mechanism is different in the present case, it can be explained almost completely by the latter. In the light of the first mechanism, an excess of saturated aldehyde will probably be formed, because the catalyst contains relatively small metal particles (~4 nm). Since this is not the case in the present study, the major role of a steric effect can be excluded. However, as mentioned above, the K-10 montmorillonite is a highly acidic support (17) and, as a result, is probably not completely inert in this reaction. According to our explanation, the acid centers of the support take part in the adsorption; that is, they anchor the substrate at its electron-rich carbonyl group. However, after NaOH treatment, the same catalyst or a catalyst containing strong Brønsted sites but no Lewis centers (Table 1) exhibited significantly lower C=O hydrogenation selectivity. These observations unambiguously demonstrate that the Lewis acid sites of the K-10 support play a crucial role in determining the chemoselectivity during hydrogenation. Since the electron density of the C=O group is significantly higher than

that of the C=C group, the cinnamaldehyde molecule will adsorb through its carbonyl oxygen on these Lewis sites. Moreover, as the experimental results show, simultaneous adsorption of the C=C and C=O groups does not occur. After anchoring the substrate, hydrogen is added, as usual, assuming that the bonding takes place close to a platinum particle. The final step is the product desorption, since the OH group is a weaker nucleophile than the C=O moiety and, as a result, C=O can displace it. After the complete hydrogenation of the carbonyl group, depending strongly on the conditions applied, the C=C group can also react. Successive C=C hydrogenation was found to be possible only at higher hydrogen pressures and/or temperatures. A representative scheme illustrating our mechanistic explanation is shown in Fig. 4.

In conclusion, the preparation and application of a 5% Pt/K-10 catalyst was described. The catalyst was found to be highly selective in the hydrogenation of cinnamaldehyde with almost exclusive formation of cinnamyl alcohol. The

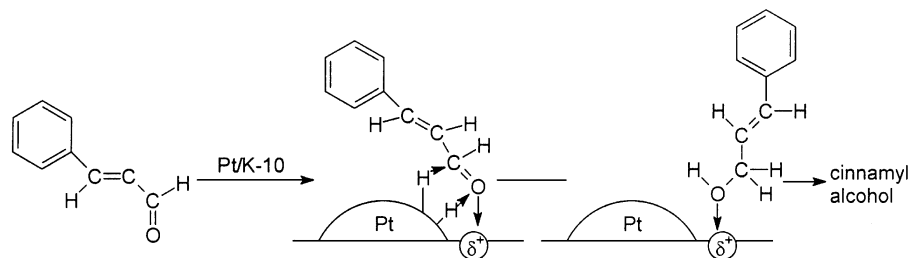


FIG. 4. Formation of cinnamyl alcohol in the hydrogenation of cinnamaldehyde over a 5% Pt/K-10 catalyst.

application of this catalyst in the hydrogenation of unsaturated carbonyl compounds proved to be a convenient, simple, and novel method for obtaining excellent chemoselectivity. The unsaturated alcohol was formed with selectivities up to 99% during cinnamaldehyde hydrogenation under moderate experimental conditions (25°C, 4 bar). The beneficial role of a significant support effect was interpreted by its Lewis acid centers, which act as anchoring sites for C=O moieties.

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