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Potassium Phosphate as a Solid Base Catalyst for the Catalytic Transfer Hydrogenation of Aldehydes and Ketones

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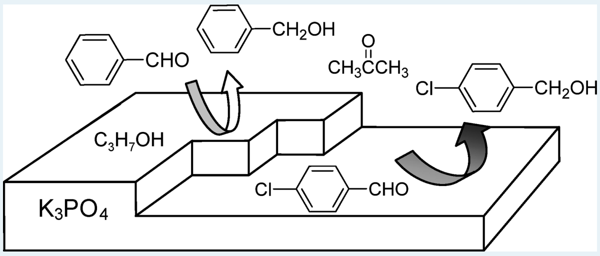

ABSTRACT: Potassium triphosphate is a surprisingly active catalyst for the catalytic transfer hydrogenation of carbonyl compounds. A pretreatment at 600 °C is critical to obtain the active material. Temperature programmed desorption of CO_2 indicates that sites of lower basicity were created after heat treatment for 5 h as compared to 1 h. With 2-propanol as hydride source, aromatic aldehydes were reduced to the corresponding alcohols with high rates. The presence of electron withdrawing chloro- and nitro-substituents at the benzene ring increases the rate of reaction compared with unsubstituted benzaldehyde, while electron donating methyl or 2-propyl groups has the opposite effect. Ketones were reduced with a lower rate of reaction than aldehydes. The role of K_3PO_4 as a heterogeneous catalyst is indicated by a complete lack of reaction in the absence of the solid base and by studies with competing substrates. The latter studies suggest that the catalytic transfer hydrogenation of benzaldehyde and chlorinated benzaldehydes takes place at different surface sites.

KEYWORDS: K_3PO_4, solid base, catalytic transfer hydrogenation, aldehydes, ketones, heterogeneous base, site differentiation

INTRODUCTION

The reduction of the carbonyl function C═O in the presence of other unsaturated groups is of considerable importance in organic synthesis.[1−3] In some cases, the reduction may be possible with molecular hydrogen and specifically treated catalysts. More generally, complex hydrides are used as reducing agents. All these reagents are used in stoichiometric conditions and many need careful handling under strictly anhydrous conditions. The Meerwein−Ponndorf−Verley (MPV) reaction offers an alternative route whereby aldehydes and ketones are selectively reduced to the corresponding alcohols by the use of a secondary alcohol such as 2-propanol.[4−6] The originally used aluminum alkoxides had to be employed in almost stoichiometric amounts. Subsequently, it was discovered that zeolites,[7−9] hydrotalcites,[10] and metal oxides and hydroxides[11−16] were good chemoselective catalysts for the reaction. In particular, Zr-zeolite beta shows extremely good activity and selectivity for the reduction of substituted cyclohexanones and α,β-unsaturated aldehydes.[17,18] Recent developments in the field of MPV and transfer hydrogenations have been reviewed by Cha.[19]

Catalytic transfer hydrogenation covers a wider range of substrates than MPV reduction, and the reaction is often catalyzed by a transition metal. Not only carbonyl compounds but also alkenes, alkynes, nitriles, and nitro compounds have been reduced with hydrogen donors such as alcohols, formic acid, and formates and hydrazine.[20] Homogeneous as well as heterogeneous catalyst systems involving ruthenium,[21−25] palladium,[26] iridium,[27] rhodium,[28] and gold[29] have been reported. A ruthenium(II) complex catalyst containing a 2-(benzoimidazol-2-yl)-6-(pyrazol-1-yl)pyridine ligand was especially selective for the transfer hydrogenation of ketones with turnover frequencies up to 59,400 h^{-1}.[30] In addition to these expensive metals and ligands, the group of Beller[31] reported a three-component catalyst system based on an iron salt, 2,2′:6′,2″-terpyridine and triphenylphosphine which was active in the chemoselective reduction of ketones. Copper nanoparticles supported on mesoporous silica were also shown to be highly selective catalysts in the reduction of aromatic ketones and aldehydes under microwave irradiation.[32] In catalytic transfer hydrogenation, the presence of a base such as NaOH, K_2CO_3, or $CsCO_3$ is required. Bäckvall[33] established that in $RuCl_2(PPh_3)_2$-catalyzed hydrogen transfer reactions, the role of the base is to form the active dihydride catalyst, $RuH_2(PPh)_3$. The presence of K_2CO_3 accelerates the reaction so that full conversion was noted within an hour as compared to the almost complete lack of reaction after 6 h in the absence of the base. The importance of the base is illustrated by Polshettiwar and Varma[34] who used KOH without any transition metal or ligands for the reduction of aromatic aldehydes and ketones by 2-propanol. Similarly, Ouali et al.[35] reported that NaOH was an active catalyst for the hydrogen transfer of a number of aromatic and aliphatic ketones. These exciting results prompted us to investigate the use of the readily available and mildly basic potassium phosphate (K_3PO_4) for the catalytic transfer hydrogenation of aldehydes and ketones (Scheme 1). In reactions, K_3PO_4 is more often used as a base in conjunction with homogeneous metal catalysts rather than as a catalyst in its own right.[36−39] However, a catalytic activity of K_3PO_4 has been observed in the Knoevenagel condensation of cyanoacetates and malononitriles,[40] the decomposition of diacetone

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Scheme 1. Catalytic Transfer Hydrogenation of Carbonyl Compounds

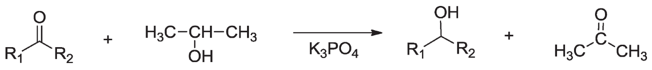


Table 1. Effect of Pretreatment on Activity of K_3PO_4 for Transfer Hydrogenation of Benzaldehyde[a]

pretreatment	conversion (%)[b]	selectivity (%)[c]
100 °C in air for 24 h	12	100
600 °C in air for 1 h	22	100
600 °C in air for 5 h	98	100

[a] Reaction conditions: 2 mmol benzaldehyde, 5 mL of 2-propanol, 0.2 g of K_3PO_4, 80 °C, under N_2. [b] After 10 h. [c] Benzyl alcohol.

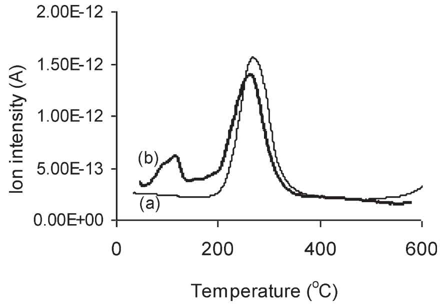


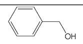
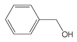
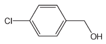
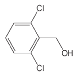
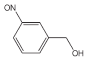
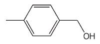
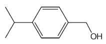
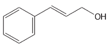
Figure 1. CO_2 TPD of K_3PO_4 after pretreatment at 600 °C for (a) 1 h and (b) 6 h.

Table 2. Alcohols Used for Catalytic Transfer Hydrogenation of 2,6-Dichlorobenzaldehyde[a]

alcohol	time (h)	conversion (%)	selectivity (%)
2-propanol	3	100	100
cyclohexanol	10	39	100
ethanol	5	63	100
1-propanol	6	76	49
hexanol	5	80	46

[a] Reaction conditions: 2 mmol of 2,6-dichlorobenzaldehyde, 5 mL of alcohol, 0.2 g of K_3PO_4, 80 °C, N_2.

Table 3. Reduction of Aromatic Aldehydes with 2-Propanol[a]

Entry	Substrate	Time (h)	Conv. (%)	Products	Sel. (%)
1	Benzaldehyde	10	98		100
2	Benzaldehyde[b]	10	98		100
3	4-chlorobenzaldehyde	3	99		95
4	2,6-dichlorobenzaldehyde	3	100		100
5	3-nitrobenzaldehyde	4	98		100
6	4-methylbenzaldehyde	6	57		100
7	4-isopropylbenzaldehyde	6	68		100
8	Cinnamaldehyde	6	72		100

[a] Reaction conditions: 2 mmol of substrate, 5 mL of 2-propanol, 0.2 g of K_3PO_4, 80 °C, under N_2. [b] 0.105 g of potassium *tert*-butoxide instead of solid K_3PO_4.

alcohol,[41] the alkylation of toluene to ethylbenzene,[42] and the cyanosilylation of carbonyl compounds.[43] More recently, K_3PO_4 has been reported as an efficient catalyst for the aminohalogenation of β-nitrostyrenes with *N*-bromoacetamide.[44] Hence, its potential catalytic activity for the transfer hydrogenation of carbonyl compounds is of interest. Being insoluble in many of the solvent systems, K_3PO_4 offers the advantages of ease of recovery from the reaction medium by mere filtration and reuse of the recovered material. The question also arises if the catalytic transfer hydrogenation reaction is truly heterogeneous, or follows a homogeneous path through the formation of soluble potassium alkoxide species.

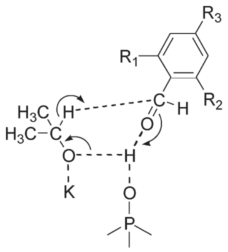
RESULTS AND DISCUSSION

Pretreatment of K_3PO_4. Prior to use, K_3PO_4 was calcined at 600 °C for 5 h. This treatment was required to produce the active catalyst; drying at 100 °C was found to be insufficient. Over the dried sample, only 12% conversion of benzaldehyde was observed after 10 h (Table 1). Benzyl alcohol was the only product formed. When K_3PO_4 was calcined for only 1 h at 600 °C, the conversion was 22%; this rose to 98% when the calcination time was increased to 5 h.

The surface basicity of K_3PO_4 was studied by temperature programmed desorption (TPD) of CO_2. After K_3PO_4 was pretreated at 600 °C for 1 h, the TPD profile showed that CO_2 desorption occurred between 170 to 350 °C with a maximum at ~260 °C (Figure 1). For K_3PO_4 pretreated at 600 °C for 5 h, the CO_2 desorption shifted to slightly lower temperature. In addition, a smaller desorption peak appeared between ~50 to 150 °C. From these observations, it can be deduced that on prolonged heating, additional sites of lower basicity are formed. It is probable that prolonged high temperature treatment results in atomic diffusion and annealing, thus forming more flat or terrace sites at the expense of kink or step sites. The total number of basic sites after calcination at 600 °C for 5 h was found to be 0.0126 mmol g^{-1}. The surface area of the samples was redetermined by N_2 adsorption after the CO_2 TPD and found to be ~0.67 $m^2\ g^{-1}$. With this surface area, the density of basic sites on the surface works out to be $1.13 \times 10^{19}\ m^{-2}$ which is close to one monolayer. This shows that a high fraction of the surface basic sites was probed by the CO_2 TPD. If the surface density had been significantly less than a monolayer, it would imply that only selected basic sites were titrated by CO_2.

Effect of Reducing Alcohols. Different alcohols were tested as hydride donors for the reduction of 2,6-dichlorobenzaldehyde to the corresponding alcohol (Table 2). The reaction was fastest with 2-propanol and full conversion was obtained after 3 h. The only products formed were 2,6-dichlorobenzyl alcohol and acetone. In comparison, cyclohexanol was less effective in reducing 2,6-dichlorobenzaldehyde and after 10 h, the conversion was only 39%. The rate of reduction was lower when primary alcohols like ethanol, 1-propanol, and hexanol were used. Furthermore,

Chart 1. Proposed Six-Membered Cyclic Transition State for the Reduction of Aromatic Aldehydes



the selectivity to 2,6-dichlorobenzyl alcohol was reduced because of the formation of hemiacetals.

Reduction of Aldehydes. The catalytic transfer hydrogenation of benzaldehyde with 2-propanol at 80 °C over K_3PO_4 occurred with 100% selectivity to benzyl alcohol (entry 1, Table 3). After 10 h, the conversion was 98%. For comparison, potassium *tert*-butoxide was also used as a homogeneous catalyst (equimolar with K_3PO_4, 0.94 mmol). In this case, the rate of reaction was comparable to that with K_3PO_4, and the conversion of benzaldehyde after 10 h reached 98% (entry 2, Table 3).

The presence of electron-withdrawing groups at the benzene ring increased the rate of reaction (entries 3−5, Table 3). Both 2,6-dichlorobenzaldehyde and 3-nitrobenzaldehyde were completely reacted within 4 h, forming the corresponding alcohols with 100% selectivity. When electron-donating groups were present, the reaction rate was decreased (entries 6 and 7, Table 3). Even after 6 h, the conversion of 4-methyl- and 4-isopropylbenzaldehyde reached only 57% and 68%, respectively. The presence of a double bond conjugated to the carbonyl function increased the rate of reduction (entry 8, Table 3). Hence, the rate of reaction for cinnamaldehyde to cinnamyl alcohol was higher than that of the alkyl-substituted benzaldehydes. These results show that K_3PO_4 can be used as a selective catalyst for the transfer hydrogenation of aromatic aldehydes. Similar electronic effects of substituents on the aromatic ring were observed when KOH was used as a homogeneous catalyst.[34] Alcohol yields of 62−75% were obtained under optimized conditions of 12 mol % KOH to 1 mmol of substrate in 3 mL of 2-propanol within the relatively short time of 30−45 min. In comparison, Ouali et al.[35] reported that the catalytic transfer hydrogenation of 1 mmol of benzaldehyde in the presence of 10 mol % NaOH gave a yield of 99% after 24 h.

The possibility that the alcohols were the product of a Cannizarro disproportonation was checked. Using dodecane as internal standard for the catalytic transfer hydrogenation of benzaldehyde, it was confirmed that the mass balance closed to better than 95%. After correcting for the flame ionization detector response, the combined counts for benzaldehyde and benzyl alcohol agree with the initial count for benzaldehyde. No benzoic acid was detected. In addition, no reaction was observed for benzaldehyde and 2,6-dichlorobenzaldehyde when 2-propanol was replaced by toluene, thus confirming that the alcohols were formed via hydrogen transfer from the alcohol, and excluding any substantial contribution by a Cannizzaro reaction. Only for the highly activated 4-chlorobenzaldehyde were some Cannizzaro products observed. 2-Propyl-4-chlorobenzoate was formed together with 4-chlorobenzyl alcohol (entry 3, Table 3). However, the selectivity to the ester was only 5%, indicating that catalytic hydrogen transfer was the main reaction.

Table 4. Catalytic Transfer Hydrogenation of Ketones over K_3PO_4[a]

entry	substrate	alcohol	temp. (°C)	conv.[b] (%)	sel.[c] (%)
1	cyclohexanone	2-propanol	80	55	100
2	4-*tert*-butylcyclohexanone	2-propanol	80	30	100
3	acetophenone	2-propanol	80	38	100
4	acetophenone[d]	2-propanol	80	68	100
5	acetophenone	2-butanol	95	32	100
6	acetophenone	2-pentanol	115	24	100
7	acetophenone	cyclohexanol	160	15	100

[a] Reaction conditions: 2 mmol of substrate, 5 mL of alcohol, 0.2 g of K_3PO_4, 80 °C, under N_2. [b] After 12 h. [c] Selectivity to alcohol. [d] 0.105 g of potassium *tert*-butoxide instead of K_3PO_4.

These results agree with the previously proposed mechanism over nontransition metals.[33] Such a mechanism has also been proposed for both homogeneous and heterogeneous catalysts such as diisobutylaluminum complexes, metal alkoxides, zeolites, zirconium hydroxide, magnesium oxide, and so forth.[8,18,19] The hydrogen transfer involves a cyclic transition state where hydrogen from the C−H bond of the alcohol is transferred to the carbonyl carbon of the acceptor. Electron-withdrawing groups on the benzene ring reinforce the partial positive charge at the carbon of the carbonyl group and facilitate the hydride transfer from the alcohol (Chart 1). This is seen in the higher rates for 4-chloro-, 2,6-dichloro-, and 3-nitrobenzaldehyde as compared to benzaldehyde (Table 3). On the other hand, electron-donating groups increase the electron density at the carbonyl carbon so that the hydride transfer is less favorable.

Although aromatic aldehydes were reduced to the corresponding alcohols, the aliphatic aldehydes, butanal, heptanal and octanal, were not reduced. Instead, they undergo aldol condensation followed by dehydration. Hence, with butanal, 2-ethylhex-2-enal was formed. The reaction was very fast, and complete conversion was obtained within an hour at 80 °C. Even at room temperature, the aldol condensation reaction for butanal reached 100% conversion within an hour, while heptanal and octanal required a slightly longer time of 2 and 3.5 h, respectively, for complete conversion. Citral and citronellal also gave the dehydrated condensation products, although the reaction was slower.

Reduction of Ketones. The reduction of cyclohexanone, 4-*tert*-butylcyclohexanone, and acetophenone was less facile than that of aldehydes. The conversion after 12 h was between 30 to 55% (entries 1−3, Table 4). The selectivity to alcohols was 100% for all three ketones. The lower rate of reduction of the ketones as compared to aldehydes may be due to both steric and electronic effects as the carbonyl moiety is linked to two alkyl groups. A higher temperature of 120−180 °C generated by microwave heating had been found to aid the reduction of ketones using lithium 2-propoxide as catalyst.[45] Hence, the reduction of acetophenone was attempted under reflux conditions with different alcohols, so that the temperature could be varied up to 160 °C (entries 5−7, Table 4). However, the highest conversion was still obtained with 2-propanol at 80 °C, probably because of the higher hydrogen donor ability of 2-propanol.

Heterogeneity of the Reaction. In catalysis, it is always important to identify the active species. K_3PO_4 is almost completely insoluble in the alcohols used as solvent. However, there is the possibility that small amounts of an alkoxide species can form by

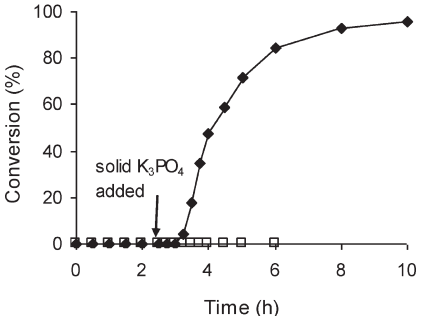


Figure 2. Requirement of solid K_3PO_4 in the reduction of benzaldehyde with 2-propanol. (□) No solid K_3PO_4 added to "potassium 2-propoxide" solution with benzaldehyde, (◆) with addition of solid K_3PO_4 after 2.5 h of reaction (indicated by the arrow).

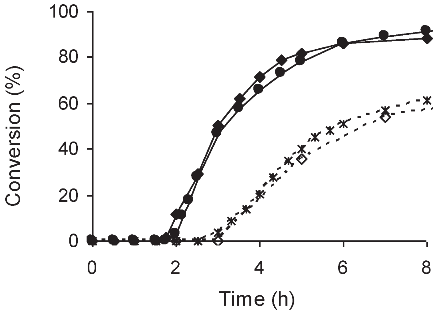


Figure 3. Reduction of benzaldehyde in (◇) air, (□) oxygen, (●) nitrogen, and (◆) freshly distilled reagents in nitrogen. Reaction conditions: 2 mmol of substrate, 5 mL of 2-propanol, 0.2 g of K_3PO_4, 80 °C, under nitrogen, oxygen, or air.

reaction with the alcohol, and that this alkoxide species is involved in the reduction of the carbonyl group. To check the possibility that potassium 2-propoxide was the actual catalyst, the 600 °C-calcined K_3PO_4 was refluxed with 2-propanol under nitrogen for 3 h. The conductivity of the solution was monitored with a conductance cell, but no change in conductance was observed. The solid K_3PO_4 was removed by hot filtration. Benzaldehyde was added to the filtrate, and the solution was heated to 80 °C. No reaction was observed even after 6 h showing that either no potassium 2-propoxide was formed under these conditions and/or the reaction is not homogeneously catalyzed by potassium 2-propoxide. However, when solid K_3PO_4 was added to the filtered solution containing benzaldehyde, formation of benzyl alcohol commenced after an induction period of 30 min (Figure 2). Potassium *tert*-butoxide was also tested for the homogeneous catalytic transfer hydrogenation of benzaldehyde (entry 2, Table 3) and acetophenone (entry 4, Table 4). The same number of moles of catalyst (0.94 mmol) was used as in the case of K_3PO_4. As potassium *tert*-butoxide is completely soluble in 2-propanol, it is expected that every molecule is catalytically active while for a heterogeneous catalyst, only the surface sites are involved in catalysis. The density of surface basic sites, as determined by the TPD of adsorbed CO_2, was found to be 0.0126 mmol g^{-1} or 0.0025 mmol for 0.94 mmol of K_3PO_4. Despite the smaller number of surface sites at K_3PO_4, the conversion of benzaldehyde was very similar to that of potassium *tert*-butoxide, reaching 98% after 10 h. The reaction rate was lower for the transfer hydrogenation of acetophenone, but the conversion of 38% over K_3PO_4 compares very well with that using potassium *tert*-butoxide, 68%. The facile transfer hydrogenation of aldehydes and ketones shows that K_3PO_4 is an active solid base catalyst. On the basis of the available active sites, the activity of the heterogeneous K_3PO_4 is more than two orders higher than that of the soluble base, potassium *tert*-butoxide.

Ivanov et al.[13] postulated that alcohol adsorption occurs on basic catalysts like magnesium oxide with the oxygen binding to the surface cation, whereas the hydrogen interacts with the basic site. The crystal structure of K_3PO_4 consists of $[KO_6]$ octahedra and $[PO_4]$ tetrahedra, with layers of potassium chains in between.[46] The exposed potassium ions in the chains and the oxygen ions are available for adsorption of the alcohol. The phosphorus is surrounded by oxygen atoms and, hence, is not exposed (Chart 1).

It was further observed in the reaction kinetics of benzaldehyde that an induction period precedes the reaction. When the transfer hydrogenation was carried out in a system open to air or with oxygen bubbled through the solution, an induction time of 2.5 to 3 h occurred before any products were detected (Figure 3). Irrespective of the reaction condition, a similar level of conversion around 60% was reached after 8 h. However, under nitrogen, the induction time was shortened to 2 h, and the reaction occurred with a higher initial rate and proceeded to reach ~90% conversion after 8 h. The use of freshly distilled reagents (benzaldehyde and 2-propanol) did not lead to further shortening of the induction time, nor did it significantly affect the rate of reaction.

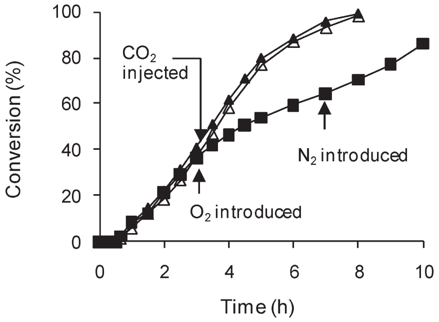


Figure 4. Reduction of benzaldehyde in (Δ) nitrogen and with introduction of (■) oxygen and (▲) CO_2. K_3PO_4 calcined at 600 °C for 5 h followed by evacuation (10^{-3} mbar) at 350 °C.

However, a significant decrease in the induction time to only 0.5 h was observed when the 600 °C-calcined K_3PO_4 was evacuated for 3 h at a pressure of 10^{-3} mbar before being used as catalyst in the reaction (Figure 4). These results suggest that species such as oxygen and/or carbon dioxide can adsorb at the surface of K_3PO_4 and reduce the reaction kinetics. This lends further support to the heterogeneity of the reaction. To test for the influence of oxygen, the reaction was conducted under a nitrogen atmosphere until the conversion reached about 20%, whereupon the gas flow was switched from nitrogen to oxygen. The reaction slowed down, but recovered slightly when the oxygen was replaced again with nitrogen after 7 h. When carbon dioxide was introduced after 3 h under a nitrogen blanket, the rate of reaction was unaffected. Hence, exposure to oxygen affects the rate of reaction, presumably via adsorption onto the K_3PO_4 surface, but the inhibitory effect can be reversed to some extent by removal of the oxygen.

Interestingly, when both benzaldehyde and 2,6-dichlorobenzaldehyde were present simultaneously in the reaction mixture,

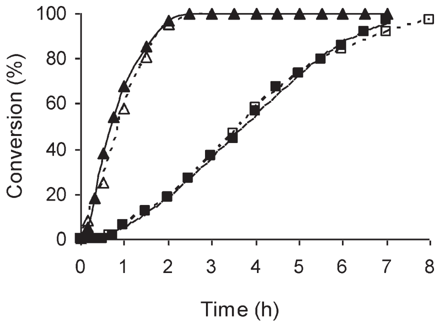


Figure 5. Conversion of benzaldehyde (□), 2,6-dichlorobenzaldehyde (Δ), and a mixture of benzaldehyde (■) and 2,6-dichlorobenzaldehyde (▲) over K_3PO_4. Reaction conditions: 2 mmol of benzaldehyde and/or 2 mmol of 2,6-dichlorobenzaldehyde; 5 mL of 2-propanol, 0.2 g of K_3PO_4 calcined at 600 °C and evacuated (10^{-3} mbar) at 350 °C, 80 °C, under N_2.

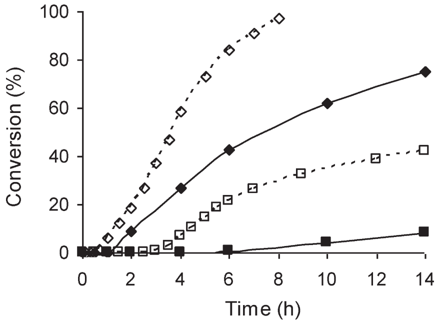


Figure 6. Conversion of benzaldehyde (◇) and acetophenone (□) and a mixture (2 mmol each) of benzaldehyde (◆) and acetophenone (■). Reaction conditions as in Figure 5.

the rate of reaction for each substrate was unaffected by the other substrate (Figure 5). It was expected that the rate of reaction of one species would be reduced because of competitive adsorption at the active sites of K_3PO_4. The observed independence of the reaction on the second component suggests that the catalytic transfer hydrogenation of benzaldehyde and 2,6-dichlorobenzaldehyde occurs at different sites on K_3PO_4. Similar observations were made for a mixture of benzaldehyde and 4-chlorobenzaldehyde.

In contrast, when an equimolar mixture of benzaldehyde and acetophenone was used, the reduction rate for both reactants decreased, consistent with a model of competitive adsorption on the surface (Figure 6). After 14 h, the benzaldehyde conversion in the mixture was 75% as compared to 97% after 8 h when it was the sole substrate. The reduction of acetophenone started only after 6 h when the conversion of benzaldehyde was already 84%. Even after 14 h, the acetophenone conversion was only 8.3%, which is about a fifth of the conversion observed when it was present alone. These results can be understood if one assumes that different basic sites are present at the surface of the solid K_3PO_4. For an activated molecule like 2,6-dichlorobenzaldehyde, sites of low basicity may be sufficient to catalyze the hydrogen transfer from 2-propanol. In contrast, nonactivated substrates such as benzaldehyde and acetophenone may need sites of higher basicity.

Reuse of K_3PO_4. Although K_3PO_4 is inexpensive and can be discarded after reaction, the possibility of reusing it was tested.

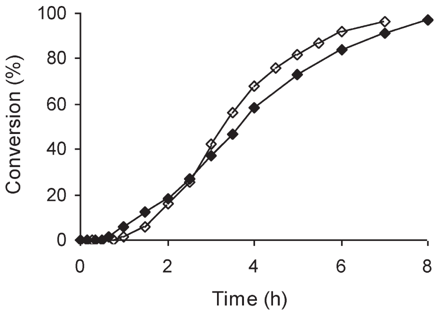


Figure 7. Catalytic transfer hydrogenation of benzaldehyde over (◆) fresh and (◇) regenerated K_3PO_4.

The solid base was recovered after reduction of benzaldehyde, washed with 2-propanol and recalcined at 600 °C. Its catalytic activity and the induction period were very similar to that of fresh K_3PO_4, and after 8 h, a conversion of 96% to benzyl alcohol was obtained (Figure 7). Reusing the catalyst will reduce waste, so that K_3PO_4 can be proposed as a green solid base catalyst for the catalytic transfer hydrogenation of aldehydes.

4. CONCLUSIONS

Potassium phosphate is an efficient solid base catalyst for transfer hydrogenation of aromatic aldehydes to the corresponding alcohols. The potassium phosphate must be pretreated at 600 °C for activation. TPD studies show that new, weaker basic sites are formed by this pretreatment. Substituted benzaldehydes with electron-withdrawing chloro- or nitro-groups have a higher rate of reaction than benzaldehyde or alkyl-substituted benzaldehydes. The reduction of ketones proceeded at a lower rate than for aldehydes. Studies with reactant pairs showed that in some cases different active sites were involved and the expected competitive inhibition on the rate of transfer hydrogenation for each reactant was not observed.

■ EXPERIMENTAL SECTION

Characterization Techniques. Potassium phosphate was obtained from Aldrich. The basicity of the sample was probed by TPD of CO_2. The sample was first pretreated in helium at 600 °C for 1 h before cooling down to room temperature. A flow of CO_2 was introduced to the sample for 0.5 h, followed by flushing in helium for 2 h to remove weakly adsorbed CO_2. The sample was then heated in helium from room temperature to 600 °C. A heating ramp of 10 °C min^{-1} was used. The evolved CO_2 was detected using an online quadrupole mass spectrometer. The CO_2 adsorption and desorption was repeated after the sample had been heated in helium at 600 °C for another 5 h. The surface area was determined after the TPD measurements by nitrogen adsorption using a Micromeritics Tristar 3000.

Catalytic Testing. The liquid chemicals were either used as received or distilled prior to use. K_3PO_4 was calcined at 600 °C in air for 5 h before use. The catalytic transfer hydrogenation was typically carried out using 2 mmol of the carbonyl substrate, 5 mL of 2-propanol as reductant, and 0.1 mmol of dodecane as internal standard. The mixture was placed in a two-neck round bottomed flask and heated under nitrogen to 80 °C whereupon 0.20 g of the calcined K_3PO_4 was added. Aliquots were removed at regular time intervals and analyzed by gas chromatography (Agilent 6890, HP 5 column). The identity of the products was confirmed by comparison with authentic samples and by gas chromatography−mass spectrometry. To test the reusability of K_3PO_4, the used sample was recovered by centrifugation after the reaction and washed with 2-propanol. After calcining at 600 °C for 5 h, it was used for another batch reaction.

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REFERENCES

(1) Smith, M. B., March, J. *March's Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*, 6th ed.; John Wiley & Sons: Hoboken, NJ, 2007.

(2) Stastná, E.; Cerný, I.; Pouzar, V.; Chodounská, H. *Steroids* **2010**, *75*, 721–725.

(3) Wu, X.; Xiao, J. *Chem. Commun.* **2007**, 2449–2466.

(4) Verley, A. *Bull. Soc. Chim. Fr.* **1925**, *37*, 537–542.

(5) Meerwein, H.; Schmidt, R. *Liebigs Ann. Chem.* **1925**, *444*, 221–238.

(6) Ponndorf, W. *Angew. Chem.* **1926**, *39*, 138–146.

(7) Creyghton, E. J.; Ganeshie, S. D.; Downing, R. S.; van Bekkum, H. *J. Mol. Catal. A: Chem.* **1997**, *115*, 457–472.

(8) De Graauw, C. F.; Peters, J. A.; van Bekkum, H.; Huskens, J. *Synthesis* **1994**, *10*, 1007–1017.

(9) Corma, A.; Domine, M. E.; Valencia, S. *J. Catal.* **2003**, *215*, 294–304.

(10) Ruiz, J. R.; Jiménez-Sanchidrian, C.; Hidalgo, J. M. *Catal. Commun.* **2007**, *8*, 1036–1040.

(11) Urbano, F. J.; Aramendia, M. A.; Marinas, A.; Marinas, J. M. *J. Catal.* **2009**, *268*, 79–88.

(12) Jyothi, T. M.; Raja, T.; Rao, B. S. *J. Mol. Catal. A: Chem.* **2001**, *168*, 187–191.

(13) Ivanov, V. A.; Bachelier, J.; Audry, F.; Lavalley, J. C. *J. Mol. Catal.* **1994**, *91*, 45–59.

(14) Kuno, H.; Takahashi, K.; Shibagaki, M.; Shimazaki, K.; Matsushita, H. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1943–1946.

(15) Liu, S. H.; Jaenicke, S.; Chuah, G. K. *J. Catal.* **2002**, *206*, 321–330.

(16) Kotani, M.; Koike, T.; Yamaguchi, K.; Mizuno, N. *Green Chem.* **2006**, *8*, 735–741.

(17) Zhu, Y.; Jaenicke, S.; Chuah, G. K. *J. Catal.* **2004**, *227*, 1–10.

(18) Chuah, G. K.; Jaenicke, S.; Zhu, Y. Z.; Liu, S. H. *Curr. Org. Chem.* **2006**, *10*, 1639–1654.

(19) Cha, J. S. *Org. Process Res. Dev.* **2006**, *10*, 1032–1053.

(20) Johnstone, R. A. W.; Wilby, A. H.; Entwistle, I. D. *Chem. Rev.* **1985**, *85*, 129–170.

(21) Baratta, W.; Rigo, P. *Eur. J. Inorg. Chem.* **2008**, *26*, 4041–4053.

(22) Sasson, Y.; Blum, J. *J. Org. Chem.* **1975**, *40*, 1887–1896.

(23) Gaikwad, A. V.; Boffa, V.; ten Elshof, J. E.; Rothenburg, G. *Angew. Chem., Int. Ed.* **2008**, *47*, 5407–5410.

(24) Liu, Z. S.; Rempel, G. L. *Chem. Eng. J.* **2009**, *147*, 366–372.

(25) Clapham, S. E.; Hadzovic, A.; Morris, R. H. *Coord. Chem. Rev.* **2004**, *248*, 2201–2237.

(26) Tao, R.; Xie, Y.; Ding, K.; Zhang, H.; Sun, Z.; Liu, Z. *J. Colloid Interface Sci.* **2010**, *351*, 501–506.

(27) Miecznikowski, J. R.; Crabtree, R. H. *Polyhedron* **2004**, *23*, 2857–2872.

(28) Jiménez, S.; López, J. A.; Ciriano, M. A.; Tejel, C.; Martínez, A.; Sánchez-Delgado, R. A. *Organometallics* **2009**, *28*, 3193–3202.

(29) He, L.; Ni, J.; Wang, L.-C.; Yu, F.-J.; Cao, Y.; He, H.-Y.; Fan, K.-N. *Chem.—Eur. J.* **2009**, *15*, 11833–11836.

(30) Zhao, M.; Yu, Z.; Yan, S.; Li, Y. *Tetrahedron Lett.* **2009**, *50*, 4624–4628.

(31) Enthaler, S.; Hagemann, B.; Erre, G.; Junge, K.; Beller, M. *Chem.—Asian J.* **2006**, *1*, 598–604.

(32) Yoshida, K.; Gonzalez-Arellano, C.; Luquec, R.; Gai, P. L. *Appl. Catal., A* **2010**, *379*, 38–44.

(33) Bäckvall, J. E. *J. Organomet. Chem.* **2002**, *652*, 105–111.

(34) Polshettiwar, V.; Varma, R. S. *Green Chem.* **2009**, *11*, 1313–1316.

(35) Ouali, A.; Majoral, J.-P.; Caminade, A.-M.; Taillefer, M. *ChemCatChem.* **2009**, *1*, 504–509.

(36) Qafisheh, N.; Mukhopadhyay, S.; Joshi, A. V.; Sasson, Y.; Chuah, G. K.; Jaenicke, S. *Ind. Eng. Chem. Res.* **2007**, *46*, 3016–3023.

(37) Lamblin, M.; Nassar-Hardy, L.; Hierso, J.-C.; Fouquet, E.; Felpin, F.-X. *Adv. Synth. Catal.* **2010**, *352*, 33–79.

(38) Popov, I.; Do, H. Q.; Daugulis, O. *J. Org. Chem.* **2009**, *74*, 8309–8313.

(39) Gerber, R.; Blacque, O.; Frech, C. M. *ChemCatChem.* **2009**, *1*, 393–400.

(40) Al-Shihry, S. S. *Molecules* **2004**, *9*, 658–665.

(41) Sodesawa, T.; Kimura, I. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2431–2432.

(42) Tada, A. *Bull. Chem. Soc. Jpn.* **1975**, *49*, 1391–1393.

(43) Higuchi, K.; Onaka, M.; Izumi, Y. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2016–2032.

(44) Chen, Z.-G.; Wang, Y.; Wei, J.-F.; Zhao, P.-F.; Shi, X.-Y. *J. Org. Chem.* **2010**, *75*, 2085–2088.

(45) Ekström, J.; Wettergren, J.; Adolfsson, H. *Adv. Synth. Catal.* **2007**, *349*, 1609–1613.

(46) Voronin, V. I.; Ponosov, Yu. S.; Berger, I. F.; Proskurnina, N. V.; Zubkov, V. G.; Tyutyunnik, A. P.; Bushmeleva, S. N.; Balagurov, A. M.; Sheptyakov, D. V.; Burmakin, E. I.; Shekhtman, G. Sh.; Vovkotrub, E. G. *Inorg. Mater.* **2006**, *42*, 908–913.