The promoting effects of CO_2 and H_2O on selective hydrogenations in CO_2/H_2O biphasic system

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The combination of CO_2 and H_2O as green solvents has been used extensively in chemical reaction and attracted much attention. The conversion and/or selectivity could be improved in the presence of both CO_2 and H_2O. In this paper, the promotion effects of CO_2 and H_2O on the selective hydrogenation reactions are shortly reviewed.

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Introduction

Utilization of green solvents is an important theme of green and sustainable chemistry. In recent years, use of compressed CO_2 and H_2O as green solvents has been studied extensively not only because both CO_2 and/or H_2O are non-toxic, nonflammable, abundant, cheap, renewable and easy to handle, but also due to they are efficient promoters in the organic catalysis reactions [1–4]. The combination of CO_2 and H_2O has attracted much attention, as the dissolution of CO_2 into H_2O will add acidic nature of the reaction solution [5,6] and this may affect the chemical reactions therein. Moreover, at the high pressure, the compressed CO_2 will dissolve into the organic phase and which will enhance the concentration of H_2 in the solution and thus dilutes the other reacting species. Furthermore, CO_2 and H_2O molecules may have interactions with reactant, intermediates and catalyst, and then modify the substrate reactivity and the product selectivity. Thus, the presence of dense phase CO_2 and H_2O will present a significant influence in the liquid-phase chemical reactions through different ways (Scheme 1) and such functions play in the catalysis selective hydrogenation reactions will be reviewed in this paper.

Acidity of the combined media of CO_2 and H_2O

In the hydrogenation of acetophenone over Pd/C, the efficiency of solvent is in order of H_2O > MeOH > EtOH > heptane ~ solventless. When introduction of 0.8 MPa CO_2 into the reaction system, the conversion increased significantly in H_2O, MeOH and EtOH solvents, and the largest conversion presented in 0.8 MPa CO_2/H_2O. The conversion in 0.8 MPa CO_2/H_2O (70%) was close to that obtained in aqueous acetic acid solution at the similar pH value of 3, which indicates that the acidity of CO_2/H_2O is an important factor in the improvement of the hydrogenation of acetophenone. It was suggested that the enhancement of reaction rate with addition of CO_2 to the aqueous solution or acetic acid was ascribed to the interaction between the oxygen atom of acetophenone with H^+ [7]. However, by contrast, in the hydrogenation of acetophenone catalyzed with Rh/C and Rh/Al$_2$O$_3$ catalysts, the pressurized CO_2 did not show any improved effect in CO_2/H_2O system, which is described to the serious catalyst deactivation by strong adsorption of CO which was formed in-situ from CO_2 and H_2 on the surface of Rh/C and Rh/Al$_2$O$_3$ catalysts, this counteracted the positive effect of acidity generated from CO_2 and H_2O [8].

For the aqueous hydrogenation of benzaldehyde and benzyl alcohol catalyzed over Ru/MCM-41 catalyst, cyclohexanemethanol was produced as main product and its yield increased significantly with the addition of 3 MPa CO_2 into the reaction system due to the increase in the acidity [9]. The similar effect was also reported for the hydrogenation of benzaldehyde to benzyl alcohol over Pd/C catalyst, the yield of benzyl alcohol increased from 46.4% to 65.6% with an increase in CO_2 pressure up to 5 MPa [10]. However, for the hydrogenation of benzoic acid, the reaction rate decreased with addition of 3 MPa CO_2 into H_2O, in which the dilution effect is predominant and the acidity of solution is discarded as the pH value of the saturated solution of benzoic acid is about 3, which is not varied with the addition of compressed CO_2 [9]. In the hydrogenolysis of benzyl alcohol to toluene over Pd/C catalyst, the conversion increased largely with addition of 1 MPa CO_2 compared to the value obtained in the absence of CO_2, and then it maintained consistently with the further increasing CO_2 pressure to 3 MPa. The acidity increases initially with addition of CO_2, while it then increases slightly at above 1 MPa with further increasing CO_2 pressure [11].

Scheme 1
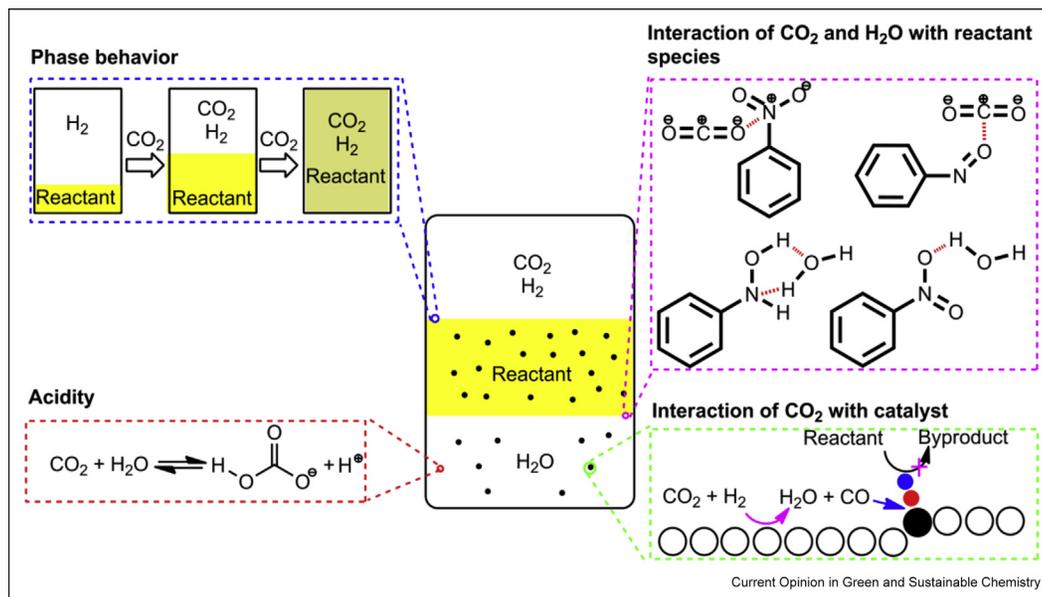
The possible promoting effects of CO_2 and H_2O in biphasic selective hydrogenations in CO_2/H_2O system.

When the hydrogenation of diphenyl ether (DPE) was carried out in compressed CO_2 and H_2O, the conversion reached 100% and it did not change within 7−18 MPa CO_2, but the product selectivity changed remarkably. The authors suggested that, at the pressure region of 7−12 MPa, the major product of cyclohexanol was produced by two steps: firstly the hydrolysis of DPE to produce phenol, then the further hydrogenation of phenol to cyclohexanol. The acidity produced by the combination of CO_2 and H_2O is important for the present reaction, it can promote the cleavage of the C−O bond in DPE molecule. At the pressure region of 12−18 MPa, the selectivity to major product of cyclohexanol decreased due to the increase in the solubility of DPE, dilution effect occurred and so lowered the hydrolysis of DPE. When the hydrogenation of DPE reaction was carried out separately in single CO_2 or in pure H_2O, dicyclohexyl ether was produced as the major product via the hydrogenation of the aromatic ring [12,13]. The similar result also presented in the hydrogenation of DPE in the CO_2 expanded organic solvents like EtOH, MeOH, PrOH, THF and hexane [14].

The effects of H_2O and CO_2 were also reported for the selective hydrogenation of benzonitrile, benzyl cyanide, 2-phenylethyl cyanide and hexanenitrile over Pd/Al_2O_3 in solventless, n-hexane, and toluene [15−17]. In these reactions, the objective product of primary amine was not detected or produced very less, however, when addition of CO_2 and H_2O, the primary amine was produced significantly although the conversion was decreased. Thus the coexistence of H_2O and CO_2 is indispensable for the high selectivity of primary amines produced in the hydrogenation of nitriles [16]. In the presence of CO_2, the carbamate salt [18], and bicarbonate or carbonate salt species will be formed, which could prevent the further reaction of primary amine with imine (intermediate) to the secondary amine, resulting in a high yield of primary amine.

Phase behavior in the presence of CO₂

In the hydrogenation of cinnamaldehyde (CAL) with $RuCl_3$/TPPTS catalyst, the much better conversion (38%) was obtained in 18 MPa CO_2/H_2O biphasic system with comparing to that (11%) in the toluene/H_2O biphasic system, since mass transfer resistance in supercritical CO_2/H_2O is lower than that in toluene/H_2O [19]. However, with increasing CO_2 pressure, the total conversion of CAL decreased marginally in the three-phase ($CO_2 + H_2$ gas, CAL liquid, H_2O) region but it decreased significantly in the two-phase ($CO_2 + H_2 + $ CAL gas, H_2O) region. At the elevated CO_2 pressures, the mole fraction of either CAL or H_2 decreased significantly, resulting in decreased conversion [20].

In the hydrogenation of 5-hydroxymethylfurfural over Pd/C in CO_2−H_2O, H_2O or scCO_2 media, almost complete conversion was achieved but the product distribution was largely different, depending on the solvent used. The 5-methy-2-furanmethanol (MFM, 95.8%) was mainly produced in pure H_2O and tetrahydro-5-methyl-2-furanmethanol (MTHFM, 95.3%) was produced in 10 MPa CO_2. In CO_2/H_2O, the selectivity of

2,5-dimethylfuran (DMF) increased to 100% with CO_2 pressure up to 11 MPa, then decreased due to the further hydrogenation of furan ring of DMF. The acidity of CO_2/H_2O is not the crucial factor for the formation of DMF due to that a low selectivity of DMF (26.1%) was obtained in aqueous acetic acid with the same pH value. The molar ratio of H_2O/CO_2 and the change of phase behavior with CO_2 pressure play important roles in determining the product distribution [21]. In the hydrogenation of furfural to furfuryl alcohol and in the further hydrogenation of furfuryl alcohol to tetrafurfuryl alcohol over Pd/C, the effect of CO_2 is significant with introduction of CO_2 into H_2O, but not into MeOH and n-heptane. In H_2O, the conversion increased with CO_2 pressure up to 10 MPa, the authors suggested that the interaction between oxygen atom of furan ring with H^+ proton generated from CO_2/H_2O may promote the adsorption of furfural on active Pd sites, resulting in the enhancement of reaction rate [22]. However, the pH values were almost constant over 1 MPa CO_2 at the same temperature, the conversion of furfural increased from $\sim$48% to 50% with increasing CO_2 pressure to 1 MPa, and it increased further to $\sim$80% with increasing CO_2 pressure to 10 MPa. So the acidity generated by CO_2/H_2O system is an important factor to influence the reaction rate, besides, the change of phase behavior with CO_2 pressure may play an important role also.

Intermolecular interactions of CO_2 or H_2O with reacting species and catalyst

Selective hydrogenation of nitrobenzene (NB) was studied over Ni/Al_2O_3 in compressed CO_2/H_2O. The conversion increased from 6% to 56% with introduction of 0.8 MPa CO_2 into H_2O. However, the pressurization with CO_2 has a drastically negative impact in EtOH and a slightly positive effect in n-hexane. The selectivity to aniline was almost 100% in the presence of CO_2 in the hydrogenation of NB. The molecular interaction was studied and the N$-$O bond of N-phenylhydroxylamine (PHA) is weakened through the interaction with H_2O [23]. The interactions of CO_2 with the reactant or intermediate compounds in the reaction decreased the reactivity of NB but increased that of nitrosobenzene (NSB) and PHA [24]. The rate of hydrogenation followed the order of PHA > NB > NSB, indicating that NB transforms to PHA directly and this step is the rate-determining one in CO_2 and H_2O. The interactions of CO_2 and H_2O with the reacting species changed the reaction process and promoted the selective hydrogenation of NB to aniline [23]. The compressed CO_2/H_2O is also effective for the hydrogenation of chloronitrobenzene [23,25] due to the interactions of CO_2 and H_2O with the reacting species [25,26].

For the hydrogenation reaction in CO_2/H_2O solvent, CO is generally produced over the Pt-group metal catalysts (Pt, Pd, Ru, Rh) [27$-$33]. In the hydrogenation of NB

to p-aminophenol (PAP) over Pt/Al_2O_3 in CO_2/H_2O, the direct hydrogenation of NB to PHA is the rate-determining step, and the rearrangement of PHA to PAP and the hydrogenation of PHA to aniline are competitive reactions, the rearrangement reaction was accelerated as the increase in acidity [34] and the hydrogenation reaction was prohibited due to the in-$situ$ generated CO in the hydrogenation in CO_2/H_2O solvent was preferentially adsorbed on the stepped and kinked sites, resulting in an increase in the selectivity to PAP (68.9%) [35]. The efficiency of CO_2/H_2O for the hydrogenation of NB to PAP without addition of solid or liquid acid was also reported over Pt$-$Sn, and Pt$-$Pb catalysts [36,37].

In the hydrogenation of levulinic acid to γ-valerolactone with $RuCl_3$/PPh_3 catalyst, the presence of formic acid and base could promote the reaction smoothly, in which the produced CO_2 from the decomposition of formic acid play an important role [38]. Both the acidity and molecular interactions of CO_2 with levulinic acid presented less influence on the reaction, however, the molecular interaction of CO_2 with $RuCl_2(PPh_3)_3$ is very significant due to $RuCl_2(PPh_3)_3$ could be changed to a more active $RuHCl(CO)(PPh_3)_3$ species in the presence of CO_2 and H_2 [39].

Conclusions

In this short review, the effectiveness of CO_2 and H_2O in the hydrogenation reactions were described, the change of acidity and phase behavior with CO_2 pressure and interaction of CO_2 and H_2O with substrate, intermediates, and catalyst are the main factors in influencing the reaction rate and product distribution, and the effective degree will be different depending on the substrate, catalyst, and reaction conditions. It is still an interesting and important research topic to study the function of CO_2 and H_2O in chemical reaction, as it is a green sustainable chemical process.

Acknowledgements

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