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A comparative study of supported aqueous– and ethylene glycol–phase catalysts in stilbene hydrogenation: Influence of the different modes of dispersion of supported liquids

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Abstract

Supported liquid phase catalysts (SLPC) containing water-soluble Pd complexes were used for hydrogenation of stilbene in toluene. When water is loaded on a silica gel support, the catalytic activity of SLPC increases with the amount of the water. In contrast, when ethylene glycol (EG) is used as the supported liquid, the activity does not depend on the amount of EG loaded. These results can be explained by differences in the mode of dispersion of the supported liquids over the support.

Keywords: supported liquid phase catalyst, metal complex, hydrogenation, catalyst preparation, palladium.

1. Introduction

Homogeneous organometallic catalysts have greater activity and selectivity in comparison to conventional heterogeneous catalysts [1]. However, homogeneous catalysts have a drawback in the catalyst separation and recycling. Davis and co-workers proposed the idea of supported liquid phase catalyst (SLPC), which is one of the methods that can overcome the drawback of the homogeneous catalysts [2–8]. In SLPC, thin polar liquid film such as water and ethylene glycol containing water-soluble organometallic complexes is supported on a hydrophilic high surface area solid such as silica gel or porous glass. The SLPC is used in a solvent immiscible with the film liquid and can be easily separated by simple filtration. A frequently used ligand for the complexes is triphenylphosphine trisulfornate sodium salt (TPPTS). Another advantage is that SLPC has a high liquid-liquid (bulk solvent) interfacial area that arises from the high surface area of the support. This is significant because overall reaction rates in biphasic systems are sometimes limited by low liquid–liquid interfacial areas and it is difficult to increase this area by mechanical agitation [9]. The concept of SLPC is well proven in the cases of hydroformylation [2–5,10–16], hydrogenation [6–8,17–20], Heck reactions [21–28] and alkylation [29]. Recently, it has also been reported that simultaneous use of two types of SLPC samples can give bi-functional catalyst systems, which are sometimes difficult to obtain by the use of mixtures of homogeneous or biphasic metal complex catalysts because of undesired negative interactions between the different metal complexes [19].

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Since reactions using SLPC are heterogeneous systems and are considered to proceed at the interface between the supported film and the reaction solvent, the overall reaction rate should depend on not only the intrinsic activity of metal complexes and on the reaction conditions used but also on such catalyst preparation variables as the quantity of liquid film and the concentration of metal complexes in the film. The present authors investigated the influence of those factors for the Heck reaction with SLPC containing palladium-TPPTS complexes using ethylene glycol (EG) as the supported film (Pd-SLPC-EG) [27,28]. It was found that the activity of Pd-SLPC-EG depends only on the concentration of the Pd-TPPTS complexes in the supported EG film, while the quantity of the supported film has no effect on the activity (Fig. 1). In contrast, the activity of SLPC containing ruthenium-TPPTS complexes using water as the supported film (Ru-SLPC-W) for the hydrogenation of *trans*-cinnamaldehyde depends not only on the complex concentration in the supported film but also on the quantity of the film (Fig. 1) [20]. The most plausible explanation for the difference between Pd-SLPC-EG and Ru-SLPC-W should invoke a difference in the state of dispersion of the two supported liquid films. However, the metal complexes employed and the reactions examined were different in those studies. Needless to say, these factors should be the same for the comparison to be significant. As the follow-up of these works, Pd-TPPTS complexes and hydrogenation of stilbene to bibenzyl were chosen and the influence of the supported liquids of water and EG on the catalytic performance of Pd-SLPC has been compared and further investigated in the present work. In the literature there are several previous works on the effects of the amount and/or the kind of supported liquids on the catalytic

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performance of SLPC [3, 7, 8, 10–15, 20, 22, 27–29]. The present authors will propose different modes of dispersion of water and EG over a silica gel support, which should be responsible for differences in the dependence of the overall rate of stilbene hydrogenation on the amounts of liquid phases loaded for the two liquids.

Figure 1

2. Experimental

Two series of SLPC samples containing Pd-TPPTS complexes were prepared using water (designated as Pd-SLPC-W) or EG (Pd-SLPC-EG) as a dispersed phase and a silica gel (Aldrich Davisil grade 646) as a support. This gel has a BET surface area of 294 m^2/g, an average pore diameter of 20 nm and a total pore volume of 0.98 cm^3/g. Desired amounts of the liquid, palladium acetate and TPPTS were added into a vessel and mixed at 60 ℃ for 1 h in ambient atmosphere to prepare Pd-TPPTS complexes. Its formation was ascertained from a change in color to dark brown. After this pretreatment, the silica gel was added to the vessel and mixed well with the Pd-TPPTS solution using a spatula. Then, the obtained mixture was moved from the vessel to a 100 cm^3 autoclave and 20 cm^3 of toluene was added. The suspension was stirred at room temperature in order for the liquid phase to contact with and disperse well on the surface of silica gel. For all the SLPC samples prepared, the concentration of palladium in the supported liquid was fixed to 50 μmol/cm^3. Similarly, the molar ratio of TPPTS/palladium was always

fixed to 4.

After the catalyst preparation, 40 cm^3 of toluene and 24 mmol of stilbene were added to the autoclave. After purging with hydrogen three times at atmospheric pressure, the autoclave was heated to 40 °C and hydrogen was further introduced up to 2 MPa under stirring. When the hydrogen pressure reached to the desired value, the reaction time was measured. During the reaction, small amounts of the reaction mixture were sampled at desired intervals and analyzed using gas chromatography. The reaction rate was determined from the decrease in the substrate concentration during the initial 20 min [20].

The state of dispersion of water and EG loaded on the support (in the absence of metal complexes) was examined by adsorption of *trans*-cinnamaldehyde (CAL) from toluene at room temperature in the same manner as used previously [20]. The CAL molecules can be adsorbed only on the bare surface of support but not onto the supported liquid phases. This adsorption was carried out at room temperature using a 50 cm^3 reactor. Two grams of silica and a certain volume of water or EG were mixed well in the reactor in the same way as used in the preparation of the SLPC samples. Then, 10 cm^3 toluene and 4.8 mmol CAL were charged into the reactor. After leaving the mixture for 30 min under stirring, the amount of CAL adsorbed by the silica sample was determined from the decrease in the concentration of CAL in the toluene phase. The adsorption of stilbene was also tried, but the amount of stilbene adsorbed was very small and so it was not significant for the present purpose.

3. Results and Discussion

Pd-SLPC-W and Pd-SLPC-EG produced only bibenzyl as the product of the hydrogenation of stilbene under the present reaction conditions. Figure 2 shows the influence of the quantity of supported liquids on the activities of Pd-SLPC-EG and Pd-SLPC-W, in which the concentration of Pd complexes in the supported liquid phases was the same (50 μmol cm^{-3}) irrespective of the amounts of the liquids used. The activity of Pd-SLPC-EG does not depend on the amount of EG loaded although the total amount of Pd-TPPTS complexes increases. In contrast, the activity of Pd-SLPC-W increases with the quantity of water supported. In separate runs, the solubility of stilbene in water and EG and the adsorption of stilbene on the bare silica support were measured at room temperature. It was found that no detectable stilbene was dissolved in water and adsorbed on the support, and that a trace amount of stilbene was dissolved in EG; however, its concentration in EG was very low (3 μmol/cm^{3}). This value was far below the stilbene concentration (400 μmol/cm^{3}) in toluene for the reaction runs. Thus, the fraction of the substrate dissolved in the supported liquid phases can be neglected; hence, the hydrogenation is considered to proceed at the interface between the supported liquid and the reaction solvent of toluene. These results strongly suggest that the modes of the liquid dispersion over silica are different between water and EG. As described above (Fig. 1), similar changes of the reaction rate with the quantity of the supported liquid characteristic to EG and water were previously observed for the Heck reaction with Pd-SLPC-EG [28] and for the CAL hydrogenation with Ru-SLPC-W [20], respectively. Hence, the difference in the dependence of Fig. 2 may

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intrinsically result from the different nature and behavior of the two supported liquids of water and EG over the silica surface.

Figure 2

The influence of liquid loading was examined by other research groups for hydroformylation [3, 11–15], hydrogenation [7,8], Heck coupling [22] and alkylation [29]. For example, Delamas and co-researchers indicated that a maximum activity of Rh-SLPC-W for hydroformylation occurred before the pore volume of the support material was fully filled with water [14]. However, those previous experiments were carried out at the conditions where the total amount of the metal complexes was kept constant; that is, the concentration of the metal complexes in the supported liquid was changed. So, the direct comparison of those previous results with the present ones is difficult.

The differences between water and EG were indicated by Wan and Davis, who prepared a SLPC sample in which the active species, [Ru(BINAP-4SO$_3$Na)(benzene)Cl]Cl, existed in EG supported on a controlled pore glass [22, 23]. The SLPC so prepared was active for asymmetric synthesis of naproxen and the use of EG is important. When water is used as a supporting liquid, a lower enantioselectivity is obtained, because the water affects the structure of active metal complexes in the dispersed liquid phase. Such results suggested that a rapid hydrolysis of the ruthenium–chloro bond occurred in the presence of water. These authors also showed that the

enantioselectivity increased with the quantity of EG used and they speculated that this could be ascribed to the increasing rotational mobility of the ruthenium complex in the liquid phase. The importance of the metal complex mobility for the Heck reaction was also suggested by Mirza et al. [22]. However, it should be noted again that both the groups carried out the reactions at constant total amounts of the metal complexes. In the present study the concentration of palladium was fixed at 50 μmol/cm^3 and the mobility of the metal complex in the liquid phases would not be important to explain the results of Fig. 2 (and Fig. 1 as well), in which the activity of Pd-SLPC-EG does not increase with the increasing amount of the liquid loaded.

To investigate the state of the supported liquid, we carried out the adsorption of CAL with the silica gel samples on which water or EG was loaded in various amounts in the absence of Pd complexes. The adsorption of stilbene on the bare silica support was also examined but no detectable adsorption was observed, so stilbene was not usable for the present purpose. Figure 3 plots the amount of CAL adsorbed against the amount of water or EG loaded. One gram of water (or EG) – free silica can adsorb 0.56 mmol of CAL. The amount of CAL adsorbed decreases nearly proportional to the amount of water loaded and reaches zero at around 1 cm^3/g of water loaded, at which the entire pore of silica is filled up with water. These observations suggest that the surface area of silica covered with water is nearly proportional to the amount of water and that CAL is selectively adsorbed on the bare silica surface. When EG is loaded on silica, the decrease in the amount of CAL adsorbed is larger than that caused by water. The loading of 0.1 cm^3/g EG (about one tenth of the total pore volume of silica) causes the amount of CAL

adsorbed to decrease drastically. At a loading level of 0.5 cm^3/g, it is less than 10% of that on

EG-free silica. These observations suggest that EG spreads over the silica surface more broadly

than water when compared at the same loading.

Figure 3

On the basis of the CAL adsorption measurements, the dispersion modes of water and EG

can be schematically illustrated as in Fig. 4. Water is supported in the form of islets on the silica

surface. When the quantity of water is increased, the islets grow in size (and may coalesce

sometimes) but the thickness of the islets remains unchanged. Consequently, the water–toluene

interfacial area increases. Thus, the catalytic activity of Pd-SLPC-W increases with the quantity

of water. On the other hand, EG is supported in the form of a thin film of a certain thickness on

silica. When the quantity of EG is increased, the EG–support contact area does not change so

much but the thickness of the EG film increases. Hence, the EG–toluene interfacial area does not

change when the quantity of EG changes. Thus, the catalytic activity of Pd-SLPC-EG changes

little with the quantity of EG (Figs. 1 and 2).

Figure 4

The concentration of Pd-TPPTS complexes in the supported liquids was the same for all the

experiments of Fig. 2. So, the turnover frequency (TOF) of Pd-SLPC-EG based on the total number of Pd atoms decreased with the increasing quantity of EG supported, as seen in Fig. 2(b). On the other hand, the TOF value of Pd-SLPC-W did not change so much with the amount of the supported water. From the viewpoint of TOF, a smaller amount of EG is better; thus the efficiency of the Pd-TPPTS complexes in EG is higher for the title reaction than that in water when a smaller amount of supported liquid (0.25 cm^3/g) is used (Fig. 2).

In conclusion, the present study demonstrates that the catalytic activities of Pd-SLPC-W and Pd-SLPC-EG for the stilbene hydrogenation depend on the quantity of the supported liquids in different fashions. This dependence can be explained by the difference in the mode of dispersion of the supported liquids. For the present reaction system, a certain small amount of EG is a better choice from the viewpoint of TOF. Generally speaking, for the choice of a suitable supported liquid, one should take into account the solubility and the diffusiveness of substrates (including gaseous substrates such as hydrogen and oxygen) in the supported liquid phase, which would influence the overall reaction rate. Additionally, the stability of the dispersed liquid phase should be considered. Reaction temperature higher than the boiling point of the supported liquid may cause the destruction of the liquid film, and the supported liquid itself may react with substrates and/or products, resulting in disappearance of the film. After choosing the supported liquid, one should optimize the catalyst preparation variables. To do this, the results obtained in the present study will be of significance.

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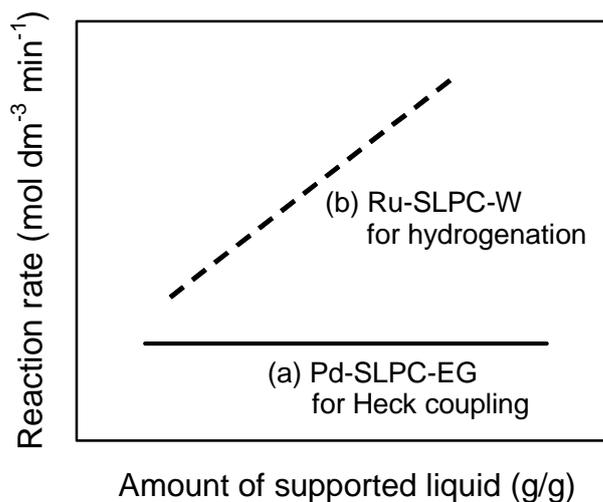
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Figure captions

Fig. 1.   A scheme for the relationship between the reaction rate (per unit volume of reaction mixture) and the amount of supported liquid (per unit weight of support) as observed previously for (a) Heck coupling with Pd-SLPC-EG [26] and (b) hydrogenation with Ru-SLPC-W [19], in which different metals and liquids are used with the same porous silica support. For those reaction runs, the amount of supported liquids used was changed while keeping the amount of bulk solvent (toluene), the weight of SiO_2 support, and the concentration of active species in the supported liquid phases unchanged.

Fig. 2.   Influence of the amount of supported liquid on the catalytic activities of Pd-SLPC-W and Pd-SLPC-EG for stilbene hydrogenation. Reaction conditions: Pd, 0.05 mmol/cm^3; silica, 1 g; stilbene, 24 mmol; toluene, 60 cm^3; H_2, 2 MPa; temperature, 40 °C.

Fig. 3.   Influence of the amount of supported liquid on the adsorption of CAL on silica. (The details of procedures are given in the text.)

Fig. 4.   Schemes for the dispersion modes of water and EG over the silica support. Metal complexes exist in the water and EG phases. ST and BB denote stilbene and bibenzyl dissolved in toluene, respectively.

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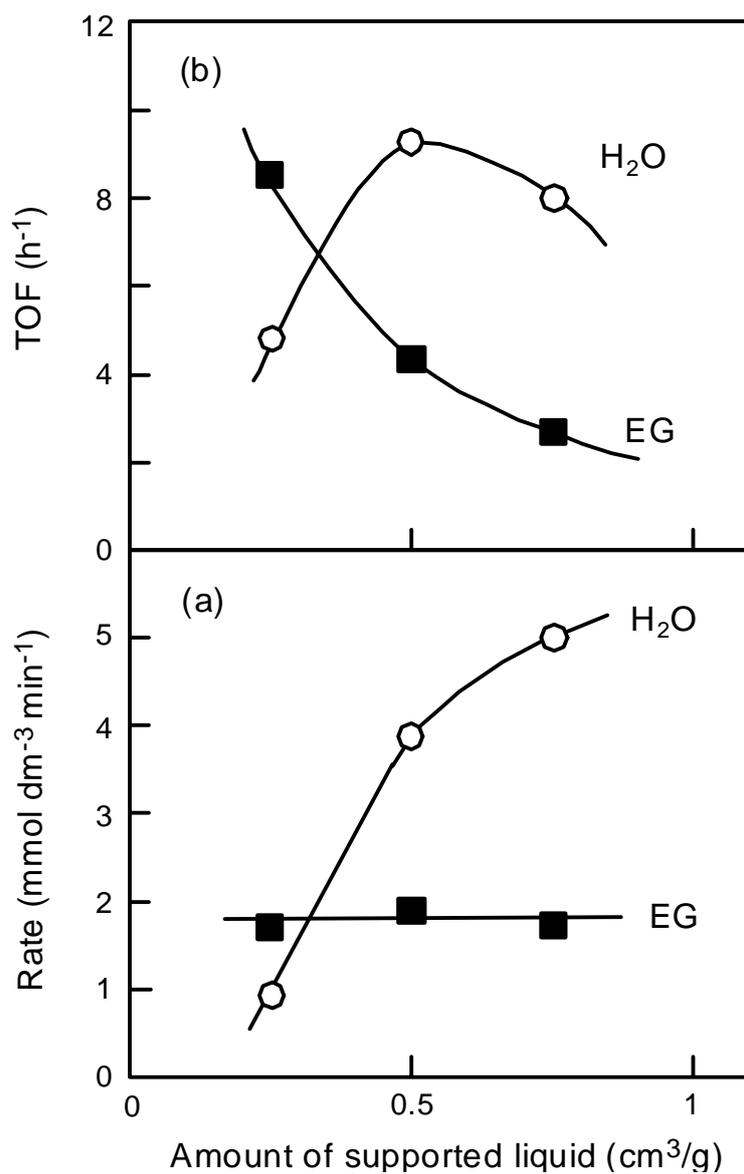
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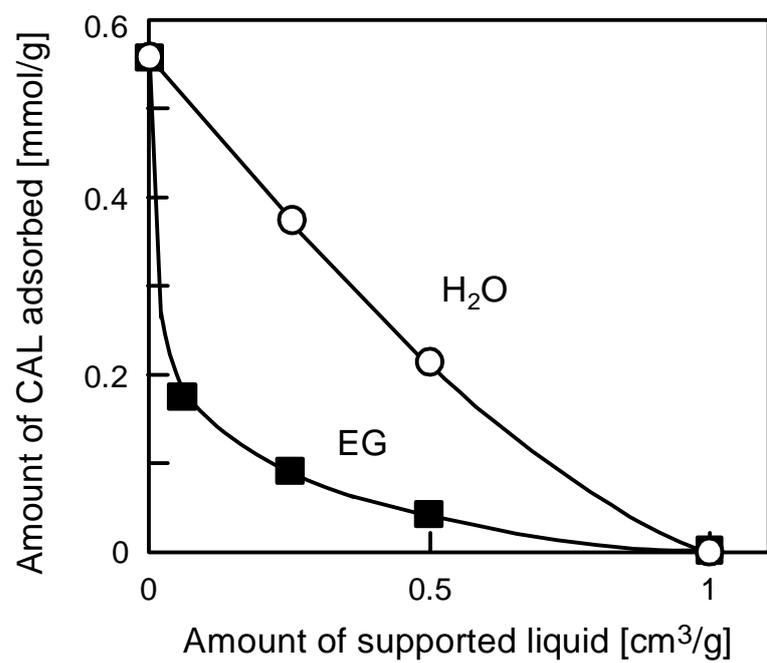
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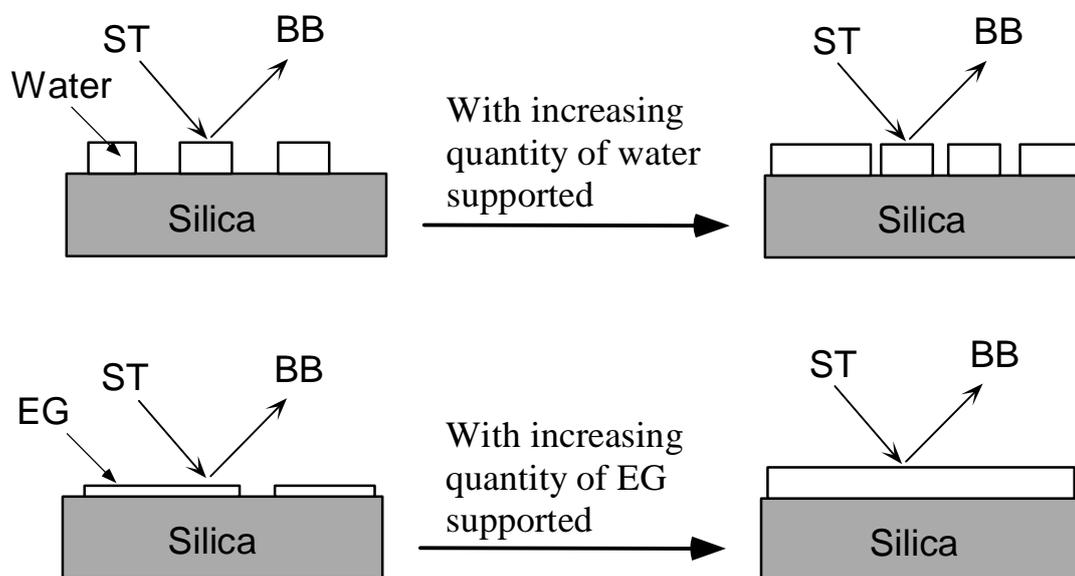
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