

Supplementary Materials: About solid phase vs. liquid phase in Suzuki-Miyaura reaction

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Table S1. Hot filtration test (Split test).

Hot filtration test (Split test)	
Description: Separation between Solid (S) and Liquid (L) phases & verification of activity (conversion) inside the homogeneous phase.	
Main hypothesis: Liquid phase contains homogeneous active species that catalyze the reaction.	
Possible Results	Possible conclusions
No change of activity after separation	Homogeneous catalysis
Homogeneous activity is higher than zero	Both mechanisms (need further verification)
No activity	Possible heterogeneous (need further verification).
Side hypothesis: No homogeneous activity because of lost (or deactivation) of homogeneous active species.	
Complimentary methods & analysis:	
<ul style="list-style-type: none"> - ICP analysis (at ppb level) for homogeneous phase before & after separation. - ICP analysis for possible adsorption of Pd at filter. - Poisoning method to check if there is homogeneous active species before separation. - Solid phase analysis (TEM) for any changes of the catalyst surface. 	
Advantages	Drawbacks
Easy and rapid to perform. Clear conclusion if the result is positive. No need for specific tools.	Many possible interpretations for negative results.

Table S2. Pd trace-analysis.

Pd trace-analysis	
Description: Analyze of homogeneous phase for Pd species (ICP, AAA)	
Main hypothesis: Leaching of homogeneous species into the solution.	
Possible Results	Possible conclusions
Detection of Pd species	Leaching of Pd into the solution
No Pd inside solution	Need further verification
Side hypothesis:	
<ul style="list-style-type: none"> - Pd concentration lower than the detection limit of analysis method. - Pd readsorbed into the support. 	
Complimentary methods & analysis:	
<ul style="list-style-type: none"> - Use of ICP-MS (ppb level). - Always use the ICP as a complimentary method with other tests. - Make analysis at different conversions (lower than 100%). - Solid analysis before and after reaction. 	
Advantages	Drawbacks
Give the quantity of Pd inside solution.	Need specific tools. No information about the homogeneous or heterogeneous activity of Pd. Leached species may be inactive.

Table S3. Reusability test.

Reusability test	
Description: Make several runs with same solid catalyst at the same experimental conditions.	
Main hypothesis: Constant activity If the catalysis is heterogeneous.	
Possible Results	Possible conclusions
Constant (or fluctuating) activity.	Possibly heterogeneous (further analysis required (F.A.R.))
Continual decrease of activity	Possibly homogeneous (F.A.R.)
Side hypothesis:	
<ul style="list-style-type: none"> - Catalyst worked for small TON. - Pd redeposit at the end of reaction. - Loss of solid. 	
Complimentary methods & analysis:	
<ul style="list-style-type: none"> - Check the higher possible value of TON. - Make run at conversion lower than 100% (50% for example). - Continually check the mass of solid catalyst. - Analyze solid phase at the end (TEM, ICP). - Analyze homogeneous phase (ICP). 	
Advantages	Drawbacks
Easy to perform. No specific tools.	Many possible conclusions. Need further methods & analysis to conclude.

Table S4. Compartmented reactor with membrane.

Compartmented reactor with membrane	
Description: Two reactors (one with catalyst & other without) separated with nanoporous membrane.	
Main hypothesis: Homogeneous mechanism if activity inside the second reactor without solid catalyst	
Possible Results	Possible conclusions
Same activity (conversion) in both reactors.	Homogeneous mechanism
No activity inside the second reactor	Possibly heterogeneous (F.A.R.)
Lower activity inside second reactor	Possibly both (F.A.R.)
Side hypothesis:	
<ul style="list-style-type: none"> - Catalyst adsorption on membrane. - Pd redeposition on the initial support. - Deactivation of homogeneous Pd species. 	
Complimentary methods & analysis:	
<ul style="list-style-type: none"> - Membrane analysis for any possible Pd deposit. - Homogeneous poisoning method for any homogeneous activity. - ICP-MS analysis for any Pd inside second reactor. 	
Advantages	Drawbacks

Qualitative conclusion	Difficult to perform & need specific tools.
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Table S5. Continuous compartmented operation (Split flow test).

Continuous compartmented operation (Split flow test)	
Description: Two reactors (first with catalyst & second without) separated by filter.	
Main hypothesis: Homogeneous contribution if conversion increases inside the second reactor	
Possible Results	Possible conclusions
Same activity inside both reactors.	Homogeneous mechanism
No activity inside the second reactor	Possibly heterogeneous (F.A.R.)
Lower activity inside second reactor	Possibly both (F.A.R.)
Side hypothesis:	
<ul style="list-style-type: none"> - Possible catalyst rapid deactivation or readsorption inside the first reactor. 	
Complimentary methods & analysis:	
<ul style="list-style-type: none"> - Check for possible catalyst deactivation (add active species stabilizers) - ICP analysis for solid & liquid phases. - Use of mathematical models. 	
Advantages	Drawbacks
Easy to perform. Work on steady state. Possible distinction of homogeneous & heterogeneous contributions using model.	Difficult to conclude if there is no activity inside the empty (second) reactor.

Table S6. 3-Phase-test.

3-Phase-test	
Description: Bond of a reagent to a support & see its conversion with solid precursor.	
Main hypothesis: Homogeneous mechanism if the desired product was detected.	
Possible Results	Possible conclusions
Complete activity	Homogeneous mechanism
No activity	Possible heterogeneous (F.A.R.)
Small activity	Possible both (F.A.R.)
Side hypothesis:	
<ul style="list-style-type: none"> - Side reaction (reagent conversion to undesired products). - Short lifetime of active species. 	
Complimentary methods & analysis:	
<ul style="list-style-type: none"> - Check for possible catalyst deactivation (add of active species stabilizers) - ICP analysis for solid & liquid phases. - Use excess of base and boronic acid. 	
Advantages	Drawbacks
Clear conclusion if result is positive	Competition with side reaction. No conclusion for negative results.

Table S7. Poisoning tests.

Poisoning tests	
Description: Use of poison that deactivate the catalyst at a desired form.	
Main hypothesis: clear conclusion if the poison doesn't stop the reaction	
Possible Results	Possible conclusions
No effect after adding the poison	Homogeneous (if Hg for example) mechanism.
No activity	Cannot conclude (F.A.R.)
Small activity	Possible both (F.A.R.)
Side hypothesis:	
<ul style="list-style-type: none"> - The poison can change the reaction conditions (viscosity, T (°C)). - The poison is not selective. 	
Complimentary methods & analysis:	
<ul style="list-style-type: none"> - Always use the poisoning test as a complimentary method with other tests. 	
Advantages	Drawbacks
Clear conclusion if result is negative Easy to perform.	Many possible interpretations if the poison stops the reaction.

Table S8. Microscopy (TEM).

Microscopy (TEM)	
Description: Take images of catalyst before & after the reaction	
Main hypothesis: If there are no variation of the catalyst surface (distribution & sizes) the catalysis is heterogeneous	
Possible Results	Possible conclusions
No variation of catalyst surface	Possible Heterogeneous mechanism (F.A.R.)
Variation of catalyst surface	Possible Homogeneous mechanism (F.A.R.)
Side hypothesis:	
<ul style="list-style-type: none"> - If there are no variations the catalyst did not work enough (small TON). - Change of surface can be due to some physical phenomenon. 	
Complimentary methods & analysis:	
<ul style="list-style-type: none"> - Always use the TEM test as a complimentary method with other tests. - Check the TON value. 	
Advantages	Drawbacks
Easy to perform.	There is no clear conclusion about the nature of the mechanism. Not very sensible.