Highly regioselective terminal alkynes hydroformylation and Pauson–Khand reaction catalysed by mesoporous organised zirconium oxide based powders†

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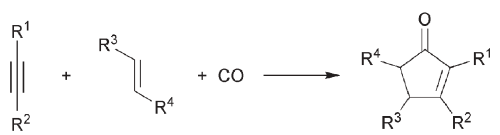
Zirconia–silica mesoporous powders act as very efficient heterogeneous catalysts for both alkyne hydroformylation and Pauson–Khand reaction and yield regioselectivities opposite to those usually observed.

Hydroformylation of alkenes is, despite the high costs of the rhodium or cobalt catalysts employed, the great success story of homogeneous catalysis, with 7 million tons of aldehydes produced every year.[1,2] On the contrary, alkynes hydroformylation is restricted to the field of academic synthesis despite the value of the resulting enals.[3–6] The reaction conditions required can compare with those of alkenes hydroformylation but the regioselectivities are usually poor,[7] except when a function like an ester or a thioester on the substrate can coordinate the catalyst and force the regioselectivity.[4] This restriction explains why industrial development of this process is still lacking. The Pauson–Khand reaction[8] which is closely related to this process, as it also involves alkynes and CO (and an alkene for a [2 + 2 + 1] cyclisation), has been thoroughly studied and constitutes one of the easiest ways to produce functionalised cyclopentenones (Scheme 1). This transformation, especially in an intramolecular version, was widely used in total synthesis.[9–11] In contrast with hydroformylation, this process is usually regioselective and catalytic intermolecular still remains an important challenge.[10] Its mechanism is not totally understood and there are still many unexplained results.[12] Development of a versatile, heterogeneous, inexpensive and selective catalyst for both reactions would, of course, be a breakthrough. In this perspective mesoporous materials, which were sometimes considered as large pore zeolites and have widely been used as catalysts,[13,14] were supposed to be good candidates.



Scheme 1 General representation of a Pauson–Khand reaction.

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Here we wish to report on the use of porous meso organised mixed zirconia silica powders for terminal alkynes and CO activation.

In a recent paper we described the use of hybrid bidentate ligands (HBL) for tandem 2,3-dimethylbut-2-ene hydroformylation.[15] HBL are hybrid materials bearing organic ligands grafted near an oxide surface so that they can bind metal centres both *via* their organic functions and *via* hydroxyl moieties close to the surface.[16] These systems are thus bridging the gap between surface organometallic chemistry[17] and standard immobilised homogeneous complexes.[13] For example, in the case of dimethylbutene hydroformylation, two processes have to be successively carried out: the isomerisation which yields 2,3-dimethyl-but-1-ene and the hydroformylation of the external double bond that finally yields 3,4-dimethylpentanal. Both steps are usually catalysed by the same homogeneous rhodium complex.[18,19] We found the way to heterogenise the catalyst and separate these steps by using a rhodium complex grafted on a zirconia-rich mesoporous material. This material was a mesoporous mixed zirconia silica powder obtained by spray drying an ethanolic sol of $ZrCl_4$ and $SiCl_4$ in a molar ratio of 4/1 with cetyltrimethylammonium bromide as surfactant. After consolidation and extraction of the organic template this powder, labelled **ZS20$_C$**, exhibited a specific surface area of 230 $m^2\ g^{-1}$ and an average pore diameter of 20 Å.[15] The Lewis acidic sites of the support were capable of isomerising the alkene, feeding the rhodium complex with a terminal olefin. Indeed, a reference run showed that an ungrafted zirconia material yielded on its own 30% of 2,3-dimethylbut-1-ene under hydroformylation conditions.† Importantly, 3% of the hydroformylation product was surprisingly detected attesting that our support could promote the hydroformylation process. This observation prompted us to investigate the catalytic activity of this support under hydroformylation conditions and 2-octene and styrene were tested.† As could be expected from the results on dimethylbutene, **ZS20$_C$** acted as a 2-octene isomerisation and hydroformylation catalyst yielding 71% of aldehydes, from which 31% were nonanal. Though this performance does not compete with homogeneous catalysts usually employed to convert internal olefins into linear aldehydes, it confirms that **ZS20$_C$** is an active hydroformylation catalyst. In the case of styrene, the conversion rate was modest (8%) but surprisingly the regioselectivity of the reaction was poor and opposite to which is usually observed for styrene:[20] 53% of linear aldehyde *vs* 47% of the branched one were obtained. This result underlined the fact that the mechanism involved was presumably not the standard one for hydroformylations catalysed by noble metals and that it could lead, through reversed regioselectivity, to interesting products.

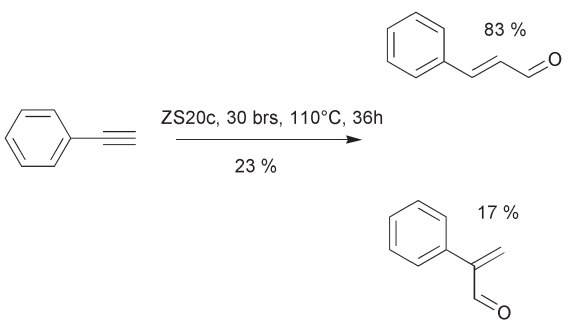
Therefore we decided to concentrate on alkynes, where there were fewer possible pathways. Three alkynes were tested under the same reaction conditions: 36 h reaction time at 110 °C in methanol under 30 bars of CO/H_2 mixture in a 1/1 ratio and 1 mol% of zirconia. The results are summarised in Table 1.

The first conclusion of these tests was that **ZS20$_C$** is a real hydroformylation catalyst for both C=C double bonds and C≡C triple bonds. The conversion rates were low except with phenylacetylene, but this could be circumvented by using harsher experimental conditions. However, it is important to keep in mind that this catalyst is the first example of a hydroformylation catalyst not featuring expensive transition metals like rhodium.‡ Furthermore it is important to note that the regioselectivity was found to be very good and in the case of phenylacetylene opposite to that expected (Scheme 2). These results give some insight into the reaction mechanism. Only terminal alkynes react and the more acidic the proton the higher the conversion rate (for example phenylacetylene has a pK_a of 23.2 in cyclohexylamine whereas *tert*-butylacetylene has a pK_a of 25.5 in the same solvent[21]). One possible pathway to rationalise both regioselectivity and acidity dependency would be a mechanism involving a deprotonation assisted by η^2-coordination of the alkyne onto the support throught its π-system. Indeed, C–C triple bonds are known to have a good affinity for zirconium(IV) species.[15,22] In a second step, one may propose that this η^2-coordination mode promotes a cooperative deprotonation of the alkyne associated with water elimination. Very likely, this step is facilitated by the Brønsted basic character of zirconia, this oxide having a point of zero charge of approximately 9. This process is probably governed by an equilibrium, strongly displaced towards the coordination of the alkyne. However if even a small part of the alkyne is deprotonated, then a carbonyl ligand, coordinated onto a neighbouring zirconium site can insert into the C–Zr bond to form a very reactive -ynalate species that can be finally cleaved with H_2 to produce the corresponding aldehyde.§ (Scheme 3)

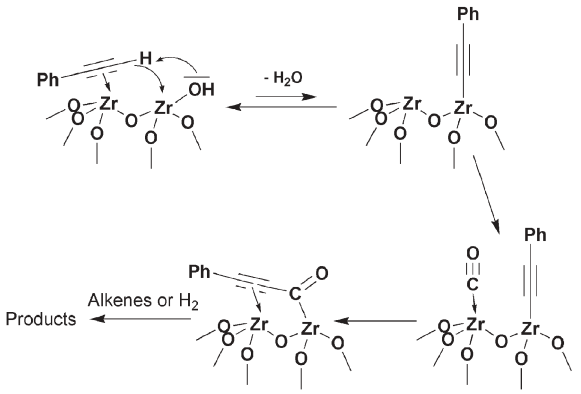
Table 1 Hydroformylation of various alkynes with **ZS20$_C$**[a]

Entry	Substrate	Conversion rate (%)[b]	Linearity (%)[b,c]
1	Phenylacetylene	23	83
2	1-Octyne	8	100
3	4-Octyne	0	0

[a] Reaction conditions: 36 h, at 110 °C in methanol under 30 bars of CO/H_2 mixture in a 1/1 ratio and 1 mol % of zirconium. [b] Conversion rates and linearities were determined by GC and confirmed by ^{1}H NMR so that the detection limit sits below 0.5%. [c] Linearity is the rate of linear aldehydes on the amount of aldehydes formed.



Scheme 2 Hydroformylation of phenylacetylene catalysed by **ZS20$_C$**.



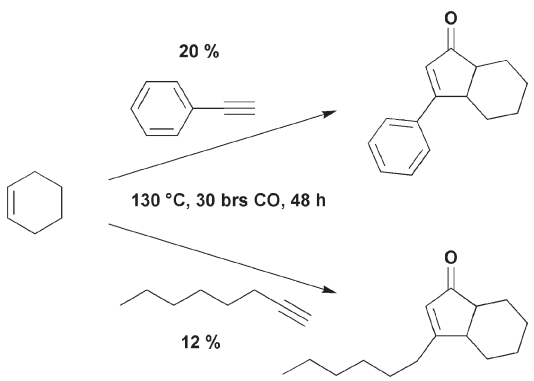
Scheme 3 A possible pathway for the first step of phenylacetylene hydroformylation catalysed by **ZS20$_C$**.

If this mechanistic proposal is true, we expected our material to be also active for catalysis of Pausond–Khand reactions. Moreover it would yield cyclopentenones in which the acetylene moiety would be located in β of the carbonyl group (such products will now on be referred to as β products). This could be very interesting as those substituents are usually placed in α position.[12] To test these two hypotheses, phenylacetylene, 1-octyne, 4-octyne and methyl butyndioate were reacted with a symmetric alkene in order to limit the potential products, cyclohexene, in presence of 4 mol % of zirconium at 130 °C under 30 bars of CO for 48 h in toluene. The results are summarised in Table 2.

Table 2 Pauson–Khand reaction of various alkynes with cyclohexene catalysed by **ZS20$_C$**[a]

Entry	Substrate	Conversion rate (%)[b]	Rate of β-product (%)[b]
1	Phenylacetylene	20	100
2	1-Octyne	12	100
3	4-Octyne	0	0
4	Methyl butyndioate	0	0

[a] The reaction conditions are: 48 h reaction time at 130 °C in toluene under 30 bars of CO and 4 mol % of zirconium. [b] The conversion rates and linearities were determined by ^{1}H NMR.



Scheme 4 Pauson–Khand reaction of terminal alkynes with cyclohexene catalysed by **ZS20$_C$**.

Results obtained for terminal alkynes were quite good regarding the relatively mild experimental conditions employed and the low catalyst loading for intermolecular Pauson–Khand reactions.[23] Such reactions have already been catalysed using group IV metal complexes but our system proves to be the first heterogeneous catalyst able to promote this transformation.[10] Interestingly, we found that internal alkynes even strongly activated ones like methyl butyndioate, do not react, thus substantiating our mechanism. Moreover the regioselectivity is totally in favour of the β-products (Scheme 4). This observation, which strongly supports the mechanism proposed, is rather unusual for this process.

The catalytic activity of a mesoporous zirconia/silica mixed powder, both in hydroformylation and Pauson–Khand processes, opens, even if the activities are still low, a wide field of investigation. The mechanism still remains unclear and requires additional investigation. On the other hand, the observed regioselectivities are rather unusual and thus interesting. We believe that catalytic application of these mesoporous materials could emphasise alkyne hydroformylation as the industrial outcomes are considerable.

Notes and references

‡ These results could naturally be assigned to traces of rhodium from previous catalyses in the autoclaves or to late transition metals leaching from the walls. When it was not possible to fit the autoclaves with a glass vessel (See Supplementary Information†), blank tests without zirconia powder were undertaken that did not afford any detectable conversion of the reactants. However it is not possible to exclude that the catalytic activity relies on traces of metal included in the silica/zirconia powders. Those pollutants could possibly be iron(III) species coming from the spraying system used for the synthesis of the powders or other metals included in $ZrCl_4$. Such chemicals could not be detected in our powders by X-ray fluorescence. But to definitely exclude such a possibility, more sensitive techniques should be used.

§ How the H_2 activation proceeds remains unclear, even if it can be admitted that dihydrogene is able to interact through σ-bonding with zirconia surface. Therefore we do not speculate on the following steps of the catalytic mechanism.

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