

DEVELOPMENT OF HETEROGENEOUS CATALYSTS FOR HYDROFORMYLATION OF 1-HEXENE IN SUPERCRITICAL CARBON DIOXIDE

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ABSTRACT

The hydroformylation of alkenes is a major commercial process used for the production of oxygenated organic compounds. Commercial hydroformylation processes may produce significant quantities of waste material. When the hydroformylation reaction is performed using a homogeneous catalyst, an organic or aqueous solvent is employed and a significant effort must be expended to recover the catalyst so it can be recycled. The hydroformylation of long-chain alkenes using homogeneous catalysts in aqueous solution is compromised because of the low-solubility of C₅ alkenes and above. Development of a selective heterogeneous catalyst would allow simplification of the process design in an integrated system that minimizes waste generation.

Supported catalysts are well-known to have minimal capacity for product selectivity. To remedy this problem, we have developed tethered rhodium-phosphine catalysts with modified silica and compared them with catalysts prepared on MCM-41 and MCM-20 supports that provide improved selectivity and conversion relative to their nonporous equivalents. Platinum and palladium catalysts analogous to those of rhodium were also investigated. Our synthesis and characterization of the rhodium, platinum and palladium complexes and evaluation of their catalytic activity and selectivity for hydroformylation in supercritical carbon dioxide will be described.

Recent studies have shown that a supercritical fluid may be used as a solvent for hydroformylation reactions. The use of carbon dioxide as a reaction solvent offers optimal environmental performance because it is non-toxic, non-flammable and renewable, and simplifies product separation. In particular, we have considered the conversion of 1-hexene to heptanal using rhodium-phosphine catalysts tethered to supports insoluble in supercritical carbon dioxide to demonstrate the advantages and understand the limitations of a solid-catalyzed process.

INTRODUCTION

Most of the current commercial hydroformylation processes use water-soluble homogeneous catalysts [1,2]. However, it is not feasible to use this method for conversion of higher alkenes (especially pentene and above), since these materials have very low water solubilities. Thus,

organic solvents are used. One of the principles of green chemistry is the elimination of organic solvents and their replacement with benign solvents. Recent studies have shown that many commercially important reactions that use organic solvents may also be performed in a supercritical fluid [3,4,5]. The use of carbon dioxide as a reaction solvent provides maximum environmental advantage because it is not ozone-depleting, and does not contribute to the formation of ground-level smog or to global warming.

In particular, we have examined the conversion of 1-hexene to heptanal. The heterogeneously catalyzed hydroformylation reaction will only be advantageous if a catalyst is developed that is both active and selective. One of the liabilities of heterogeneous catalysts is the inability to control selectivity. However, we are currently investigating two means of attaining high activity and selectivity:

- 1) the use of support and ligand modifiers, and
- 2) the use of mesoporous supports (MCM-41 and MCM-20).

In this work we developed rhodium-, platinum-, and palladium-phosphine heterogeneous catalysts and evaluated their performance for catalytic hydroformylation using supercritical carbon dioxide (scCO₂) as the solvent.

I. EXPERIMENTAL

Synthesis of catalysts:

The activity of a heterogeneous catalyst depends (at least in part) on the nature of the support. Although a CO₂-philic support surface may be appropriate for use in scCO₂, a more hydrophobic silica surface may interact more effectively with the hexene substrate. We prepared a series of phosphinated supports by condensation of Si(OEt)₄ and (EtO)₃Si(CH₂)₂PPh₂ in ethanol and water. Hydrophobic supports were obtained by incorporating (EtO)₃Si(CH₂)₉CH₃ in the above synthesis whereas the incorporation of (EtO)₃Si(CH₂)₂(CF₂)₇CF₃ led to the production of CO₂-philic supports [6]. The modified phosphinated supports were combined with rhodium catalyst precursors in ethanol to prepare a catalyst with a rhodium-to-phosphorus ratio of 1:2. The phosphinated supports were used in combination with platinum and palladium catalyst precursors [7] in toluene to prepare catalysts with a metal-to-phosphorus ratio of 1:2.

In order to improve the selectivity of our heterogeneous rhodium catalysts, we synthesized a series of mesoporous siliceous MCM-41 supports. Siliceous MCM-41 and MCM-20 supports have been prepared following the synthesis of Beck et al. [8] and modified by refluxing a suspension containing the calcined siliceous MCM-41 or MCM-20 support and (EtO)₃Si(CH₂)₂PPh₂ in toluene. Surface modification of the phosphinated MCM-41 support was accomplished by incorporation of (EtO)₃Si(CH₂)₉CH₃ or (EtO)₃Si(CH₂)₂(CF₂)₇CF₃ to produce hydrophobic phosphinated MCM-41 and CO₂-philic phosphinated MCM-41 support, respectively. Modified phosphinated MCM-20 material was neither prepared nor evaluated within the experimental protocol. The phosphinated MCM-41 and MCM-20 supports were reacted with [RhCl(1,5-cod)]₂ and with PtCl₂{Ph₂P(CH₂)₂Si(OEt)₃}₂ to obtain catalysts with a

metal-to-phosphorus ratio of 1:2. The phosphinated MCM-41 supports were also used in the preparation of palladium catalysts with Pd:P of 1:2.

The supports and resulting catalysts presented in Table 1 were characterized using CP/MAS ^{13}C and ^{31}P NMR spectroscopy and elemental analysis.

Catalyst number	Properties	BET surface area (m^2/g) (duplicate analysis)
1	Rh on phosphinated silica	8.60; 9.16
2	Rh on hydrophobic phosphinated silica	31.23; 32.44
3	Rh on CO_2 -philic phosphinated silica	35.32; 40.01
4	Rh on phosphinated MCM-41	642.11; 651.70
5	Rh on hydrophobic phosphinated MCM-41	721.37; 828.22
6	Rh on CO_2 -philic phosphinated MCM-41	843.89; 912; 28
7	Rh on phosphinated MCM-20	829.45; 856.84
8	Pd on phosphinated silica	226.21; 234.75
9	Pd on phosphinated MCM-41	1086.33; 1282.94
10	Pt on phosphinated silica	250.20; 252.35
11	Pt on phosphinated MCM-41	715.55; 708.33
12	Pt on phosphinated MCM-20	645.94; 654.15

Table 1: Properties and BET surface areas of the different metal catalysts.

Hydroformylation reactions:

The hydroformylation of 1-hexene was performed using a batch reactor. The catalyst was contained in a nylon mesh envelope and placed in a basket attached to the stirrer shaft. The CO , H_2 and CO_2 gases were added in the desired proportions and samples were regularly collected from the reactor and analyzed by gas chromatography. The activity and selectivity of each catalyst were determined for hydroformylation of 1-hexene in supercritical carbon dioxide. The activity was defined as moles of total aldehydes produced per initial mole of 1-hexene per mole of rhodium. The selectivity was calculated as moles of linear aldehyde (heptanal) per mole of branched aldehydes (2-ethylpentanal and 2-methylhexanal).

II. RESULTS AND DISCUSSION

The catalyst performance was evaluated in terms of activity and regioselectivity. Figure 1 shows the activity (total yields of aldehydes per mole of rhodium) of each catalyst as a function of time. Figure 2 shows the regioselectivity of each catalyst expressed as linear-to-branched ratio (L:B). Figures 3 and 4 represent the total aldehydes yields per mol of metal and the regioselectivities with the different metal precursors, respectively.

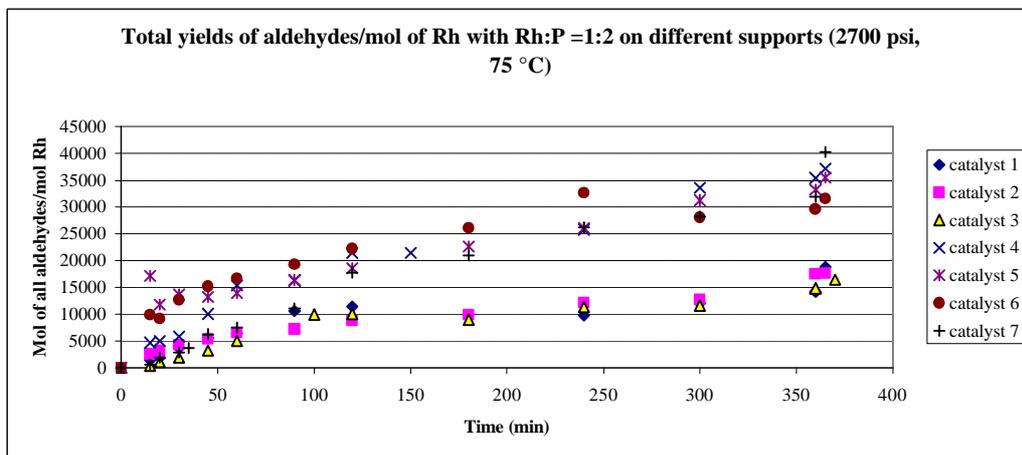


Figure 1: Comparison of aldehyde yields normalized to the rhodium content obtained at 100 °C and 184 atm.

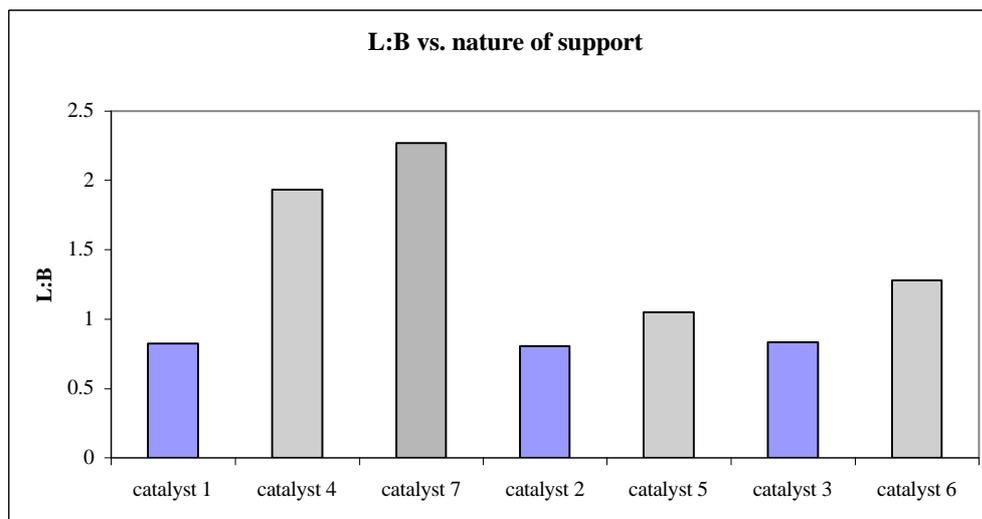


Figure 2: Comparison of average regioselectivity obtained with catalysts anchored on silica vs. MCM supports.

Based on the yield of aldehydes per mole of metal, the catalysts tethered on MCM supports clearly provided higher activity than the catalysts anchored on silica. In addition, the

Commentaire : Is it possible to add a legend that indicates which fill is associated with each support?

regioselectivity to heptanal was higher with catalysts prepared on the MCM materials than with the catalysts prepared using the phosphinated silica support.

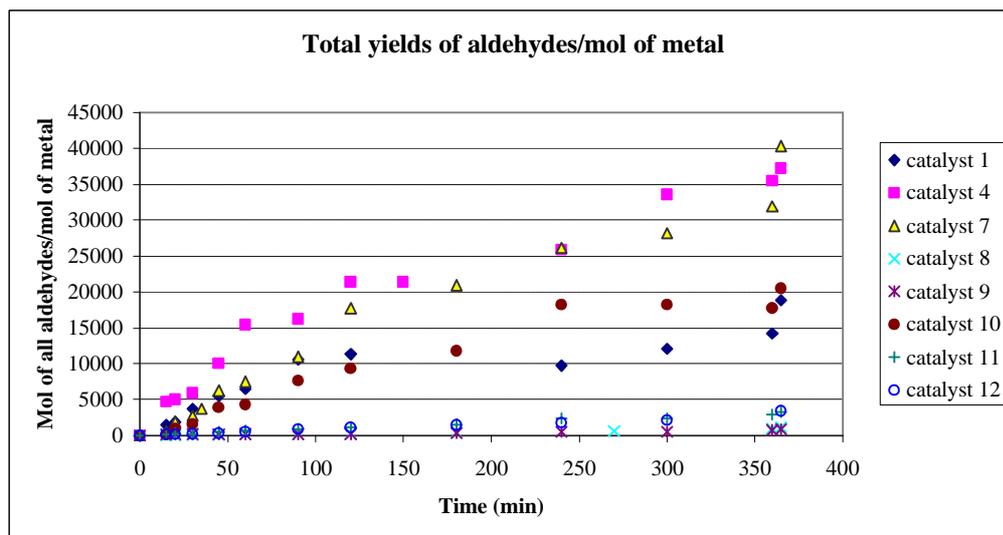


Figure 3: Comparison of aldehydes yields obtained with different metal catalysts

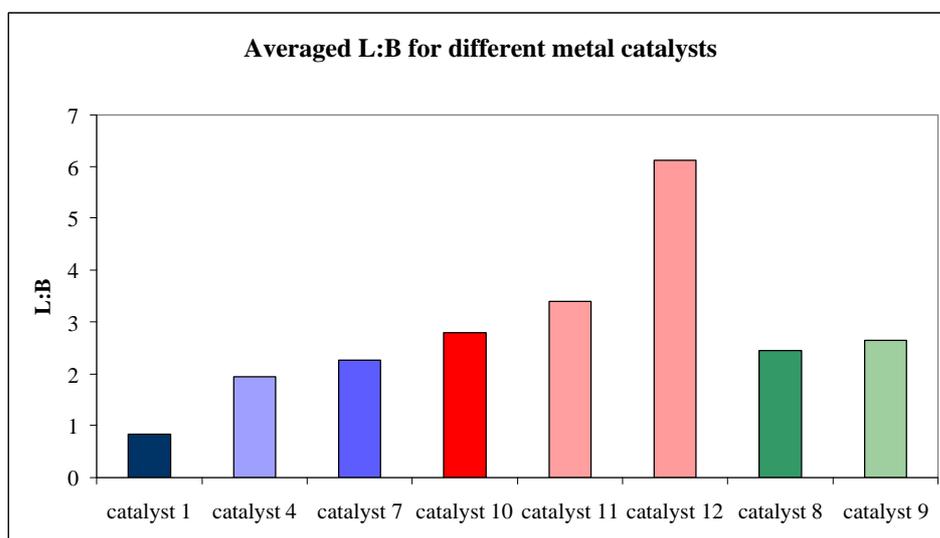


Figure 4: Comparison of the average regioselectivity obtained with different metal catalysts.

The improvement in the yield and regioselectivity arose from the combination of properties of heterogenized catalysts and structural properties of MCM-type supports. Solid-state NMR spectroscopy revealed interesting characteristics of the MCM-41 supports. For example, CP/MAS ^{13}C NMR spectra of the catalyst precursors Rh/P/SiO₂ and Rh/P/MCM-41 after hydroformylation were compared to those of the fresh catalyst precursors. No change was noticed for the catalysts anchored on silica. However, an increase in the intensity of the resonances between 20 and 35 ppm was observed for Rh/P/MCM-41. Solid-state NMR analyses revealed that heptanal was trapped in the pores of the MCM-41 supports during the catalytic reaction.

III. CONCLUSION

Supported catalysts have been developed and used for the hydroformylation of 1-hexene in scCO₂. The performance (activity and selectivity) of the catalysts are affected by the type of support material. Catalysts prepared using mesoporous siliceous MCM-based supports showed improved performance relative to those prepared on silica. The highest regioselectivity was obtained with the MCM-supported platinum complexes whereas the highest yield of aldehydes was achieved with the MCM-supported rhodium complexes. Solid-state NMR analyses were helpful in understanding the behaviour of catalysts supported on MCM-41.

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REFERENCES

- [1] HERRMANN, W.A.; KOHLPAINTNER, C.W., *Angew. Chem. Int. Ed. Engl.*, Vol. 32, **1993**, p. 1524.
- [2] SON, S.U.; HAN, J.W.; CHUNG, Y.K., *Journal of Molecular Catalysis A*, Vol. 135, **1998**, p. 35.
- [3] RATHKE, J.W.; KLINGER, R.J.; KRAUSE, T.R., *Organometallics*, Vol. 10, **1991**, p. 1350.
- [4] MEEHAN, N.J.; SANDEE, A.J.; REEK, J.N.H.; KAMER, P.C.J.; VAN LEEUWEN, P.W.N.M.; POLIAKOFF, M., *Chem. Comm.*, **2000**, p. 1497.
- [5] BACH, I.; COLE-HAMILTON, D.J., *Chem. Commun.*, **1998**, p. 1463.
- [6] (a) TADD, A.R.; MARTEEL, A.; MASON, M.R.; DAVIES, J.A.; ABRAHAM, M.A., *Ind. Eng. Chem. Res.*, Vol. 41, **2002**, p. 4514 (b) TADD, A. R.; MARTEEL, A.; MASON, M.R.; DAVIES, J.A.; ABRAHAM, M.A., *J. Supercrit. Fluids*, Vol. 25, **2003**, p. 183 (c) HEMMINGER, O.; MARTEEL, A.; MASON, M.R.; DAVIES, J.A.; TADD, A.R.; ABRAHAM, M.A., *Green Chemistry*, Vol. 4, **2002**, p. 507.
- [7] BEMI, L.; CLARK, H.C.; DAVIES, J.A.; FYFE, C.A.; WASYLISHEN, R.E., *J. Am. Chem. Soc.*, Vol. 104, **1982**, p. 438.
- [8] BECK, J.S.; VARTULI, J.C.; ROTH, W.J.; LEONOWICZ, M.E.; KRESGE, C.T.; SCHMITT, K.D.; CHU, C. T-W.; OLSON, D.H.; SHEPPARD, E.W.; MCCULLEN, S.B.; HIGGINS, J.B.; SCHLENKER, J.L., *J. Am. Chem. Soc.*, Vol. 114, **1992**, p. 10834.