From gas-phase to liquid-phase hydroformylation over a solid rhodium catalyst

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Highlights

- Potential advantages of incorporating a liquid phase during heterogeneous hydroformylation
- Better distribution of the surface concentrations is achieved by the presence of a solvent
- Bridging heterogeneous hydroformylation from short to long-chain olefins via liquid-phase experiments

1. Introduction

Hydroformylation is the main commercial route towards aldehyde production. In the presence of a metal such as Rh or Co, olefins react with syngas to produce aldehydes, as well as paraffins, and to a lesser extent, alcohols, as by-products. Rhodium is the most active metal for the catalysis of hydroformylation, allowing for the use of mild temperatures (100 to 200°C) and total pressures (10 to 30 bar). Most of the research on heterogeneously catalyzed hydroformylation is focused on short-chain olefins, such as ethylene, where all the reactants are in the gas phase. In contrast, homogeneously catalyzed hydroformylation occurs in the liquid phase, irrespective of the olefin's carbon number.

The present work has focused on heterogeneously catalyzed hydroformylation over a rhodium catalyst, aiming at filtering out potential effects induced by the difference in phase of operation between homogeneously and heterogeneously catalyzed hydroformylation. To this purpose, small olefin hydroformylation has been performed at gas-phase conditions, as well as in the presence of a paraffin mixture solvent (liquid phase) [1]. An adequate understanding of such phase effects will allow for a more reliable extrapolation of the hydroformylation behavior as observed for short-chain olefins towards that of long-chain olefins.

2. Methods

Ethylene hydroformylation was carried out in a HTK setup equipped with a plug-flow reactor of 900 mm length and 16 mm internal diameter. Commercial rhodium nanoparticles supported on alumina were pelletized, crushed and sieved, and the 500 – 710 μm fraction was employed to create the fixed bed in the reactor. C_2H_4, along with CO and H_2 were fed from an equimolar mixture bottle by a thermal flow controller. A paraffinic mixture, named Halpasol®, containing linear paraffins from C9 to C15 was fed by means of an HPLC pump. The experiments were performed within the following boundaries of operating conditions: total pressures from 10 to 60 bar and temperatures ranging from 120 °C to 150 °C at space times between 50 and 100 kg s/mol.

3. Results and discussion

In simple agreement with the Arrhenius relationship, the temperature was found to enhance the ethylene conversion in a similar manner at gas-phase and liquid-phase conditions, see Figure 1.a. Yet, the ethylene conversion at liquid phase conditions was between 1.5 and 2 times higher than at gas-phase conditions. An exposure of the catalyst to different reactant concentrations, originating from differences in solubility of the three reactants, i.e., ethylene, CO and H_2, in the Halpasol solvent, is believed to be at the origin of this behavior, with ethylene being the most soluble one, followed by CO and H_2. These observations are in accordance with previous studies that have already demonstrated a positive correlation between ethylene conversion and ethylene partial pressure[2]. During gas-solid operation with an equimolar gas mixture, in which the catalyst is, hence, 'equally exposed' to the three reactants, CO has been found to be the *Most Abundant Surface Intermediate* (MASI) as a result of its high heat of adsorption ($-\Delta H_{CO}$ = 156 KJ/mol), and correspondingly acts as an inhibitor for the hydroformylation reaction. The better solubility of ethylene in the paraffinic solvent, hence, seems to favor the interaction between ethylene and the catalyst, resulting in a higher reaction rate.

The ethylene hydroformylation experiments mainly led to the production of the desired propanal (hydroformylation product), along with ethane (hydrogenation product) as undesired byproduct via two parallel reactions. Given the low ethylene conversion and the absence of consecutive reactions, the selectivity response to temperature can be assumed to reflect the actual impact of the temperature and not to be disguised by conversion effects. Figure 1.b shows the negative impact of temperature on the aldehyde selectivity for both gas-phase and liquid-phase C_2H_4 hydroformylation. A stronger dependance on temperature was observed for liquid-phase operation (going from 72% at 120 °C to 62% at 140 °C in liquid-phase operation), exhibiting higher aldehyde selectivity at low temperatures compared to the gas phase. At liquid-phase conditions, the temperature effect on solubility reinforces the temperature impact on selectivity. The ethylene-to-syngas molar ratio in the liquid phase decreases from approximately 5 at 100°C to <4 at 140°C as a result of the reduced ethylene solubility at higher temperatures. Figure 1.c presents experimentally the observed apparent activation energies: 91 kJ/mol for hydrogenation and 68 kJ/mol for hydroformylation at gas-phase conditions; 66 kJ/mol for hydrogenation and 37 kJ/mol for hydroformylation at liquid-phase conditions. The lower activation energy of hydroformylation over hydrogenation stems from the decreasing aldehyde selectivity with increasing temperatures. For both reactions, the apparent activation energy was lower at liquid-phase conditions, indicative of lower surface coverages of CO on the catalyst as opposed to that at gas-phase conditions. The paraffin solvent, hence, appears to act as an efficient moderator to control the surface intermediate concentrations on the catalyst [3].

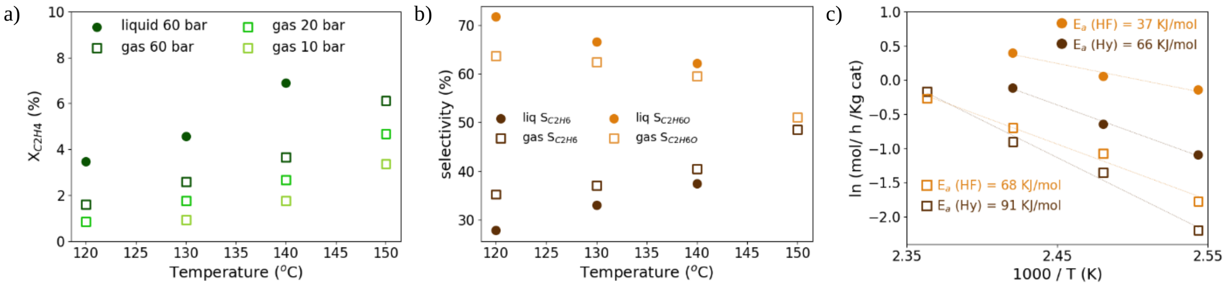

Figure 1. Temperature effect on ethylene conversion (a), selectivity (b), ethylene rate over time and catalyst mass (c) during gas (□) / liquid (●) hydroformylation.

4. Conclusions

The presence of an organic solvent during olefin hydroformylation allows for the tuning of the hydroformylation performance towards aldehydes by increasing conversion and selectivity. The molar ratio of the reactants to which the catalyst is exposed differs at gas-phase and liquid-phase conditions, which was attributed to differences in solubility of the three reactants in the paraffinic solvent. The higher solubility of ethylene as compared to CO, which on its turn has a higher solubility than H_2, enhances both reaction rates, yet particularly that of hydroformylation. Apparent activation energies were lower at liquid-phase compared to gas-phase conditions, allowing for the operation at lower reaction temperatures, potentially even below 120°C, where hydroformylation is favored over hydrogenation.

References

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Keywords
Rhodium catalyst; heterogeneous hydroformylation; paraffinic solvent; ethylene