Selective hydroformylation of styrene over rhodium supported on layered and exfoliated transition metal dichalcogenides

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Highlights

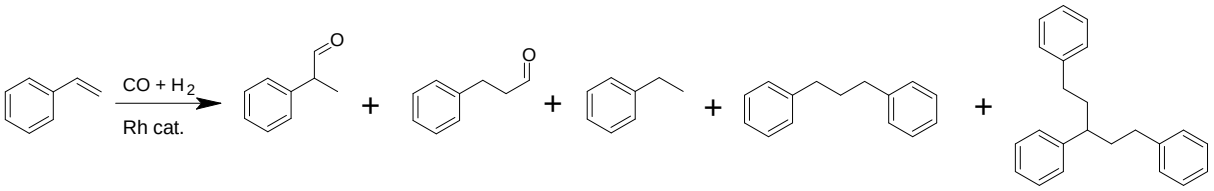
- Rh successfully supported on TMDs and their exfoliated analogues
- Rh/TMDs ensured high aldehyde selectivities (> 81%), similar to Wilkinson catalyst
- Rh/exfoliated-WS_2 revealed the highest hydroformylation activity but lower stability

1. Introduction

Hydroformylation (oxo process) is an important industrial reaction that converts alkenes into aldehydes via the addition of syngas (CO/H_2).[1] Since its discovery in 1938, it has become one of the major homogeneous catalytic processes, with aldehydes serving as key intermediates for alcohols, amines, acids, polymers, surfactants, and pharmaceuticals.[1,2]

Hydroformylation has traditionally been carried out with homogeneous catalysts dominated by Rh–phosphine catalysts, such as Wilkinson complex, which provide excellent activity and regioselectivity. However, homogeneous systems are difficult to separate from products, sensitive to impurities and prone to deactivation, which makes them economically and environmentally problematic. This creates a strong need for heterogeneous catalysts that would be easily recoverable, more stable, and reusable, ideally matching the performance of homogeneous analogues. Supported Rh catalysts, however, often show lower selectivity, higher hydrogenation rates, and metal leaching. Transition metal dichalcogenides (TMDs) are emerging as promising supports because their layered structure, sulphur vacancies, and tunable electronic properties enable strong metals anchoring.

Styrene, serving as the model reactant within our study, is a valuable probe substrate due to its electronic and steric complexity.[2] Hydroformylation produces two aldehydes, linear 3-phenylpropanal and branched 2-phenylpropanal, while undesired hydrogenation yields ethylbenzene and oligomerization styrene dimers and trimers (Scheme 1).



Scheme 1: Hydroformylation of styrene toward desired aldehydes and competing ethylbenzene, product of hydrogenation

2. Methods

The catalysts were prepared using rhodium chloride as metal precursor and conventional wet impregnation performed at different temperatures (20 h).[3] Selected catalysts additionally underwent calcination at 300 °C (12 h). Next to commercial MoS_2 and WS_2 (Sigma Aldrich), high-pressure homogenization was employed as exfoliation technique for producing few-layer TMDs nanosheets (named Ex-MoS_2 and Ex-WS_2).

Prepared catalysts were thoroughly characterized using XRF (AXIOS XRF spectrometer), XRD (Bruker-Phaser 2nd Generation diffractometer), SEM (TESCAN LYRA3GMU), SEM/EDS (EDS analyzer equipped with SDD detector), TEM (EFTEM Jeol 2200 FS) and N_2 physisorption (NOVA 2000e Surface Area and Pore Size Analyser, Quantachrome Instruments).

Hydroformylation tests were performed in a 50 mL autoclave (Parr Instrument) using syngas ($CO:H_2$ = 1:1) at a pressure of 3 MPa and a temperature of 100 °C for 6 h. Homogeneous Wilkinson's catalyst (chlorido-tris(triphenylphosphine)-rhodium(I)) was used as a reference for catalytic performance.

3. Results and discussion

Successful preparation of Rh/TMD catalysts was confirmed by several characterization methods. XRF showed that actual Rh loadings were slightly lower than the nominal values, with deposition efficiency declining once the target loading exceeded 5 wt%. The Mo/S and W/S ratios of the supports increased after any thermal treatment (during high-temperature impregnation or calcination), indicating sulphur loss and possible formation of oxides or sulphur-deficient phases (MoS_{2-x} and WS_{2-x}). XRD was used to confirm the TMDs crystal structure and assess the effects of Rh loading and thermal treatments. All samples showed the characteristic reflections of hexagonal 2H-TMDs, and no crystalline Rh, Rh oxides, or Rh chlorides were detected, indicating that Rh is highly dispersed. SEM shows that the Rh/TMD catalysts retain their hexagon-like plate morphology, with no Rh particles visible. In contrast, TEM reveals small, well-dispersed Rh nanoparticles across the TMD surfaces, overcoming SEM's resolution limits.

Catalytic hydroformylation performance was evaluated from styrene conversion after 6 h, with selectivity determined toward the desired aldehydes. Ethylbenzene was the main side product formed via styrene hydrogenation, and dimer and trimer formation was also detected. As a benchmark, Wilkinson's homogeneous Rh catalyst gave 98 % styrene conversion with 85 % selectivity to aldehydes. Results obtained using selected Rh/TMDs catalysts are compared in Table 1.

Table 1: Hydroformylation results for selected Rh/TMDs catalysts (non-calcined) and Wilkinson´s catalyst

Catalyst	Support	Conversion (%)	Selectivity (%)		
			Aldehydes	Ethylbenzene	Dimers + trimers
2 wt% Rh / TMDs (RT)	Wilkinson	97.7	85.4	12.9	0.0
	MoS_2	23.2	75.5	20.4	0.7
	Ex-MoS_2	53.5	9.9	0.0	90.1
	WS_2	32.3	80.9	16.0	3.1
	Ex-WS_2	40.1	91.4	0.0	8.6

4. Conclusions

A series of Rh-modified commercial and exfoliated TMDs catalysts with varying Rh loadings and different impregnation/calcination treatments were systematically studied for styrene hydroformylation.

Catalysts prepared using commercial disulphides achieved ~30 % styrene conversion with aldehyde selectivities comparable to Wilkinson's catalyst. The best performance was obtained with exfoliated WS_2, which showed exceptionally high aldehyde formation (~90 %) due to strong suppression of the competing hydrogenation reaction. In contrast, Rh/Ex-MoS_2 displayed very low hydroformylation activity and predominantly produced dimers and trimers.

Overall, the results highlight the need to optimize Rh loading, thermal treatment and support morphology to obtain stable, selective Rh/TMDs hydroformylation catalysts and provide guidance for designing efficient heterogeneous systems.

References

[1] B. Zhang, D. Peña Fuentes, A. Börner, ChemTexts 8 (2021) 2.
[2] R. Franke, D. Selent, A. Börner, Chemical Reviews 112 (11) (2012) 5675-5732.
[3] M. Pitínová, A. Krnáčová, A. Shafiq, I. Danylo, L. Koláčný, M. Veselý, Catal Today 460 (2025), 115473.

Keywords
Rhodium catalysts; MoS_2 and WS_2-supported catalysts; Styrene hydroformylation

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