

Hydrogenation of Styrene Catalyzed by Immobilized Mo Complexes

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Introduction

Immobilized transition metal complexes into polymers combine the good activity, selectivity and reproducibility typical of homogeneous catalysts with the easy product separation and catalyst recovery characteristic of heterogeneous catalysts.

Studies in our laboratories have long been concerned with the use of transition metal compounds immobilized on poly(4-vinylpyridine) as catalysts for the hydroesterification and hydroformylation of 1-hexene under CO/H₂O, water-gas shift reaction, and hydrodechlorination of chlorobenzene under CO/H₂O [1], due to their easy preparation, good stability, high or moderate catalytic activities.

We report in the present study the influence of some reaction parameters ((P(H₂), and T) in the catalytic hydrogenation of styrene to ethylbenzene by the immobilized complexes formed in the reaction between [Mo(CO)₃(CH₃CN)₃] and poly(4-vinylpyridine) (P(4-VP)) in contact with 2-ethoxyethanol.

Materials and Methods

2-Ethoxyethanol (Aldrich) was distilled from anhydrous stannous chloride. Styrene was distilled prior to use. Triphenylphosphine from Stream Chemical was used as received. Poly(4-vinylpyridine)/divinylbenzene(2%) (P(4-VP)), was used as provided by Reilly Industries. The immobilized Mo complexes were synthesized as reported [2]. This material will be referred herein as Mo/P(4-VP).

Catalytic runs were performed in a 30 mL mechanically stirred and electrically heated stainless steel Parr reactor. In a typical run, 0.5 g of the catalyst ([Mo] = 2 wt. % (1 x 10⁻⁴ mol)), 0.54 g (5.2 x 10⁻³ mol) of styrene, 0.1 g of toluene (internal standard), triphenylphosphine (typically 0.09 g, 3.3 x 10⁻⁴ mol) and 10 mL of 2-ethoxyethanol were added to the glass reactor vessel, then flushed with nitrogen to remove all the air from the system and thereafter flushed with hydrogen to remove all nitrogen from the system. The reaction vessel was charged with H₂ at the desired pressure (30 atm), and then electrically heated at 90 - 110 °C for 24 h. After 24 h, the reaction was stopped; the reactor was cooled to room temperature, excess pressure was vented and products analyzed by GC and GC-MS techniques. The GC-MS of the ethylbenzene (molecular ion peak at m/e = 91 and base peak at m/e = 106) product is similar to a pure sample of ethylbenzene.

Results and Discussion

The [Mo(CO)₃(CH₃CN)₃] immobilized on P(4-VP) in contact with 2-ethoxyethanol catalyzes the hydrogenation of styrene to ethylbenzene under hydrogen atmosphere in presence of triphenylphosphine (PPh₃). The turnover frequencies for

ethylbenzene production were calculated as mol of ethylbenzene per mol of [Mo(CO)₃(CH₃CN)₃] in 24 h (TF(ethylbenzene) = [(mol of ethylbenzene)/((mol of Mo) x (rt))] x 24 h, where (rt) = reaction time in hours). The calculated catalytic activity defined as TF(ethylbenzene) was reproducible to ca. 10 % for a series of experimental runs. Furthermore, control experiments show that no reaction was detected in the absence of the polymer-immobilized Mo complex. The reaction conditions were: [Mo] = 2 wt. % (1 x 10⁻⁴ mol), 0.5 g of P(4-VP), [styrene] = 0.54 g (5.2 x 10⁻³ mol), styrene/Mo = 50, 10 mL of 2-ethoxyethanol under P(H₂) = 5 - 30 atm at 90 - 130 °C in 24 h. The data obtained from these studies are reported in Table 1.

Table 1. Catalysis by Mo/P(4-VP)^a

T (°C)	P(CO) (atm)	Conv. (%)	TF(ethylbenzene)
90	30	3.2	1.6
100	30	10.0	5.2
110	30	14.7	7.3
120	30	9.6	4.7
130	30	7.1	3.5
110	5	1.7	1.0
110	10	6.7	3.3
110	20	8.3	4.1

^a0.5 g of Mo/P(4-VP); [Mo] = 2% wt.; styrene = 0.54 g (5.2x10⁻³ mol); 2-ethoxyethanol = 10.75 mL (0.12 mol); S/C = 50; PPh₃/Mo = 3; rt = 24 h.

The results show that TF(ethylbenzene)/24 h values and the overall yields increased from 1.6 to 7.3 (24 h)⁻¹ and from 3.2 to 14.7.1% respectively, reaching the highest point at 110 °C and then decreased. Formation of polystyrene over 110 °C was observed. As can be observed from Table 1, increase in carbon monoxide pressure on the 5-30 atm range is accompanied by a linear improvement in TF/24 h values.

Significance

In this work we carried out the catalytic transformation of styrene, which is present in about 15% in a typical pyrolysis gasoline, in saturated compounds under H₂ atmosphere and this approximation constitutes a promissory work for a future industrial catalytic process for gasoline improving.

Acknowledgments

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References

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