Selectivity in phenol hydrogenation to cyclohexanone over Rh/SiO$_2$ catalysts

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Abstract: A silica-supported rhodium catalyst for the selective hydrogenation of phenol to cyclohexanone at room temperature and 1 atm H$_2$ pressure is developed. The conversion decreased with Rh loading whereas the initial selectivity to cyclohexanone increased. Direct hydrogenation to cyclohexanol occurred in parallel with partial hydrogenation to cyclohexanone. The negative correlation between selectivity and Rh particle size suggests that direct hydrogenation occurs at low coordination sites whereas partial hydrogenation occurs at higher coordinated terrace sites. By blocking the low coordination edges and steps through grafting with (3-mercaptopropyl)methoxysilane, the cyclohexanone selectivity was improved from 82 to 93 % at 100 % conversion.

Keywords: Phenol hydrogenation, Rh catalyst, selectivity.

1. Introduction

Cyclohexanone is an important intermediate in the synthesis of caprolactam for nylon-6 and adipic acid for nylon-6,6 with about 97 % of the annual production being devoted for this purpose.[1]. The balance is used as building block in the synthesis of pharmaceuticals, herbicides, insecticides and as a specialty solvent for resins and lacquers. Commercially, cyclohexanone is prepared by the catalytic oxidation of cyclohexane or via the hydrogenation of phenol in either a one- or two-step process.[2]. In the two-step process, phenol is fully hydrogenated to cyclohexanol followed by an endothermic dehydrogenation step to cyclohexanone. A one-step process where phenol is selectively hydrogenated to cyclohexanone is certainly preferred due to savings in costs and energy.

In general, palladium catalysts show good selectivity to cyclohexanone although the activity is not high.[3] Therefore, high hydrogen pressure (> 5 bar), temperature (> 50 °C) and low phenol/Pd molar ratios of 5 – 20 are typically used. In comparison, rhodium has high activity for hydrogenation of the aromatic ring under very mild conditions.[4]. However, there are only a few studies on its use for phenol hydrogenation due to poor selectivity to cyclohexanone.

2. Experimental

Silica-supported samples of 0.5 to 15 wt.% Rh were prepared by wet impregnation using different concentration of RhCl$_3$ solutions. After drying, the samples were calcined at 400 ºC for 4 h in air. The 5 wt.% Rh/SiO$_2$ sample was grafted with molecules of different chain length and chemical groups including 3-mercaptopropyl trimethoxysilane (molar ratio to Rh = 2:1). Nitrogen adsorption isotherms, x-ray powder diffraction, x-ray photoelectron spectroscopy, thermogravimetric analysis, transmission electron microscopy and elemental analysis were measured. The reaction was typically carried out in a two-necked round bottom flask containing 1.5 mmol phenol in 25 ml of cyclohexane at ambient temperature (25 °C) at 1 atm H$_2$. The catalyst at a Rh:phenol mole ratio of 1:100 was added. Unless otherwise stated, the catalyst was pretreated in a H$_2$:He gas flow (2:18 ml min^{-1}) at room temperature for an hour prior to use. Reactions were also carried out in a Berghof HR100 autoclave at 1 bar H$_2$ gauge (pressure maintained by periodic topping up) and 30 ºC. The reaction mixture consisting of 3 mmol (0.282 g) in 50 ml of cyclohexane as solvent was placed in a Teflon liner and an amount of catalyst corresponding to Rh:phenol mole ratio 1:100 was added.

3. Results and discussion

A low Rh loading of 0.5 wt. % resulted in a highly active catalyst with all phenol being converted after only 3.5 h (Table 1). The initial selectivity to cyclohexanone was ~ 75 % and remained fairly constant until all the phenol was consumed whereupon rapid hydrogenation of cyclohexanone to cyclohexanol occurred. Similar kinetic profiles were observed for 2 – 10 wt. % Rh/SiO_2 although full phenol conversion required longer times of 5 to 8 h (Fig. 1a). The initial cyclohexanone selectivity increased to 82 – 85 % with higher Rh loading. In contrast, the initial cyclohexanone selectivity was high, 86 %, for 15 wt. % Rh/SiO_2 but it decreased with increasing conversion to only 35 % at 100 % conversion.

Table 1. Selective hydrogenation of phenol over Rh/SiO_2 catalysts at 30 °C and 1 bar (gauge) H_2.

Entry	Rh (wt. %)	Time (h)	Conv. (%)	Sel. (%)	Conv.[a] (%)	Sel.[a] (%)	TOF [b] (h^{-1})
1	0	24	0	0	0	-	0
2	0.5	3.5	100	69.1	12.5	75.6	4142
3	2	5	100	73.2	10.3	81.4	3748
4	5	5	100	80.5	8.5	83.8	3791
5	10	7	100	65.3	6.3	84.8	3643
6	15	15	100	35.1	3.1	86.2	2644

[a]Conversion and selectivity to cyclohexanone after 0.5 h. [b]Phenol converted after 0.5 h per surface atom.

Based on the reaction kinetics, we propose that at least two different sites are involved for phenol hydrogenation. Sites comprising low coordinated Rh atoms at corners and edges catalyze the direct hydrogenation to cyclohexanol while atoms at terraces or planes catalyze hydrogenation via cyclohexanone. Grafting of surface hydroxyl groups on SiO_2 with (3-mercaptopropyl)methoxysilane resulted in an enhancement in the cyclohexanone selectivity to 91 – 93 % at 100 % conversion (Fig. 1b). This was attributed to a steric effect where the low coordinated sites on the Rh particles are blocked by grafted (3-mercaptopropyl) moieties located within its vicinity.

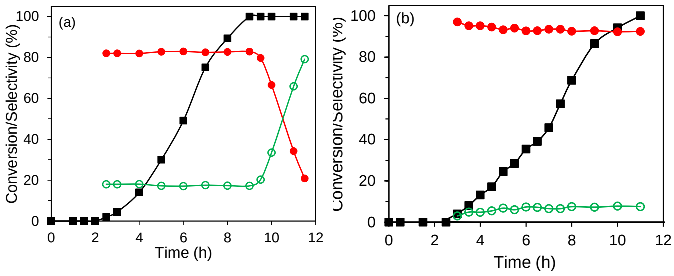

Figure 1. (a) Reaction kinetics for (a) 5 wt.% Rh/SiO_2 and (b) grafted 5 wt.% Rh/SiO_2. (■) Conversion and selectivity to (●) cyclohexanone and (○) cyclohexanol. Reaction conditions: phenol (1.5 mmol), cyclohexane (25 ml), catalyst (0.03 g), 1 atm H_2 in balloon at 25 °C.

4. Conclusions

Silica supported Rh catalysts were active for the hydrogenation of phenol to cyclohexanone at room temperature and 1 atm H_2 pressure but the selectivity to cyclohexanone at 100 % conversion was low. By grafting with (3-mercaptopropyl)methoxysilane, the cyclohexanone selectivity was improved to 93 %. The mild reaction conditions together with *in-situ* activation offer ease of use of this recyclable catalyst.

References

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