

Review of a Cyclohexane Oxidation Reaction Using Heterogenous Catalyst

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Abstract - Cyclohexane oxidation is an important chemical reaction for industrial application. Cyclohexanol and cyclohexanone, also known as K-A oil, are important intermediate products for the production of nylon 6 and nylon 6,6 using oxidation of cyclohexane. A current process uses various metal salt. Commercially-practiced process is operated with very low conversion level, i.e. 4-6 % conversion due to severe selectivity problems. Due to higher reactivity of intermediate desired products, e.g. cyclohexanol and cyclohexanone, compared to cyclohexane leads to many byproducts formation and reduces selectivity drastically at higher conversion level. So it is restricted to operate at lower conversion level to achieve about 70-85% selectivity for K-A oil. Various metal salts like cobalt, gold, silver etc have been used as catalysts for cyclohexane oxidation. Due to stable nature of C-H bond results in higher activation energy required to carry out this reaction at higher temperature. Due to very less solubility of oxygen higher pressure is also desired. This paper discusses about the detail literature survey for cyclohexane oxidation reaction carried out using mainly oxygen or air as an oxidizing agent. With better understanding, it is expected that catalyst with better selectivity towards intermediate products will provide commercially feasible operation.

Keywords - Cyclohexane, selective oxidation, heterogeneous catalyst, cyclohexanol, cyclohexanone, K-A oil

I. INTRODUCTION

Nylon fibers production process is an important commercial process using cyclohexanol and cyclohexanone as intermediate products. Direct oxidation of cyclohexane is a process to produce cyclohexanol and cyclohexanone. Recent review discusses about challenges present for current research [1]. Current commercial processes involve use of manganese or cobalt salts as homogenous catalysts. Process operates at about 425 to 435 K and 10 to 20 bar oxygen or air pressure. Due to stable nature of cyclohexane and higher reactivity of intermediate desired products, large amount of byproducts are generated at higher conversion level. It is desired to keep byproduct formation to reduce separation cost of desire product, K- A oil. Commercial processes are operated at about 4-6% conversion level to keep 70-85% selectivity to cyclohexanol and cyclohexanone [2]. Apart from selectivity, separation of homogeneous catalyst is a major issue. To enhance selectivity and reduce catalyst separation cost, recently many heterogeneous catalytic processes. Being cheapest raw material, air can be considered as desired oxidizing material but other oxidizing materials like oxygen, hydrogen peroxide or tert-butyl hydrogen peroxide have been tried for cyclohexane oxidation reactions. However, due to very high cost of hydrogen peroxide or tert-butyl hydroperoxide, compared to air or oxygen, such processes are economically not viable. Economical the oxidant higher than that of the product [3], further emphasis is given on the catalytic oxidation in liquid phase with the cheaper oxygen as oxidant [4]. Using molecular oxygen as oxidant, some transitional metals such as Ti, V, Cr, Co, Mn, Fe, Mo, Au and metal oxides contained in or on various supports have been extensively studied as the cyclohexane oxidation catalyst [5]. Up to now, the development of new heterogeneous catalysts for the oxidation of cyclohexane is still of considerable commercial and academic interest.

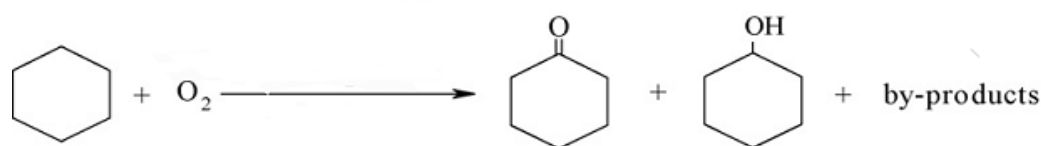


Figure 1. Cyclohexane oxidation reaction to produce K-A oil mixture and other by-product.

Many homogeneous catalytic systems have been tried in the said reaction. Heterogeneous catalysis had also found to be very effective in enhancing selectivity. Most of the mesoporous materials have been successfully used in the selective oxidation of various aromatics. Supported, site-isolated metal oxide materials are considered as an important class of heterogeneous, selective oxidation catalysts. High-surface-area supports like SBA-15 afford highly dispersed metal oxide species which are the key parameter in the rather difficult oxidation of cycloalkanes. Optimization of various reaction conditions leads to the formation of products with high selectivity and yields. The adopted procedure was simple, greener and more efficient to cyclohexene oxidation. SBA-15 materials enabled a better accessibility of active sites to bulky substrate molecules which is reflected in the high conversions of cyclohexene and better selectivity to the epoxide or diol over these novel catalysts [6].

With nano gold catalyst, it is observed that it can produce K-A oil with higher selectivity and cyclohexane conversion [7-10]. Due to higher activation energy of C-H bonds in cyclohexane is known to be very difficult to achieve selectively at temperatures below 100 °C [11].

II. LITERATURE REVIEW

Table1: Results for cyclohexane oxidation reaction [1-14].

Sr No.	Catalyst	Conditions	Yield (%)	conversion (%)	Selectivity (%)	References
1.	Ag/MCM-41	Cyclohexane 0.1 mol, catalyst 0.042 g, O ₂ 1.4 Mpa, 413 K, stirrer, reaction time 3h.	-	10.7	83.4	[1]
2.	Ag/TS-1	Cyclohexane 0.1 mol, catalyst 0.042 g, O ₂ 1.4 Mpa, 413 K, stirrer, reaction time 3h.	-	6.1		[1]
3.	Ag/Al ₂ O ₃	Cyclohexane 0.1 mol, catalyst 0.042 g, O ₂ 1.4 Mpa, 413 K, stirrer, reaction time 3h.	-	2.7		[1]
4.	Au/SiO ₂	cyclohexane 20 ml, catalyst 50 mg; 150 °C, 1.5 MPa; PTFE-lined reactor, reaction time 3h	-	9.2	82.6	[2]
5.	Au/TiO ₂ /SiO ₂	cyclohexane 20 ml, catalyst 50 mg; 150 °C, 1.5 MPa; PTFE-lined reactor, reaction time 3h	-	8.7	88.8	[2]
6.	Au/ZSM-5	cyclohexane 20 ml, catalyst 50 mg; 150 °C, 1.5MPa;reaction time 1hr	-	8.8	-	[2]
7.	AlPO-5	2 ml cyclohexane, 10 mg catalyst, 0.5 MPa O ₂ , at 413 K, 4 h.	-	2.0	86.1	[3]
8.	Ce-AlPO-5	2 ml cyclohexane, 10 mg catalyst, 0.5 MPa O ₂ , at 413 K, 4 h.	-	9.9	95.4	[3]
9.	Sm-AlPO-5	2 ml cyclohexane, 10 mg catalyst, 0.5 MPa O ₂ , at 413 K, 4 h.	-	9.4	93	[3]
10.	Dy-AlPO-5	2 ml cyclohexane, 10 mg catalyst, 0.5 MPa O ₂ , at 413 K, 4 h.	-	10.6	92.6	[3]
11.	Y-AlPO-5	2 ml cyclohexane, 10 mg catalyst, 0.5 MPa O ₂ , at 413 K, 4 h.	-	8.4	94	[3]
12.	La-AlPO-5	2 ml cyclohexane, 10 mg catalyst, 0.5 MPa O ₂ , at 413 K, 4 h.	-	10.1	85.6	[3]
13.	Gd-AlPO-5	2 ml cyclohexane, 10 mg catalyst, 0.5 MPa O ₂ , at 413 K, 4 h.	-	13.1	87.6	[3]
14.	Gd-AlPO-5	2 ml cyclohexane, 10 mg catalyst, 0.5 MPa O ₂ , at 413 K, 6 h.	-	12.8	91.1	[3]
15.	1% Au/graphite	70 °C, 10 mL cyclohexane, 0.05 g additive, 0.12 g catalyst, 0.08 g TBHP, 17 hr	--	3.7	23.1	[4]
16.	2% Au/graphite	70 °C, 10 mL cyclohexane, 0.05 g additive, 0.12 g catalyst, 0.08 g TBHP, 17 hr	-	7.3	9.9	[4]
17.	0.5% Au/ graphite.	70 °C, 10 mL cyclohexane, 0.05 g additive, 0.12 g catalyst, 0.08 g TBHP, 17 hr	-	6.0	17.2	[4]
18.	0.5 %Au/graphite modified with Bi	70 °C, 10 mL cyclohexane, 0.05 g additives, 0.12 g catalyst, 0.08	-	2.1	18.8	[4]

		g TBHP, 17				
19.	0.2% Au/Al ₂ O ₃	cyclohexane 20 ml, catalyst 50 mg; 150 °C, 1.5 MPa, 3 h; 100 ml PTEE-lined autoclave.	-	12.6	84.7	[5]
20.	0.6% Au/ Al ₂ O ₃	cyclohexane 20 ml, catalyst 50 mg; 150 °C, 1.5 MPa, 3 h; 100 ml	-	11.5	86.7	[5]
21.	1.0% Au/ Al ₂ O ₃	cyclohexane 20 ml, catalyst 50 mg; 150 °C, 1.5 MPa, 3 h; 100 ml	-	10.9	84.3	[5]
22.	0.55% Au/ZSM-5	cyclohexane 2 ml, catalyst 5 mg; 150 °C , 1.0 MPa O ₂ , 3 h.	-	7.0	91.0	[5]
23.	Au/SBA-15-im	2 h of reaction	-	8.7	80.3	[6]
24.	Au/F-SBA-15-im	2 h of reaction	-	8.4	79.2	[6]
25.	Au/F-SBA-15-co	2 h of reaction	--	16.6	92.4	[6]
26.	Bi-SBA-15	413 K, 1MPa O ₂ , 4 h	15.7	16.9	93	[7]
27.	Ti ₈₅ Zr ₁₀ Co ₅	cyclohexane 8ml, catalyst 40 mg, oxygen 2MPa, temperature 413 K, time 6 h.	-	2.0	99.6	[8]
28.	Ti ₈₀ Zr ₁₀ Co ₁₀	cyclohexane 8ml, catalyst 40 mg, oxygen 2MPa, temperature 413 K, time 6 h.	-	2.6	99.5	[8]
29.	Ti ₅ Zr ₇₅ Co ₂₀	cyclohexane 8ml, catalyst 40 mg, oxygen 2MPa, temperature 413 K, time 6 h.	-	6.5	86.9	[8]
30.	Ti ₁₀ Zr ₇₀ Co ₂₀	cyclohexane 8ml, catalyst 40 mg, oxygen 2MPa, temperature 413 K, time 6 h.	-	6.9	82.6	[8]
31.	Ti ₂₀ Zr ₆₀ Co ₂₀	cyclohexane 8ml, catalyst 40 mg, oxygen 2MPa, temperature 413 K, time 6 h.	-	6.3	85.5	[8]
32.	Ti ₃₀ Zr ₅₀ Co ₂₀	cyclohexane 8ml, catalyst 40 mg, oxygen 2MPa, temperature 413 K, time 6 h.	-	6.1	86.8	[8]
33.	Ti ₄₀ Zr ₄₀ Co ₂₀	cyclohexane 8ml, catalyst 40 mg, oxygen 2MPa, temperature 413 K, time 6 h.	--	6.8	83.2	[8]
34.	Ti ₅₃ Zr ₂₇ Co ₂₀	Cyclohexane 8ml, catalyst 40 mg, oxygen 2MPa, temperature 413 K, time 6 h.	-	5.1	88.0	[8]
35.	Ti ₆₅ Zr ₁₅ Co ₂₀	cyclohexane 8ml, catalyst 40 mg, oxygen 2MPa, temperature 413 K, time 6 h.	-	5.8	95.8	[8]
36.	Ti ₇₀ Zr ₁₀ Co ₂₀	cyclohexane 8ml, catalyst 40 mg, oxygen 2MPa, temperature 413 K, time 6 h.	-	6.8	90.4	[8]
37.	Ti ₇₅ Zr ₅ Co ₂₀	cyclohexane 8ml, catalyst 40 mg, oxygen 2MPa, temperature 413 K, time 6 h.	-	5.9	93.7	[8]
38.	Ti ₆₀ Zr ₁₀ Co ₃₀	cyclohexane 8ml, catalyst 40 mg, oxygen 2MPa, temperature 413 K, time 6 h.	-	4.6	76.9	[8]
39.	Ti ₅₀ Zr ₂₀ Co ₃₀	cyclohexane 8ml, catalyst 40 mg, oxygen 2MPa, temperature 413 K, time 6 h.	-	4.5	84.8	[8]

40.	Ti ₅₀ Zr ₁₀ Co ₄₀	cyclohexane 8ml, catalyst 40 mg, oxygen 2MPa, temperature 413 K, time 6 h.	-	4.3	73.5	[8]
41.	The presence of carbamated modified silica gel supported bis(maltolato)oxovanadium complex [VO(ma) ₂]	catalyst = 20 mg, O ₂ pressure = 10 atm, cyclohexane = 5.0 ml, 175 °C, 20 h, in an autoclave	-	15.8	11.2	[9]
42.	Co-ZSM-5	temperature, 373 K; pressure, 1.0 MPa O ₂ ; time, 4 h; the amount of catalyst, 200 mg	-	7.50	92.4	[10]
43.	Fe-ZSM-5	temperature, 373 K; pressure, 1.0 MPa O ₂ ; time, 4 h; the amount of catalyst, 200 mg	-	6.47	74.5	[10]
44.	Mn-ZSM-5	temperature, 373 K; pressure, 1.0 MPa O ₂ ; time, 4 h; the amount of catalyst, 200 mg		6.19	71.1	[10]
45.	Cu-ZSM-5	temperature, 373 K; pressure, 1.0 MPa O ₂ ; time, 4 h; the amount of catalyst, 200 mg		6.29	75.2	[10]
46.	Ni-ZSM-5	temperature, 373 K; pressure, 1.0 MPa O ₂ ; time, 4 h; the amount of catalyst, 200 mg		2.48	54.4	[10]
47.	Cr/ZSM-5	temperature, 373 K; pressure, 1.0 MPa O ₂ ; time, 4 h; the amount of catalyst, 200 mg		2.54	75.9	[10]
48.	Na-ZSM-5	temperature, 373 K; pressure, 1.0 MPa O ₂ ; time, 4 h; the amount of catalyst, 200 mg		0.69	53.6	[10]
49.	Co ₃ O ₄	Temp.: 130 °C; Pressure: 1.0 MPa O ₂ , Time: 2 h; Catalyst: 200 mg		11.1	89.3	[11]
50.	Co/ZSM-5	Temp.: 130 °C; Pressure: 1.0 MPa O ₂ , Time: 2 h; Catalyst: 200 mg		7.2	96.1	[11]
51.	3%Co/SiO ₂	Temp.: 130 °C; Pressure: 1.0 MPa O ₂ , Time: 2 h; Catalyst: 200 mg		7.3	86.3	[11]
52.	3% Co/Al ₂ O ₃	Temp.: 130 °C; Pressure: 1.0 MPa O ₂ , Time: 2 h; Catalyst: 200 mg		6.2	90.4	[11]
53.	3% Co/MgO	Temp.: 130 °C; Pressure: 1.0 MPa O ₂ , Time: 2 h; Catalyst: 200 mg		4.8	98.7	[11]
54.	CoAlPO-11	Temp.: 130 °C; Pressure: 1.0 MPa O ₂ , Time: 2 h; Catalyst: 200 mg		5.5	83.2	[11]
55.	FeAlPO-11	Temp.: 130 °C; Pressure: 1.0 MPa O, Time: 2 h; Catalyst: 200 mg		7.5	89.5	[11]
56.	Au/ZSM-5	423 K, 1 MPa O ₂ , 4 h	14.7	16	92	[12]
57.	Ce/AlPO-5	413 K, 0.5 MPa O ₂ , 4 h	11.8	13	91	[12]

58.	Co/ZSM-5	373 K, 1 MPa O ₂ , 4 h	6.9	7.5	92.4	[12]
59.	Fe/AlPO	403 K, 2 MPa air, 24 h	7.0	5.5	93.6	[12]
60.	Bi-MCM-41	423 K, 1 MPa O ₂ , 4 h	15.5	17	91	[12]
61.	Au/MCM-41	423 K, 1 MPa O ₂ , 6 h	17.9	19	94	[12]
62.	Au/SBA-15	423 K, 1 MPa O ₂ , 6 h	16.7	18	93	[12]
63.	[Cr]MCM-41	388 K, 1 MPa O ₂ , 6 h	<9	<10	90	[13]
64.	FeAlPO-5	403 K, 1 MPa air, 8 h	1.5	2.5	59	[13]
65.	FeAlPO-5	403 K, 1 MPa air, 24 h	3.4	6.6	51.7	[13]
66.	MnAlPO-5	403 K, 1 MPa air, 8 h	2.5	2.7	92.9	[13]
67.	MnAlPO-5	403 K, 1 MPa air, 24 h	3.8	6.2	61.3	[13]
68.	CoAlPO-5	403 K, 1 MPa air, 8 h	0.9	1.6	56.7	[13]
69.	CoAlPO-5	403 K, 1 MPa air, 24 h	1.6	2.0	82.8	[13]
70.	C ₂₇ ClC ₁₅ Chromium- containing small pore mesoporous silica	393 K, 2.7 MPa air, 6 h	7.4	8.0	92	[14]
71.	[Cr]MCM-48	388 K, 1 MPa O ₂ , 6 h	<9	<10	90	[14]

III. SUMMARY

Development of new process for direct oxidation of cyclohexane in presence of oxygen or air with higher conversion and good selectivity is the main objective of the current researcher. It is also have lots of commercial significance. Due to more stable nature of cyclohexane and more reactivity of intermediate products like cyclohexanol and cyclohexanon, selective oxidation is a major challenge. Literature survey suggests that the air oxidation of cyclohexane produces only limited conversion, about 10-19% with 80-95% selectivity with gold metal and different supports like ZSM-5, MCM-41, SBA-15. Further efforts and understanding is required to reduce activation energy and replace the traditional process of cyclohexane oxidation to K-A oil.

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