

A New Route to Control Product Selectivity in the Oxidative Dehydrogenation of Cyclohexane and Cyclohexene

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The product selectivity can be controlled by adding acetic acid in feed over vanadium phosphate (VPO) in gas phase oxidative dehydrogenation (ODH), in which cyclohexane and cyclohexene are oxidized to cyclohexene and 1,3-cyclohexadiene (1,3-CHD), respectively, at almost 100% selectivity. This approach is also an efficient method to capture the very unstable intermediates in the mechanism study.

The selective catalytic oxidative dehydrogenation has been the subject of many studies due to the importance of refining and reforming process in the petroleum industry, but there are very few practical processes for converting hydrocarbons directly to more valuable products.¹ This is attributed to the relatively inert C–H bond in the hydrocarbons and the desired products are relatively active, which will result in very low selectivity of the desired products or must keep at very low conversion.² Here we show a new route to control product selectivity in the oxidative dehydrogenation by adding acetic acid (HOAc) in feed over phosphates catalysts.

In recent years, it has been the focus topics to exploit Earth's resources more efficiently and cleanly.² A new process to produce adipic acid (the precursor for Nylon-6,6) by oxidation of cyclohexene with H₂O₂ has been reported.³ It is a green process and is completely different from the traditional process to produce adipic acid from cyclohexene as raw material. In the practical process of the hydrogenation of benzene to cyclohexene, it is not only the low yield of cyclohexene (≈30%), but also the low selectivity of cyclohexene (≈60%)⁴ because the complete hydrogenation of benzene to cyclohexane is much more favorable in thermodynamics.⁵ Considering the oxidation of cyclohexene to adipic acid with H₂O₂, it might need another process to obtain cyclohexene by oxidative dehydrogenation of cyclohexane in gas phase. But only a mixture of maleic anhydride (MA) and benzene generally is obtained over vanadium phosphate (VPO) under conventional conditions.⁶ It is well known that vanadium phosphorous oxides have been widely investigated for partial oxidation and oxidative dehydrogenation of hydrocarbons.⁶

It is found that VPO catalysts⁷ also show very strong ability to abstract H-atom in partial oxidation of cyclohexane in gas phase in our experiments as shown in Table 1. In the absence of acetic acid, the main products in cyclohexane oxidation are benzene, maleic anhydride (MA), CO_x and no cyclohexene at various temperatures.⁶ In this study, it is found that the selectivity of products appears a huge change when acetic acid is added in the feed. The selectivity of the main product changes from MA to benzene, 1,3-cyclohexadiene, and then to cyclohexene as shown in Table 1. Besides, almost ≈100% selectivity to cyclohexene can be obtained when the mole ratio of acetic acid

to cyclohexane is up to 12.9:1 at 723 and 773 K, the conversion of cyclohexane is at 6.9% and at 11.9%, respectively. When the mole ratio of acetic acid to cyclohexane is from 5.3:1 to 7.7:1, cyclohexene, 1,3-CHD (trace 1,4-CHD), benzene, maleic anhydride and CO_x can appear simultaneously at 723 K. These results indicate that both cyclohexene and 1,3-CHD are intermediates in the oxidative dehydrogenation of cyclohexane to benzene and then benzene is oxidized further to MA.

Table 1. The results of cyclohexane ODH to cyclohexene adding different quantity of HOAc at 723 K⁸

HOAc/C ₆ H ₁₂ /mole ratio	Conversion /mole %	Selectivity/mole %			
		C ₆ H ₁₀	1,3-CHD	C ₆ H ₆	MA, CO _x
0	24.7	0	0	63.0	37.0
2.4	16.9	0.70	0	68.1	31.2
5.3	14.5	50.0	8.1	23.7	18.2
7.7	11.8	83.4	2	13.7	0.9
10.3	7.5	95.5	0.5	4.0	0
12.9	6.9	100	0	0	0

Reaction condition: catalyst, 0.20 g; cyclohexane, 9.25 mmol·h⁻¹; air, 40 mL·h⁻¹.

In the meanwhile, the disadvantage in the new route is that about 2–3% acetic acid has been oxidized into CO_x at 723 K.

Considering very low stability of 1,3-cyclohexadiene in thermodynamics as an intermediate in the oxidative dehydrogenation of cyclohexane,⁹ the above approach is also applied to the preparation of 1,3-CHD by the oxidative dehydrogenation of cyclohexene. It is well known that 1,3-CHD-based polymers are a very interesting class of materials due to their good heat, weather, impact, abrasion, and chemical resistances, low water absorption, birefringence, and excellent transparency and rigidity.¹⁰ Nowadays, many methods for preparation of 1,3-CHD have been reported in the literature.¹¹ These preparation methods are not suitable to produce 1,3-CHD in large scale, and they are lower efficient and non-environmental-friendly. In the catalytic methods, Amano reported that cyclohexene is dehydrogenated with only 3–32% selectivity to 1,3-CHD over C/Al₂O₃ under non-oxidative conditions.¹² Iwasawa reported only 16% selectivity to cyclohexadiene under 2.55% conversion to cyclohexene over polynaphthoquinone catalyst in the presence of oxygen.¹³

In the absence of HOAc, no 1,3-CHD can be detected in products even if both conversion and reaction temperatures keep lower.

Table 2 gives the result of the oxidative dehydrogenation of cyclohexene with the various amount of HOAc over VPO catalyst⁷ at 723 K. When the molar ratio of HOAc to cyclohexene in feed varies from 0 to 1:1, a small amount of 1,3-CHD and a large amount of benzene appear in the products with a decrease of conversion. With an increase of HOAc amount, the selectivity to 1,3-CHD also gradually increases. The high selectivity to

1,3-CHD (almost 100%) appears in the molar ratio of HOAc to cyclohexene above 12.1:1 at 3.8% conversion. These results indicate that addition of HOAc in feed can adjust very efficiently the oxidation of 1,3-CHD to benzene. Like the oxidation of cyclohexane, $\approx 2.5\%$ HOAc is also oxidized to CO_x in this reaction.

Table 2. The results of cyclohexene ODH to 1,3-CHD adding different quantity of HOAc at 723 K⁸

HOAc/C ₆ H ₁₀ /mole ratio	Conversion /mole %	Selectivity/mole %		
		1,3-CHD	C ₆ H ₆	MA, CO _x
0	99.9	0	55.8	44.2
0.40	95.0	0	68.2	31.8
1.0	85.0	<1.00	76.8	22.2
2.2	14.8	1.00	74.0	25.0
4.7	10.0	11.0	80.0	9.00
7.2	8.10	47.8	47.2	5.00
9.6	5.00	77.5	22.5	0
12.1	3.80	100	0	0

Reaction condition: catalyst, 0.20 g; cyclohexane, 9.86 mmol·h⁻¹; air, 40 mL·h⁻¹.

In general, these results show that the above process can be used to obtain the unstable intermediates in oxidative dehydrogenation of cyclohexane and cyclohexene. No trace amount of the oxygenated products (such as cyclohexanol, cyclohexanone) can be detected in above both reactions. To explain the action of acetic acid in the oxidative dehydrogenation of cyclohexane and cyclohexene, a series of experiments on the change of the space velocity are carried out. The results show that $\approx 100\%$ selectivity to 1,3-CHD corresponding to only 0.62% conversion to cyclohexene can be obtained when the space velocity is increased to 160 times as the primary. Besides, N₂ as diluent is also fed in the reactor, but the products selectivity do not obviously vary with the flow rate from 20 to 120 mL min⁻¹. These results indicate that acetic acid is not like diluent but interacts with the active centers on catalyst as adsorptive species. So we suggest that acetic acid should be adsorbed on the active sites of VPO catalyst to precede reactants (cyclohexane, cyclohexene) so that there is almost no adjacent active site for the oxidative dehydrogenation of reactants. The isolated active site thus formed is attributed to forbidding the further oxidation of desired products,¹⁴ which is very similar to the active center in enzymes. As a result, the primary product could be desorbed very quickly from the catalyst surface to avoid the further oxidation because of the strong adsorption of acetic acid on the active sites of VPO catalyst. So we suggest that the action of acetic acid should not be thought as per-acid with oxygen because the activity is decreased after the addition of HOAc in the feed.

The above results indicate that the new route can obtain efficiently the very unstable intermediates in oxidative dehydrogenation. It is possible to utilize the approach to produce the valuable and unstable chemicals, but it can be more important as a new method to investigate the mechanism and determine initial intermediates. In the activation of alkane molecules, there can be two routes in the reaction pathway when a hydrogen atom was first abstracted from the substrate molecules on the catalyst surface; (1) consecutively abstract the second H atom to form an olefin or (2) alternatively interact with oxygen from the lattice oxygen or from the gas phase oxygen, which can form an oxygenated intermediate. However, there is still little information

on the described process. If a trace amount of primary species, olefin and/or oxygenated intermediate, can be captured by adding acetic acid in the feed over different catalysts, thus, it provides the information on the reaction mechanism and distinguishes the function of the catalyst in catalytic selective oxidation. This work will be described in elsewhere.

The new route shows that HOAc in the feed can efficiently adjust the oxidation ability of catalysts and can be applied into the production of very unstable intermediates with high selectivity. Besides, the process could also be thought to be the new way to investigate the mechanism in oxidative dehydrogenation because it can capture efficiently the unstable intermediates, which also prove the powerful information to understand the mechanism in oxidation dehydrogenation. It takes a new inspiration how to control selective oxidation of alkane.

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