Selective Oxidation of Cyclohexane at Low Temperature by Fe-Pd Bicatalytic Systems; FeCl₂-Pd/alumina System and Pd/Fe₂O₃ System

Ki-Won Jun, Lingaiah Nakka, Sang-Bum Kim, and Kyu-Wan Lee*

Chemical Technology Lab. I, Korea Research Institute of Chemical Technology,
P.O. Box. 107, Yusong, Taejon 305-600, Korea
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The system which employs iron, palladium, molecular oxygen and hydrogen as a model mono-oxygenase, has been investigated to develop a new method for selective cyclohexane oxidation under mild conditions. This system provides much higher yield and selectivity for the formation of cyclohexanol and cyclohexanone compared to that of the existing industrial method. When the catalytic system, FeCl₂-Pd/alumina, was employed, the oxidation system required acetone as a solvent to be efficient and acidifying the solvent by a little addition of acetic acid or HCl made the system more efficient. The Pd catalyst was recyclable without a significant deactivation but the recycling of ferrous chloride showed the decrease in the activity. On the other hand, the heterogeneous catalytic system, Pd/Fe₂O₃ could be recovered easily and reused after drying treatment.

Introduction

Many efforts have been made to develop an efficient method for oxidation of unactivated C-H bonds of alkanes because of importance in view of both industrial and synthetic aspects.[1-7] The existing oxidation processes usually require severe reaction conditions and a mixture of products is formed in the vast majority of cases. In a typical industrial process, cyclohexane oxidation is carried out at 160 °C and 15 bar using a Co(II) catalyst, giving only 4% conversion with 80% selectivity for cyclohexanone and cyclohexanol.

In contrast with the industrial process, the selective functionalization of non-activated C-H bonds of saturated hydrocarbons takes place *via* enzymatic catalysis in living organisms. Many enzyme-mimetic systems also allow the selective oxidation of hydrocarbons under mild conditions.[8-10] However, they mostly require the complicated metal complexes such as metallo-porphyrins, which are often less durable during the reaction. Furthermore, many of them employ mono-oxygen donor agents such as iodosobenzene in stead of molecular oxygen. The Gif systems[1,2] developed by Barton and co-workers, seem so attractive because they consist of simple and readily available reagents. For example, the Gif^V system consists of iron(II), molecular oxygen, acetic acid as a proton source, zinc dust as a reducing agent and requires the pyridine-acetic acid mixture as a solvent.

Although using molecular oxygen in place of the mono-oxygen donors should have significant advantages, it generally requires a proton source and a metallic reducing agent to activate oxygen molecule, which is dissolved into the reaction mixture and ultimately makes the catalyst recovery difficult. In this work, we have sought to establish procedures through which molecular oxygen could be used without a metallic reducing agent.

First, we used iron chlorides like Gif type reactions, but we did not use any metallic agents and organic proton sources, instead hydrogen gas was added together with a Pd/

alumina catalyst to activate molecular oxygen. We already reported our initial results on the selective oxidation of cyclohexane.[11] The study has been pursued further and we report here the data that were obtained from our supplementary research. Attention is also given to the catalyst recycling.

Experimental

Commercial Pd/alumina (Pd=1 wt%) catalyst was obtained from Aldrich and used without any modification. Palladium supported on iron oxide (Fe-Pd) catalysts (Pd=10 wt%) were prepared by impregnation method. The required amount of PdCl₂ was added to Fe₂O₃ in aqueous medium. The excess water was removed by using rotary evaporator at 60 °C and the catalyst masses were dried at 120 °C for 2h. The dried samples were calcined at different conditions to prepare four types of catalysts (Table 1). For convenience, the four samples were labeled (H), (HA), (A) and (AH) to denote calcination environment (H=5% H₂ in N₂, A =air).

The X-ray Diffraction (XRD) measurements for the prepared Fe-Pd samples were performed on a Rigaku D/MAX III B diffractometer with a copper target. The X-ray photoelectron spectroscopy (XPS) measurements were carried out on a VG Escalab MK II photoelectron spectrometer,

Table 1. Calcination methods and surface areas of prepared Fe-Pd samples

Catalyst code	Calcination method		BET surface area (m²/g)
	1st treatment	2nd treatment	
(H)	at 500 °C for 6h in 5%H₂/N₂	–	4.5
(HA)	at 500 °C for 6h in 5%H₂/N₂	at 500 °C for 6h in air	4.9
(A)	at 500 °C for 6h in air	–	6.5
(AH)	at 500 °C for 6h in air	at 100 °C for 6h in 5%H₂/N₂	7.0

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*To whom correspondence should be addressed.

which was equipped with a magnesium anode operated at 15 kV and 20 mA.

The reaction was carried out in a round bottom flask equipped with a gas bubbler and a refrigerated condenser (maintained at $-$ 20 °C) at 30-35 °C under atmospheric pressure. Iron chloride and Pd/alumina were added to cyclohexane in a solvent and the gases of hydrogen and oxygen were bubbled through the stirred reaction mixture. The palladium on iron oxide catalysts were also examined instead of iron chloride+Pd/alumina. As a solvent, acetone was mainly used. In order to prevent an explosion, precautions were taken to ensure that there was no ignition source. After completion of the reaction, acetophenone as an internal standard was added into the mixture and the solid catalysts were separated by filtration. The reaction mixture was analyzed by a gas chromatography using 5% OV-17 on a chromosorb column (1/8"×5') with a flame ionization detector. The yields were calculated based on cyclohexane. In this reaction, mainly cyclohexanol and cyclohexanone were formed and the formation of other organic products was negligible.

Results and Discussion

Iron chloride-Pd/alumina system. The reaction results using iron chloride and the Pd/alumina catalysts in various solvents are shown in Table 2. The mixed solvent of pyridine and acetic acid, which is originally the Gif-type solvent, gave high ketone selectivity like the Gif reactions. When the mixed solvent of acetone and acetic acid was used, the reaction showed an improved conversion to cyclohexanol+cyclohexanone and high alcohol selectivity. However, the addition of pyridine into the acetone solvent made the reaction system much less efficient.

There are many factors that would be involved in the solvent effects such as the reactant solubility, the solvent polarity, the ligand effects of solvents and the ability of stabilizing reactants or intermediates. Generally, it is very difficult to elucidate the solvent effects clearly because of its complication. For the effective oxidation, the solvent should have the ability of dissolving all the reactants, hydrogen, oxygen, cyclohexane and hydrogen peroxide for transferring

the reactant species to the catalysts. In this reaction, it is likely that one of the important solvent effects is related to the formation and stabilizing of hydrogen peroxide. This speculation is supported by the fact that acetone favors the direct production of hydrogen peroxide from O_2 and H_2 on Pd catalysts.[12]

The solubility of iron chloride is one of the factors to be considered with the effect of acetic acid. The solubility of $FeCl_2 \cdot 4H_2O$ is very low in acetone but it is enhanced considerably when acetic acid is added to acetone. In our previous paper,[11] however, we reported that the promoting effect of acetic acid was also found with $FeCl_3 \cdot 6H_2O$ and the total amount of $FeCl_3 \cdot 6H_2O$ used in the reaction was dissolved completely even in pure acetone. Therefore, the promoting effect of acetic acid is not likely due to simple enhancement of iron chloride solubility. Moreover, in the comparison reactions under the same conditions as the oxidation except that cyclohexane was not added, we could not find an evidence of increasing hydrogen peroxide formation by acetic acid addition; the addition of acetic acid did not increase the concentration of hydrogen peroxide accumulated during the reaction.[11] It is known that iron complex bearing carboxylate bridges is formed from acetic acid and iron chloride in Gif^{IV} system.[1] It is unlikely that the active species of the present system is exactly same as that of the Gif system because of the different product selectivity of two reactions: the Gif system gives high selectivity to ketones. However, we can not completely exclude the possibility of promoting by acetate ligand.

In the acetone-acetic acid solvent system, iron metal and various iron halides were examined in this reaction (Table 3). The results show that only iron chlorides are efficient in the reaction.

It is expected that the use of a stabilizer of hydrogen peroxide would possibly make the oxidation system more efficient. Some acids like hydrochloric acid was reported as the stabilizers that inhibit the decomposition of H_2O_2, thereby improving the H_2O_2 formation further.[13,14] In this study, therefore, we investigated the effects of acid addition into the acetone solvent. The results using the acid-modified solvent systems are listed in Table 4. From the results, it should be noted that the addition of a small amount of acid like HCl to acetone leads to considerable improvement in yield. It is more likely that chloride ion has a kind of pro-

Table 2. Cyclohexane oxidation with $FeCl_2$ and Pd/alumina in various solvents[a]

Solvent (amount, mL)	Conversion[b] (mole %)	Selectivity (mole %)	
		cyclo-hexanol	cyclo-hexanone
Pyridine (20)	0.48	20.8	79.2
Acetic acid (20)	0.78	74.4	25.6
Acetone (20)	1.57	82.8	17.2
Acetonitrile (20)	0.66	51.5	48.5
Pyridine (20)+acetic acid (2)	1.54	9.7	90.3
Acetone (15)+pyridine (5)	0.23	65.2	34.8
Acetone (17)+acetic acid (3)	4.77	82.6	17.4

[a] Conditions: cyclohexane (59.4 mmole), $FeCl_2 \cdot 4H_2O$ (1.5 mmole), Pd/alumina (1 g), H_2 (20 mL/min), O_2 (20 mL/min), reaction temp.=30 °C, reaction time=3 h. [b] Conversion is based on cyclohexane.

Table 3. Cyclohexane oxidation with various type of iron compounds[a]

Iron compound	Conversion[b] (mole %)	Selectivity (mole %)	
		cyclohexanol	cyclohexanone
Fe metal	1.90	71.1	28.9
$FeF_3 \cdot 3H_2O$	2.47	68.0	32.0
$FeCl_2 \cdot 4H_2O$	4.77	82.6	17.4
$FeCl_3 \cdot 6H_2O$	5.02	84.1	15.9
$FeBr_3$	0	–	–
FeI_2	0.41	–	100

[a] Conditions: cyclohexane (59.4 mmole), Fe compound (1.5 mmole), Pd/alumina (1 g), acetone (17 ml)+acetic acid (3 mL), H_2 (20 mL/min), O_2 (20 mL/min), reaction temp.=30 °C, reaction time=3 h. [b] Conversion is based on cyclohexane.

Selective Oxidation of Cyclohexane

Bull. Korean Chem. Soc. **1997**, Vol. 18. No. 12   1271

Table 4. Cyclohexane oxidation with $FeCl_2$ and Pd/alumina in acid-modified solvents[a]

Solvent (amount, mL)	Conversion[b] (mole %)	Selectivity (mole %)	
		cyclo-hexanol	cyclo-hexanone
Acetone (20)	1.57	82.8	17.2
Acetone (19)+acetic acid (1)	4.12	85.0	15.0
Acetone (19)+HCl 37% (1)	7.18	88.2	11.8
Acetone (20)+H_2SO_4 (0.3)	2.24	99.6	0.4
Acetone (20)+HNO_3 70% (0.3)	1.91	86.9	13.1

[a] Conditions: cyclohexane (59.4 mmole), $FeCl_2 \cdot 4H_2O$ (1.5 mmole), Pd/alumina (1 g), H_2 (20 mL/min), O_2 (20 mL/min), reaction temp.= 30 °C, reaction time=3 h. [b] Conversion is based on cyclohexane.

moting effects as observed in the effects of anions (Table 3). The promoting effect of acetic acid also seems to be related to the effect of HCl, which can be formed from the counter ion exchange between iron chloride and acetic acid.

Through the experiments using $FeCl_2$-Pd/alumina for extended reaction time, we have already shown that the conversion increased with the time and then reached up to *ca.* 12 mole %.[11] Here, we investigated how high yield can be obtained by the increase in $FeCl_2$ amount. Figure 1. shows the effect of $FeCl_2$ amount in this reaction. The conversion increased initially with $FeCl_2$ amount but remained almost constant above the $FeCl_2$ amount of 1.5 mmole. This system was designed to utilize hydrogen peroxide formed *in situ* by the palladium catalyzed combining of molecular oxygen and hydrogen. Therefore the reaction seems to proceed *via* two steps: hydrogen peroxide is formed from O_2 and H_2 by the Pd/alumina and then hydrogen peroxide is used for the oxidation of cyclohexane by the iron ion. The rate of each step would be affected by the amount of the catalyst that is responsible for the step. As increasing the amount of $FeCl_2$, the rate of the second step would be increased till the reaction is controlled by the first step. As the higher amount of $FeCl_2$ is employed, the additional in-
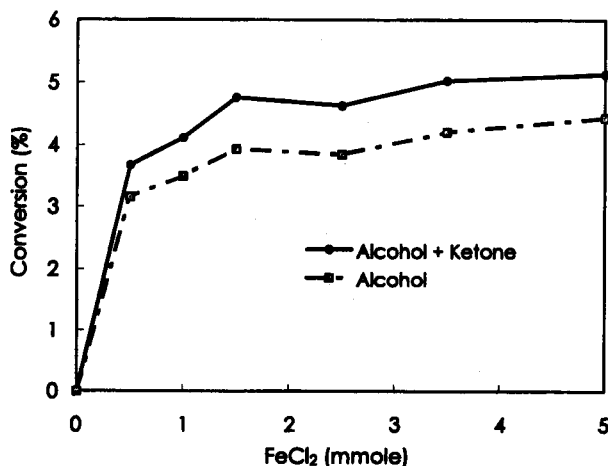
Figure 1. The effects of $FeCl_2$ amount in the reaction. Conditions: cyclohexane (59.4 mmole), Pd/alumina (1 g), acetone (17 mL)+acetic acid (3 mL), H_2 (20 mL/min), O_2 (20 mL/min), reaction temp.=30 °C, reaction time=3 h.
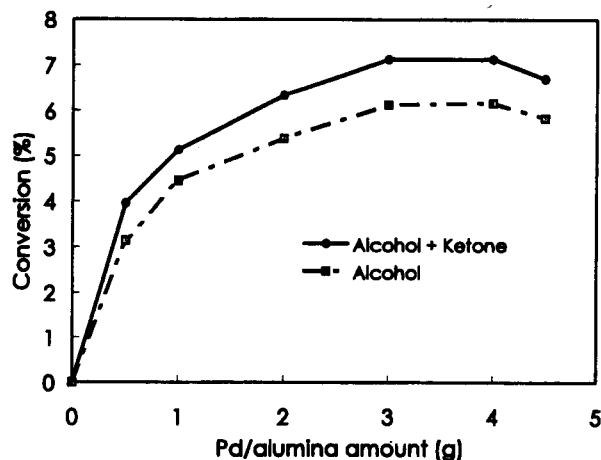
Figure 2. The effects of Pd/alumina amount in the reaction. Conditions: Cyclohexane (59.4 mmole), $FeCl_2$ (5 mmole), Pd/alumina (1 g), acetone (17 mL)+acetic acid (3 mL), H_2 (20 mL/min), O_2 (20 mL/min), reaction temp.=30 °C, reaction time=3 h.

crease in the conversion seems to be limited by the step of H_2O_2 formation.

While the large amount of $FeCl_2$ being employed, the effect of Pd/alumina amount was also investigated (see Figure 2). The oxidation conversion increased with the increase up to 3 g of the Pd/alumina amount and then decreased slightly. Increased conversion, achieved by additional use of Pd/alumina, should be the result of relieving the constraint at the H_2O_2 formation step. However, over-use of Pd/alumina resulted in the decrease of the conversion. In the presence of large amount of Pd/alumina, the supply of H_2 and O_2 should be limited because of their restricted solubility in the solvent. Under the condition of limited supply of dissolved H_2 and O_2, excess Pd/alumina would lead to decrease in H_2O_2 concentration rather than increase because of its ability of decomposing H_2O_2. The Pd metal is also known to be active in the decomposition of hydrogen peroxide into water and oxygen.[15]

In the $FeCl_2$-Pd/alumina system, the repeated use of catalytic system was examined. First Pd/alumina was recycled. After the reaction Pd/alumina catalyst was filtered and dried at oven temperature (120 °C) and reused with fresh iron chloride in the reaction. The results of the repeated use were presented in Table 5. The results show that there was ·

Table 5. Cyclohexane oxidation using recycled Pd/alumina[a]

No. of use for Pd/alumina	Conversion[b] (mole %)	Selectivity (mole %)	
		cyclohexanol	cyclohexanone
1	7.12	86.1	13.8
2	7.14	87.8	12.0
3	7.14	83.5	16.5
4	6.69	85.7	14.5
5	6.42	84.9	15.1
6	6.73	86.2	13.8

[a] Conditions: cyclohexane (59.4 mmole), $FeCl_2 \cdot 4H_2O$ (5 mmole), Pd/alumina (3 g), acetone (17 mL)+acetic acid (3 mL), H_2 (20 mL/min), O_2 (20 mL/min), reaction temp.=30 °C, reaction time=3 h. [b] Conversion is based on cyclohexane.

not so significant decrease in the catalyst activity upon repeated use.

Recycling of iron chloride has been also attempted. After the reaction the iron salt was recovered by evaporating all the organic materials for the repeated use experiments. These results were presented in Table 6. A considerable decrease in the conversion was observed upon the recycling up to 2 times but there was not additional decrease in the subsequent recycling. Atomic absorption spectroscopy analysis showed that only 52% of original iron ions was dissolved in the solution after the repeated reactions, indicating the activity loss is due to the formation of insoluble iron salts. These results suggest that the use of a heterogeneous catalytic system should be more desirable way for its easy recovery and stability.

Iron oxide-Pd system. As shown in Table 1, there was no big variation in the surface areas of Fe-Pd catalysts due to pretreatment conditions.

In the XRD experiments, it was found that the Fe_2O_3 phase was predominant in all the catalysts except in the catalyst (H). In case of the catalyst (H) calcined under a hydrogen atmosphere, Fe_3O_4 phase was found to be predominant. XRD results for all the catalysts did not show any Pd phases, suggesting that palladium species exist in the amorphous phase.

The XPS binding energies of Fe $2p_{3/2}$ and Pd $3d_{5/2}$ electrons along with Fe/Pd atomic ratios are presented in Table 7.

The XPS binding energies of $2p_{3/2}$ electrons of iron of all the catalysts were almost identical with iron oxides (Fe_2O_3 or Fe_3O_4). The B. E. values for Fe_2O_3 and Fe_3O_4 are too close to distinguish them with the help of XPS. The Pd $3d_{5/2}$ binding energies of the catalysts (H) and (AH) corresponded to Pd metal, indicating that $PdCl_2$ was reduced

under a H_2 atmosphere. The catalysts (HA) and (A) show the binding energy values which are close to $PdCl_2$ (338.0 eV) rather than PdO (336.4 eV). Since palladium chloride is known to be decomposed above 680 °C,[16] palladium chloride on the iron oxide would not be changed during the calcining at 500 °C in air. This is in agreement with the result that the catalyst (A) shows the binding energy of $PdCl_2$. In case of the catalyst (HA), palladium metal species would be formed during the first calcination under the reductive atmosphere, and then the surface would be oxidized during the 2nd calcination in air. It is known that palladium acquires a superficial coating of oxide when heated in air from 350 to about 790 °C.[16] However, the binding energy obtained in the catalyst (HA) was different from that of PdO. A possible explanation for the higher value in the binding energy is that surface palladium oxidic species is different from bulk PdO. This seems to be related with PdO_2 species bearing higher binding energy (337.6 eV) for Pd $3d_{5/2}$ electrons. In the results of Pd/Fe ratios, the catalysts (HA) and (A) show much higher value than the catalysts (H) and (AH), suggesting that the calcination in air gives higher dispersion of Pd on iron oxide than that in H_2/N_2.

Figure 3 shows variations in the activity of four kinds of Fe-Pd catalysts. For comparison, the reaction was carried out using only $PdCl_2$/silica or only Fe_2O_3. However, either reaction gave no oxygenation product. These findings are in support with the idea that the catalytic ability is founded on combining individual functions of two metal species. The Fe-Pd catalytic system seems to function by direct combination of H_2 and O_2 at the Pd site followed by migration of the H_2O_2 to the iron site where the oxidation of substrate occurs. Although it is premature to discuss the precise mechanism at the present stage, it may be suggested that the reaction proceeds through the formation of an analogue of the FeO^{3+}, which is the potent oxidant of the natural enzyme cytochrome P-450 [17]: $H_2O_2 + Fe(III) \rightarrow FeO^{3+} + H_2O$.

As shown in Figure 3, the order of activity was (HA) > (A) > (AH) > (H). The catalysts (A) and (HA), which were calcined under oxidative condition at the final stage, gave higher activity compared to the other catalysts. This results can be explained in terms of the high Pd/Fe surface ratio observed by XPS (Table 7). The XPS data show higher Pd/Fe
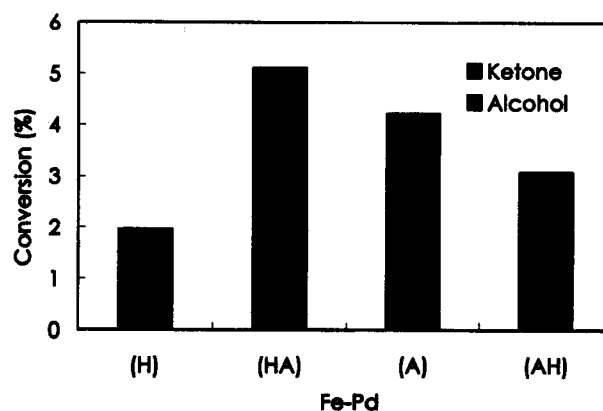
Table 6. Cyclohexane oxidation using recycled iron chloride[a]

No. of use for FeCl₂	Conversion[b] (mole %)	Selectivity (mole %)	
		cyclohexanol	cyclohexanone
1	5.13	86.5	13.5
2	4.09	84.8	15.2
3	2.75	84.0	16.0
4	2.84	87.3	12.7
5	2.70	85.9	14.1

[a] Conditions: cyclohexane (59.4 mmole), $FeCl_2 \cdot 4H_2O$ (5 mmole), Pd/alumina (1 g), acetone (17 mL)+acetic acid (3 mL), H_2 (20 mL/min), O_2 (20 mL/min), reaction temp.=30 °C, reaction time=3 h. [b] Conversion is based on cyclohexane.

Table 7. XPS Binding energy data and surface Pd/Fe ratio of Fe-Pd samples

Catalyst	Pd/Fe ratio[a]	Fe $2p_{3/2}$ (eV)	Pd $3d_{5/2}$ (eV)
(H)	0.15	710.36	335.50
(HA)	0.53	710.65	337.40
(A)	0.47	710.96	337.80
(AH)	0.15	711.16	335.57

[a] The surface ratios were calculated from the normalized peak area and the sensitivity factor.

Figure 3. Catalytic activity of Fe-Pd sample in the cyclohexane oxidation. Conditions: cyclohexane (59.4 mmole), Fe-Pd (1 g), acetone (20 mL), H_2 (20 mL/min), O_2 (20 mL/min), reaction temp.=35 °C, reaction time=6 h.

Table 8. Cyclohexane oxidation using recycled Fe-Pd (HA)[a]

No. of use for Pd/Fe₂O₃	Conversion[b] (mole %)	Selectivity (mole %)	
		cyclohexanol	cyclohexanone
1	5.11	83.9	16.0
2	4.09	74.3	25.7
3	4.89	73.0	27.0
4	5.26	70.9	29.1

[a] Conditions: cyclohexane (59.4 mmole), Fe-Pd (HA) (1 g), acetone (20 mL), H₂ (20 mL/min), O₂ (20 mL/min), reaction temp.=35 °C, reaction time=6 h. [b] Conversion is based on cyclohexane.

Table 9. Cyclohexane oxidation using recycled Fe-Pd (A)[a]

No. of use for Pd/Fe₂O₃	Conversion[b] (mole %)	Selectivity (mole %)	
		cyclohexanol	cyclohexanone
1	4.22	85.3	14.7
2	4.04	82.9	17.3
3	4.32	75.0	25.0
4	3.66	75.1	24.9
5	3.58	76.3	23.7
6	3.52	71.0	29.0
7	4.02	76.6	23.3
8	3.70	72.4	27.6

[a] Conditions: cyclohexane (59.4 mmole), Fe-Pd(A) (1 g), acetone (20 mL), H₂ (20 mL/min), O₂ (20 mL/min), reaction temp.=35 °C, reaction time=6 h. [b] Conversion is based on cyclohexane.

surface ratio for these catalysts indicating that oxidic Pd is dispersed better than metallic Pd on iron oxide. The well dispersed Pd seems to be responsible for higher formation of H_2O_2 and favorable subsequent oxidation. The poor dispersity of Pd in (H) and (AH) should reduce the formation of H_2O_2. The catalyst (H), treated in a H_2 atmosphere, showed especially low activity. The catalyst (AH), where we tried to reduce only Pd, showed better activity than the catalyst (H) although both had similar dispersion of Pd. With (H) Fe_3O_4 phase was observed predominantly in XRD. It seems that the Fe_3O_4 phase is not preferable for the oxidation.

The Fe-Pd (HA) and (A) which showed relatively high activity in the reaction for 6 h (Figure 3), were examined for extended oxidation time (16 h): the catalysts (HA) and (A) gave 11.2% and 9.3% of conversions to cyclohexanol+cyclohexanone, respectively. These results are noteworthy as considering the fact that the conversion is restricted because of by-product formation in the existing industrial process of cyclohexane oxidation.

With Fe-Pd (HA) and (A), the catalyst recycling was investigated (Table 8 and 9). The used catalyst was filtered, dried at 120 °C and reused for the reaction. From the results, it is apparent that the catalysts can be reused without a significant decrease in the activity. It is to be noted that the catalysts can be used repeatedly after only drying treatment.

Conclusions

An attempt has been made to develop a new method for cyclohexane oxidation. With the oxidation system $FeCl_2$-Pd/Al_2O_3-H_2O_2, it has been found that acetone solvent is preferable. A little addition of small quantities of acids like acetic acid and HCl gave higher conversion. Recycling the palladium catalyst showed no decrease in the activity but the recycling of iron catalysts gave lower activity. The use of the heterogeneous system, Pd/Fe_2O_3 permitted much easier separation and recycling of catalyst, showing the possibility of being a potential alternative to the present industrial process due to the mild reaction conditions, relatively high conversion and high selectivity.

Now, work is still in progress to provide more practical low-temperature oxidation, taking efficiency of catalysts and hydrogen into account.

References

1. Barton, D. H. R.; Ozbalik, N. In *Activation and Functionalization of Alkanes*; Hill, C. L., Ed.; John Wiley: New York, U. S. A., 1989; p 281.
2. Barton, D. H. R.; Beviere, S. D.; Chavasiri, W.; Csuhai, E.; Doller, D.; Liu, W.-G. *J. Am. Chem. Soc.* **1992**, *114*, 2147.
3. Barton, D. H. R.; Chavasiri, W. *Tetrahedron* **1994**, *50*, 19.
4. Schuchardt, U.; Carvalho, W. A.; Spinac, E. V. *Syn. Lett.* **1993**, 713.
5. Spinacé, E. V.; Pastore, H. O.; Schuchardt, U. *J. Catal.* **1995**, *157*, 631.
6. Schuchardt, U.; Pereira, R.; Kräembuhl, C. E. Z.; Rufo, M. Buffon, R. *Appl. Catal. A* **1995**, *131*, 135.
7. Lee, K.-W.; Kim, S.-B.; Jun K.-W.; Shim E.-K. *New J. Chem.* **1993**, *17*, 409.
8. Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245.
9. Mansuy, D.; Battioni, P. In *Activation and Functionalization of Alkanes*; Hill, C. L., Ed.; John Wiley: New York, U. S. A., 1989; p 195.
10. Mansuy, D.; Bartoni, J. F.; Chottard, J. C.; Lange, M. *Angew Chem. Int. Ed. Engl.* **1980**, *19*, 909.
11. Kim, S. B.; Jun, K.-W.; Kim, S. B.; Lee K.-W. *Chem. Lett.* **1995**, 535.
12. Hooper, G. W. *U.S. Patent* 3,361,533.
13. Izumi, Y.; Miyazaki, H.; Kawahara, S. *U.S. Patent* 4, 279,883.
14. Brill, W. F. *U.S. Patent* 3,336,112.
15. Miyake, T.; Hamada, M.; Sasaki, Y.; Oguri, M. *Appl. Catal. A* **1995**, *131*, 33.
16. Kirk-Othmer *Encyclopedia of Chemical Thechnology*, 3rd ed.; John Wiley & Sons: New York, U. S. A, 1982; Vol. 18, p 248.
17. Herron, N. *New J. Chem.* **1989**, *13*, 761.