Covalantly bonded Schiff base cobalt complex catalyst for the selective oxidation of linear alkanes using molecular oxygen

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Abstract

A Schiff base [1,2-bis(salicylidene amino)-phenylene] cobalt complex catalyst bonded on carbamate modified silica gel has been prepared for one step liquid-phase oxidation of alkanes with molecular oxygen. At moderate temperatures (150 °C) and low oxygen pressure (16 atm), the oxidation of *n*-hexane and *n*-heptane were studied. In the case of *n*-hexane, it was found that isomerization, dehydrocyclization as well as oxidation products both were formed, while for *n*-heptane, there was no cracking or reforming reaction and the oxidation products are principally 4-heptanone, 2-heptanone, 2-heptanol and heptanoic acid. For *n*-hexane, if the reaction is carried out in nitrogen atmosphere, only isomerization and dehydrocyclization products are formed in high yield (∼74.0%) with no 2,2-dimethyl butane (2,2-DMB) and 2,3-dimethyl butane (2,3-DMB). It is thus seen that the catalyst reported in this work can also be used for reforming of *n*-hexane and requires much lower temperature. The thermogravimetric analysis (TGA) analysis shows that it is stable up to 211 °C and the atomic absorption spectroscopy (AAS) shows a negligible loss of metal in 50 h use of the catalyst upto 180 °C reaction temperature.
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1. Introduction

Alkanes are most abundant and least expensive hydrocarbon feedstock available. They are relatively unreactive (due to higher ionization energy, pK_a values and low electron affinity) and in forming their oxidative products (alcohol, aldehyde, ketones and acids), the challenge faced is selectivity [1–3]. Oxidation of alkanes at low temperatures can be carried out in presence of solid catalysts using hydrogen peroxide as the oxidizing agent [1,4]. This has the advantage of preserving its molecular structure (i.e. absence of isomerization and cracking reaction), but commercially, oxidation using molecular oxygen is more attractive proposition. This normally requires high temperature, pressure and suitable catalysts and at these conditions, it can undergo additional reactions viz., cracking, isomerization, dehydrogenation, dehydrocyclization, aromatization [5,6]. In fact this property has been utilized industrially through catalytic reforming in which *n*-hexane and *n*-heptane in presence of Pt/Al$_2$O$_3$ catalyst [7] (350–500 °C) and hydrogen atmosphere form several products. These are lower alkanes by cracking (methane, ethane, propane, butane, etc.), monobranched materials through isomerization (2- and 3-methyl pentanes (2- and 3-MP), etc.), dibranched materials (2,2-dimethyl butane and 2,3-dimethyl butane), cyclized alkanes through dehydrocyclization (MCP and CH, etc.), olefins by dehydrogenation (ethylene, propylene, etc.) and aromatics by aromatization (benzene, toluene, etc.).

The oxidation of *n*-hexane in presence of molecular oxygen has been carried out in the temperature

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range of 150–200 °C by Thomas et al. [8], in which there is no isomerization or cracking. The catalysts tested have been cobalt and manganese deposited on aluminophosphate zeolite (Co-AlPO$_4$) and the product consists of various alcohols, acids, aldehyde and ketones of *n*-hexane. The main disadvantage is extremely low conversion and similar results were obtained for oxidation of *n*-pentane and *n*-octane. The LaMO$_3$ (M: Mn, Fe, Co) perovskite catalyst [9] (in the temperature range of 200–350 °C) and Pt, Ni/Al$_2$O$_3$ operating in the temperature range of 350–500 °C have been used for total combustion of *n*-hexane [10]. Catalyst reformation of *n*-hexane is an important industrial reaction and the commonly used catalyst is platinum supported on alumina (Pt/Al$_2$O$_3$) in hydrogen atmosphere operating in temperature range of 350–500 °C [11,7]. The main steps in reforming reaction consist of cracking, isomerization, dehydrocyclization and aromatization, which compete with each other during the reaction.

There are fewer studies on the oxidation of *n*-heptane. Molecular Sieves (SAPO-5, SAPO-11, BEA and MCM-41) have been used for partial oxidation in the temperature range of 300–400 °C and the products formed are 2,3- and 4-heptanones and hetrocyclic compounds (cyclohexanol (CHol), benzyl alcohols, furans and pyrans) [12]. Other reactions involving *n*-heptane are hydrocracking using Ni supported ZSM-5 zeolite (in temperature range of 160–200 °C) and cracking using MCM-22 catalyst (in the range of 450–550 °C) [13,14]. Catalytic pyrolysis of *n*-heptane giving alkenes in larger proportion has also been reported [15] and catalytic reforming on Pt/Al$_2$O$_3$, Sn/Al$_2$O$_3$ in hydrogen atmosphere in the temperature range of 350–550 °C has been studied [16]. The study shows the formation of hydrocracking products (formation of C$_1$–C$_6$ compounds), isomerization products, cyclization products and aromatization products (benzene and toluene).

In this paper, we report a nonzeolite heterogeneous catalyst formed by bonding a well defined coordinated complex on a carbamate-silica gel that oxidizes alkanes using molecular oxygen at moderate reaction conditions and gives an entirely different product distribution. This work is in line with a recent review on surface organometallic complexes chemistry. In this, several catalysts have been described, which give lowering of reaction temperature and new product distribution [17]. The reaction products formed

by our catalyst have been identified by GC–MS analysis (Shimadzu QP-2000, GC Column: ULBAN HR-1, fused silica capillary—0.25 m × 50 m). The study of the oxidation products formed for *n*-hexane showed that isomerization, dehydrocyclization as well as oxidation occurred during the reaction. However, the yield of the oxygenated products was very small and the former two dominated the overall reaction. As a result of this, the product consisted of 2-methylcyclopentanol (2-MCPol) as well as cyclohexane. In the nitrogen atmosphere, the catalyst has high selectivity for isomerization and dehydrocyclization with no cracking and aromatization. As opposed to this, for *n*-heptane, there was no cracking reaction and only oxygenated products were formed. The oxygenated products for this case was found to be 4-heptanone, 2-heptanone, 2-heptanol and 1-heptanoic acid with selectivity of 8.4, 33.6, 16.3 and 6.3%.

2. Experimental section

2.1. Material and methods

The *n*-hexane and *n*-heptane used in our study were obtained by fractionating the LR grade chemicals (Ranbaxy Chemicals, India). The catalyst loaded with [1,2-bis(salicylidene amino)-phenylene] cobalt complex has been synthesized [18] and the reaction steps are given below.

2.1.1. Preparation of carbamate modified silica gel

Silica gel (5.0 g) was washed with distilled water, then with acetone and dried at 60 °C under vacuum. This was then refluxed with 50 ml of HCl (35%) in a flask for 4 h and the hydroxylated silica gel [19] was separated and washed with distilled water several times. Phenyl isocyanate (p. 656, [20] for the reaction, the product confirmed by its IR and ^{13}C-NMR) was prepared by the reaction of sodium azide, (16.8 g, 0.26 g mole) with an equivalent number of moles of benzoyl chloride (35.0 g, 0.26 g mole) in a benzene medium (20 ml) at 0 °C. Phenyl isocyanate readily react with hydroxyl and amine groups (p. 686, [20]) and this is utilized in functionalizing silica gel. The reaction mass separates into two phases, the liquid phase was filtered and was reacted with 5.0 g of silica gel.
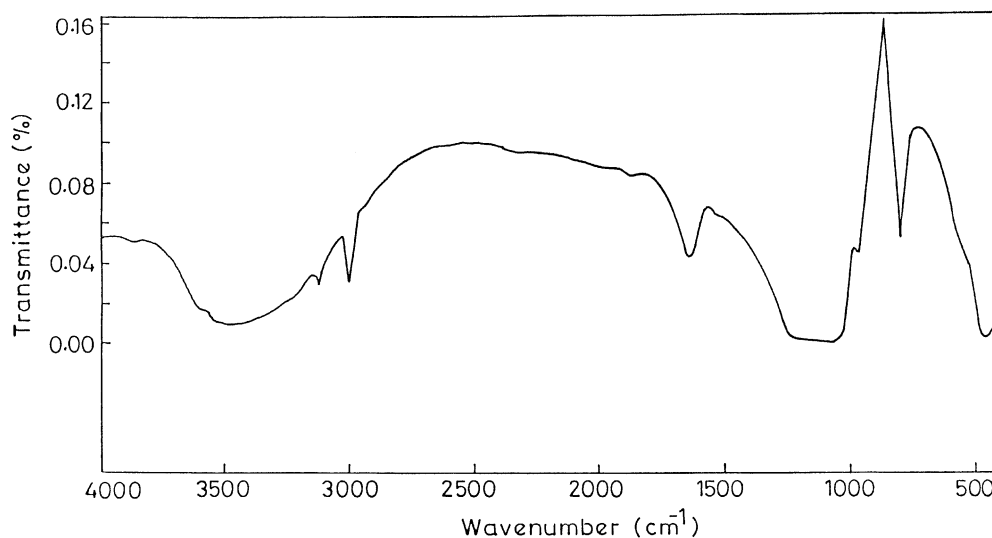
Fig. 1. FTIR spectrum of covalently bonded cobalt complex catalyst.

The reaction mass was stirred at $40\,°C$ for 6 h and the carbamate bonds on the silica gel was confirmed by FTIR (aromatic –CH at $3027\,cm^{-1}$, –NH group at $1595\,cm^{-1}$, C=O at $1690\,cm^{-1}$). The extent of reaction was estimated by determining the amine group concentration on silica gel using (0.26 meq./g) butyl amine method [21].

2.2. Preparation of cobalt complex [22,23]

The complexing agent [1,2-bis(salicylidene amino)-phenylene] was prepared by the condensation reaction of (p-phenylene diamine (0.1 g, 0.1 g mole) with salicylaldehyde (21.20 ml, 0.2 g mole) in absolute alcohol solvent for 3 h. After the completion of the reaction, a yellow precipitate of the product appeared, which is filtered and dried. In the next step, this (3.0 g, 9.5 m mole) and $CoCl_2·6H_2O$ (12 g, 0.5 m mole) are dissolved in acetonitrile (100 ml) solvent. The solution was then refluxed ($80\,°C$) for 2 h and after the completion of the reaction, a red–brown color precipitate of the cobalt complex was formed. The complex was washed several times with acetonitrile for purification and dried at $80\,°C$. The IR spectrum of the complex shows the aliphatic and aromatic –CH group at 2927 and $3053\,cm^{-1}$, respectively, >C=N isocyanate at $1640\,cm^{-1}$ and –OH group at $3610\,cm^{-1}$.

2.2.1. Formation of bonded cobalt complex on modified silica gel

The carbamate groups of the modified silica gel (2.0 g) is reacted with dichloroethane (50 ml) by refluxing ($60\,°C$) it in presence of a Lewis acid, $ZnCl_2$ catalyst, (5.0 mg, 0.037 g mole) for 2 h. The FTIR of the product showed the alkyl group –CH_2 at $2940\,cm^{-1}$ and the chloride group at $749\,cm^{-1}$ on the silica gel, confirming that the reaction has occurred. As a result of this reaction, the support material (modified silica gel) now has –CH_2CH_2Cl groups possibly at the phenyl and the secondary amine groups of the carbamate and the chloride groups of these react with the cobalt metal complex (formed in step (ii)) dissolved in acetonitrile. This is subsequently refluxed ($80\,°C$) for additional 3 h to give the desired heterogeneous [1,2-bis(salicylidene amino)-phenylene] cobalt complex chemically bound to the modified silica gel. The FTIR of the catalyst is shown in Fig. 1, which shows aliphatic and aromatic –CH at 2940 and $3030\,cm^{-1}$, C=O group shifted to $1644\,cm^{-1}$ with the characteristic peaks of metal complexing at $1509\,cm^{-1}$ with the absence of chloride group. If we represent the hydroxyl group of the silica gel molecule as (Si) –OH, then the formation of the catalyst can be written as

$$NaN_3 + C_6H_5COCl \longrightarrow C_6H_5-N=C=O$$
$$(\text{Phenylisocyanate})$$

(Silica gel Supprted Co Catalyst)
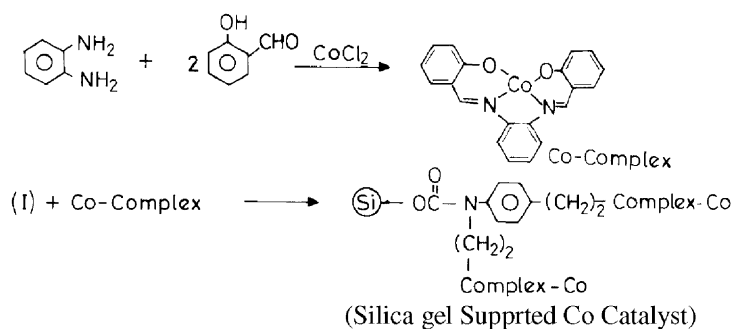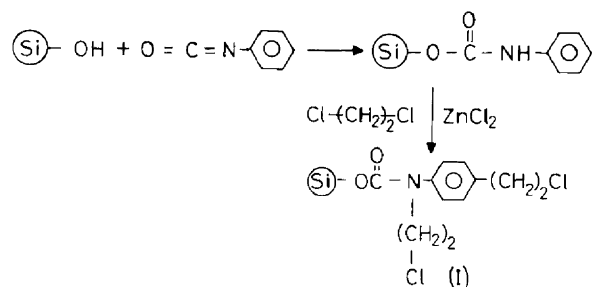
The cobalt metal content in the catalyst was determined by atomic absorption spectroscopy (AAS) to be 0.47%. The stability of the catalyst was measured by the thermogravimetric analysis (TGA) using Stanton Redcroft Instrument at a heating rate of 10 °C/min under N_2 atmosphere. The oxidation state of the cobalt metal of the heterogeneous catalyst was analyzed by an electron paramagnetic resonance (EPR) equipment (E-Line Century Series EPR Spectrometer Model 109, X-band).

2.3. Oxidation reaction procedure

The oxidation reactions were performed in high-pressure stainless steel batch reactor. An autoclave-rocking reactor having capacity of 500 ml, gas delivery, and sampling line was employed for the oxidation of alkane. An on/off controller was used for controlling the temperature with a chrome alloy thermocouple for temperature sensing. The catalyst was originally red-brown in color, which after the oxidation reaction turned into dark brown in color and the catalyst was separated by the filter paper. The product

of oxidations were analyzed by gas chromatography using a capillary column fused silica capillary column 0.25 mm × 50 m film thickness 0.25 μm with flame ionization detector and the products identified by the GC/MS (Shimadzu QP-2000) instrument.

2.4. Results and discussion

2.4.1. n-Hexane oxidation

The oxidation of *n*-hexane using molecular oxygen was studied in a batch reactor in the temperature range of 150–200 °C for 8 h of reaction time. It was found that when the product mixture was directly analyzed by GC, some compounds did not show up due to their low concentrations. To overcome this problem, the product mixture was distilled at 75 °C and the residue as well as the distillate were analyzed separately. The GC–MS analysis of the distillate showed four products as 2-MP, 3-MP, methyl cyclopentane (MCP) and cyclohexane (CH). Adding pure components to the product and taking its gas chromatograph again further authenticated these components. The analysis of the residue showed these four

compounds along with the following additional four compounds 2-hexanone (2-Hone), 2-hexanol (2-Hol), 2-methylcyclopentanol (2-MCPol) and cyclohexanol (CHol). From the overall material balance, the overall conversion has been determined. For example, at 200 °C, 8 h reaction time, the yields are determined to be 21.83% 2-MP, 17.74% 3-MP, 19.6% MCP, 10.21% CH, 0.059% 2-Hone, 0.04% Hol, 0.08% 2-MCPol and 0.03% with the overall conversion of 73.6% and the results have been summarized in Table 1.

From the experimental data, the effect of temperature (150–200 °C) on the overall conversion is shown in Table 1, which appears to continue to rise from 64.0 to 73.6%. The yields of the 2-MP, 3-MP, MCP and CH with temperature and the yields of 2-MP and 2-MP, 3-MP fall while those of MCP and CH rise. As opposed to this, the yields and selectivity (Table 1) of 2-Hone, 2-Hol, 2-MCPol and CHPol rise with the increase of temperature. As the temperature is increased beyond 200 °C, the yield of unidentified products increases, e.g. at 200 °C it is 2.94% (which is close to zero at 180 °C). As a result of this, higher temperatures were not investigated. Thus we see that with the cobalt catalyst reported in this work, n-hexane undergoes isomerization (giving 2-MP, 3-MP) and dehydrocyclization (giving MCP and CH) along with the

oxidation reaction (giving 2-Hone, 2-Hol, 2-MCPol and CHol). The yields of oxidized products are small and the dominating reactions are the former two.

It appears that isomerization and dehydrocyclization reaction of n-hexane using our catalyst are relatively faster than the oxidation reaction and the MCP and CH (isomerized products) are formed in higher concentrations first which are further oxidized in presence of oxygen to MCPol and CHol. As a result of this the combined yield of 2-MCPol and CHol is greater than the combined yield of 2-Hone and 2-Hol. Next, we examine the effect of total amount of oxygen fed as obtained by varying the initial pressure of oxygen before the reactor is heated to the furnace temperature. The reaction temperature was chosen to be 180 °C as the amount of unidentified product for this temperature was negligibly small. The total conversion and yields of isomerization products are given in Fig. 2 and those of oxygenated products in Fig. 3. The yields and the selectivities of 2-MP and 3-MP decrease although the fall in their values are small. For n-hexane, the yield of methyl cyclopentane and cyclohexane increase with the increase in oxygen pressure. On the other hand, the selectivity of the isomerized product decreases and we see that oxygen pressure favors dehydrocyclization reaction to some extent but

Table 1
Effect of temperature on the yield and selectivity of the products formed by the catalytic oxidation of n-hexane and n-heptane

| Products	150 °C		160 °C		180 °C		200 °C	
	Yield (%)	Selectivity (%)	Yield (%)	Selectivity (%)	Yield (%)	Selectivity (%)	Yield (%)	Selectivity (%)
n-Hexane overall conversion (%)	63.45		66.38		69.97		73.22	
2-Methylpentane	28.32	44.57	27.01	40.68	24.86	35.56	21.87	29.86
3-Methylpentane	23.1	36.35	21.89	32.97	20.00	28.58	18.78	25.64
Methylcyclopentane	10.19	16.03	14.02	21.31	17.48	24.98	20.64	28.20
2-Hexanone	0.01	0.02	0.01	0.02	0.02	0.03	0.06	0.08
2-Hexanol	0.01	0.02	0.01	0.02	0.02	0.03	0.45	0.62
2-Methylcyclopentane	0.01	0.02	0.02	0.03	0.04	0.06	0.08	0.12
Cyclohexane	1.89	2.97	3.41	5.15	7.53	10.76	11.31	15.44
Cyclohexanol	0.01	0.02	0.01	0.02	0.02	0.03	0.03	0.04
Unidentified products	–	–	–	–	–	–	2.94	–
n-Heptane overall conversion (%)	5.08		5.28		8.10		9.48	
4-Heptenone	0.65	12.79	0.08	1.52	1.20	14.83	1.50	5.82
Heptanoic acid	0.50	9.84	0.60	11.37	0.65	8.02	0.73	7.71
2-Heptenol	1.30	25.59	1.50	28.04	2.0	24.69	2.25	32.73
2-Heptanone	2.63	57.78	3.10	58.71	4.25	52.46	5.0	52.74
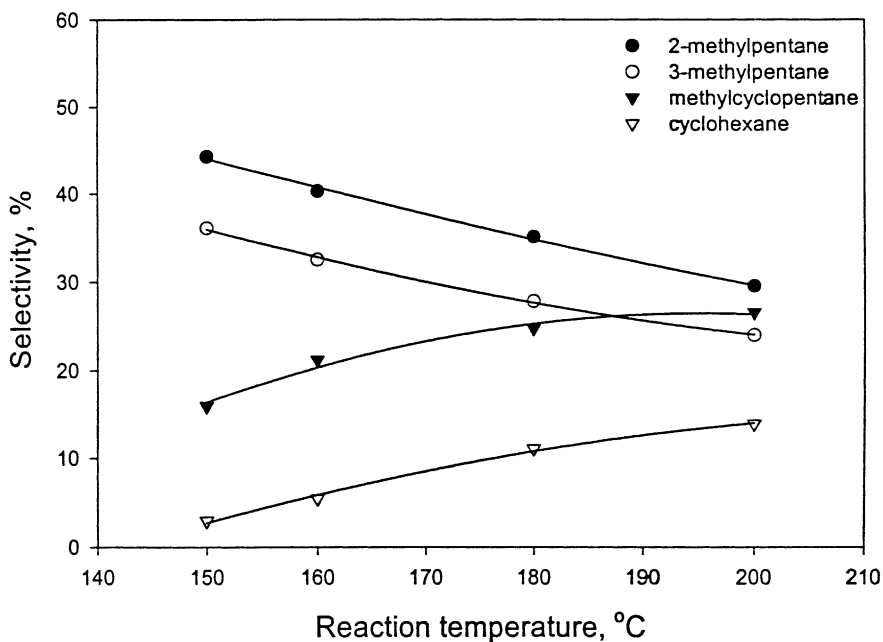
Fig. 2. Effect of temperature on the selectivity of the products formed by the catalytic isomerization of *n*-hexane in nitrogen atmosphere.
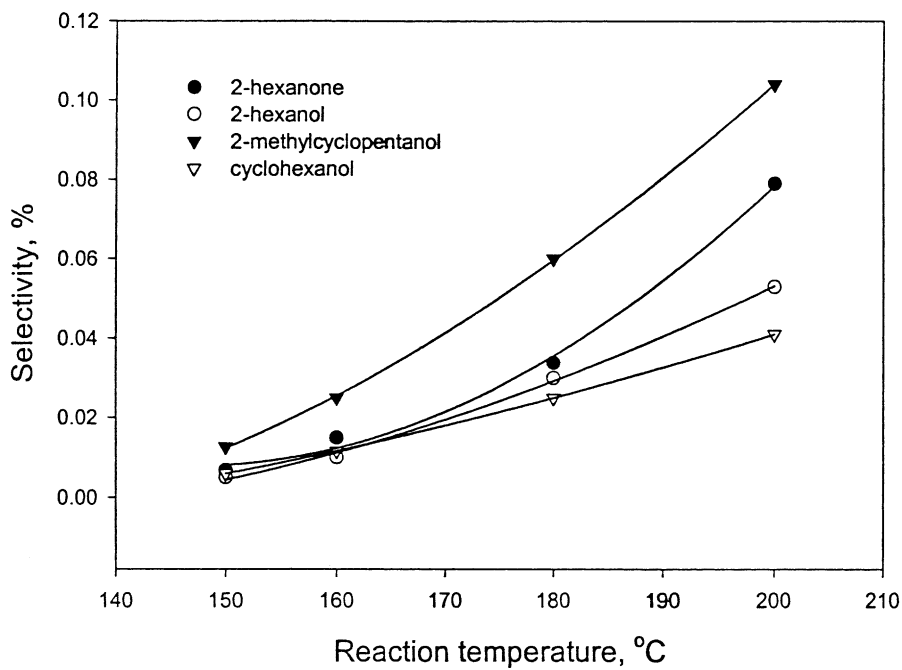

Fig. 3. Effect of temperature on the selectivity of the oxidative products formed by the *n*-hexane oxidation.

selectivity decrease due to significant oxidation of *n*-hexane. The variation in the yield and selectivity of the products (2-Hone, 2-Hol, 2-MCPol and CHol) are shown in Table 1. Both these are seen to increase with the increase in the initial oxygen pressure.

From the results presented above, the selectivity of the reforming reactions (i.e. isomerization and dehydrocyclization) for *n*-hexane is calculated to be about 94%. These reactions are very important in the frame of petroleum industry to increase the octane number of low octane gasoline. To avoid the oxidation of *n*-hexane, when nitrogen was used in place of oxygen, same isomers (2- and 3-MP) and dehydrocyclized products (MCP and CH) were formed. The overall conversion at 200 °C (73.6%) was found to be almost same but the overall yield (71.7%) and selectivity (97.5%) of the reformed products increased. Thus, we see that in presence of N_2, the overall conversion and the selectivity were high. It may be observed that industrially, catalytic reforming is carried out in presence of hydrogen and the catalyst used is platinum adsorbed on alumina surface (Pt/Al_2O_3 system). For this catalyst, the temperature required is 350–500 °C and the main steps of the reactions consist of cracking, isomerization, dehydrocyclization and aromatization competing with each other equally [7,11]. For *n*-hexane, it gives cracking products (C_1–C_5), isomerization products (2-MP, 3-MP, 2,2-DMB and 2,3-DMB), dehydrocyclized products (MCP) and aromatic products (benzene). The cobalt catalyst reported in this work is found to respond in nitrogen atmosphere and is more specific compared to the industrial Pt/Al_2O_3 catalyst.

2.4.2. n-Heptane oxidation

The oxidation of *n*-heptane has been similarly studied in the same batch reactor keeping the mass of the catalyst (0.5 g) constant at different temperatures (between 150 and 200 °C), pressures (between 100 and 220 atm) for reaction period of 8 h shown in Table 1. The product of one of the runs has been analyzed using gas chromatograph and a total of five major peaks were observed. The identification of these compounds has been done by mass spectra of the pure compound, corresponding to peaks in the GC. This comparison gives peak-1 in the GC as *n*-heptane (90.5%), peak-2 as 4-heptanone (0.8%), peak-3 as 2-heptanone (3.2%), peak-4 as 2-heptanol (1.6%) and peak-5 as heptanoic

acid (0.6%), respectively. We observe that at 160 °C reaction temperature, the overall conversion of the reaction was 9.5%. Thus, the selectivity of 4-heptanone, 2-heptanone, 2-heptanol and heptanoic acid was 8.4, 33.6, 16.8 and 6.3%, respectively, and the overall selectivity of the reaction was 65.3%. Here, we notice that the main reaction was oxidation of *n*-heptane and not isomerization and dehydrocyclization as we found for *n*-hexane. Thermal oxidation reactions are generally run at very high temperatures (350–1000 °C) and the selectivity of these reactions is usually very low. On the other hand, for this catalyst, the temperature (160 °C) was low while the selectivity was high (Table 1). Now, we can say that the catalyst has played a very important role in the oxidation of *n*-heptane.

The effect of the temperature on the conversion as well as the product distribution was studied in the temperature range of 150–200 °C keeping initial oxygen pressure (100 psi) and reaction time (8 h) constant. The conversion of heptane with temperature for fixed reaction time is shown in Fig. 4, which increases with increase in temperature. The variation of yield and selectivity of the products (4-heptanone, 2-heptanone, 2-heptanol and heptanoic acid) formed on the oxidation of *n*-heptane is shown in Table 1. The yield of these compounds increases with increase in temperature, but the selectivity of the individual compound decreases with temperature due to occurrence of other side reactions giving several unidentified products.

On application of the pressure, some oxygen goes to the solution in *n*-heptane and the dissolved oxygen plays an important role in the oxidation. On further increasing the reaction pressure (100–200 psi), the solubility of oxygen increases giving higher *n*-heptane conversion (1.36% at 140 psig, 5.3% at 160 psig, 5.73 at 180 psig and 6.05% at 200 psig). At 220 psi the maximum conversion is seen to be 6.12% and further increase in pressure (250 psi) does not change the final conversion attained. The conversion increases with reaction time (4.7% at 6 h, 5.3% at 8 h, 5.9% at 10 h and 6.0% at 12 h) as expected and the yield of these compound increases with increase in reaction time. Initially, the yield increases rapidly but for long time approaches an asymptotic value (6.1% at 20 h). We have varied the amount of support bound cobalt catalyst (2.3% at 0.5 g, 5.3% for 1.0 g, 5.6% for 1.5 g and 5.94% for 2.0 g). We find that the conversion does not change beyond 2.0 g. The catalyst is likely to play
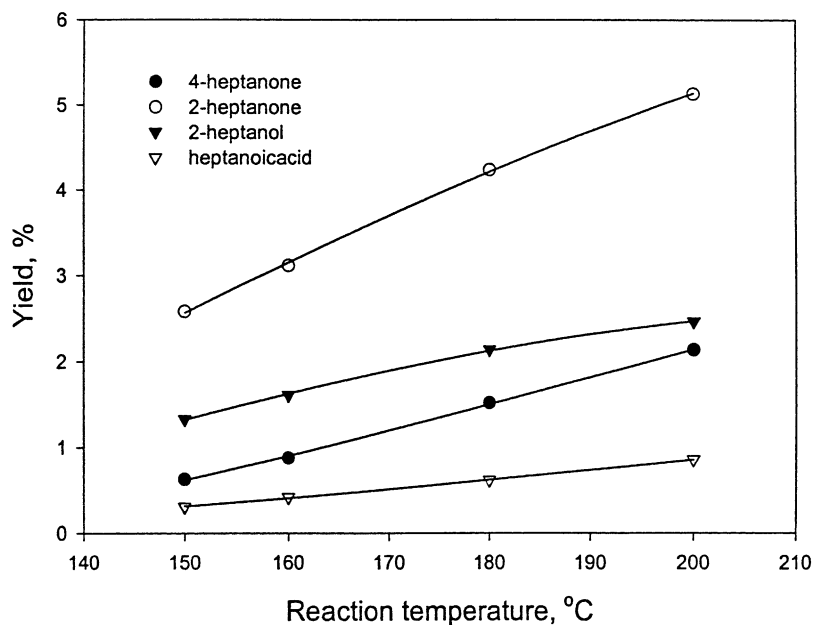
Fig. 4. Effect of temperature on the yield of the oxidative products formed by the *n*-heptane oxidation.

a dual role in the initiation and termination reaction steps and this may be responsible for this observation of the amount of the catalyst dependent kinetics.

2.4.3. Catalyst characterization

In order to find out that the loaded complex on the silica gel is stable at the reaction temperature, the TGA of the catalyst has been carried out and the results are given in Fig. 5. In this figure the complex breaking is

seen to occur at 211 °C and is to found to be stable upto 180 °C. The AAS of the fresh catalyst shows the cobalt metal content to be 0.48%. After using this catalyst for 50 h at 180 °C the metal content is found to decrease to 0.39%, but the activity of the catalyst remained unaltered.

The experiments have shown that no reaction occurs in absence of the silica gel catalyst or in presence of free cobalt metal or cobalt complex. It was further
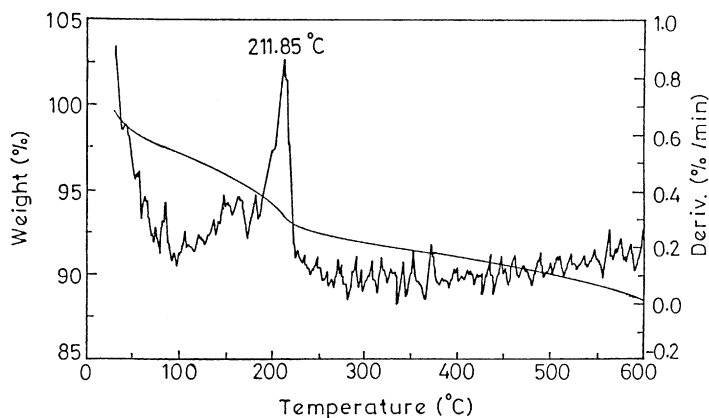

Fig. 5. TGA of the fresh heterogeneous cobalt catalyst with the heating rate 10 °C/min under N₂ atmosphere.
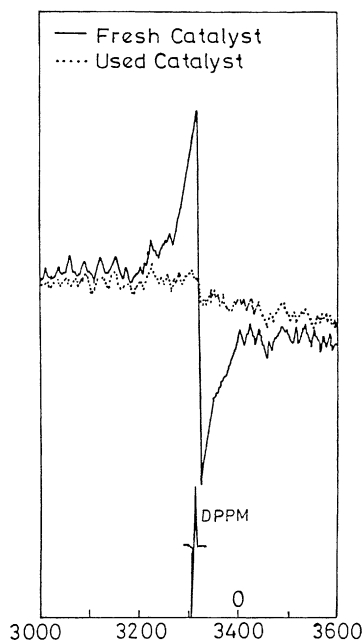
Fig. 6. The EPR of the freshly prepared bound and used cobalt complex catalyst at room temperature. The used catalyst is EPR silent.

observed that the red brown color of the fresh catalyst becomes dark brown after the reaction in presence of molecular oxygen. In the determination of the EPR of the catalyst, diphenyl picryl hydrazyl (DPPH) has been used as the standard for the g value ($g = 2.0023$) for the lone pair electron. The EPR spectrum of the fresh catalyst (Fig. 6) is silent due to absence of any paramagnetic species and this also confirms that cobalt is present at in the +2 oxidation state. After the oxidation reaction and the change of color, the catalyst gives an EPR spectra (Fig. 6), which suggests that the cobalt now is in the +3 oxidation state. The catalyst seems to play a dual role in the initiation as well as termination steps of the accepted reaction mechanism [1,24,25] of functionalization of alkanes using cobalt metal. The oxidation of alkanes with molecular oxygen in presence of the cobalt complex catalyst could occur through (i) autooxidation of free radicals (ii) the metal ion followed by reoxidation of the reduced metal or (iii) catalytic oxygen transfer. In order to show that the reaction is not occurring via free radical mechanism, we carried out the oxidation of alkane in presence of free radical initiator,

like for example, benzoyl peroxide (BPO) and found negligible effect on the initial slow phase or the final conversion reached. In addition to this, we also carried the oxidation reaction in presence of free radical scavengers like, hydroquinone and once again found no effect upon the final conversion reached.

3. Conclusion

We conclude that the oxidation reaction of linear alkanes (*n*-hexane and *n*-heptane) with molecular oxygen occurs in presence of silica gel supported [1,2-bis(salicylidene amino)-phenylene] cobalt complex catalyst. The *n*-hexane undergoes isomerization as well as oxidation while *n*-heptane undergoes only oxidation reaction. The TGA analysis of the catalyst shows that the bonded metal complex was stable upto 211 °C and the AAS analysis gives that the metal does not leach out for at least 50 h of experimentation at 180 °C.

Acknowledgements

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