

# Direct oxidation of *n*-heptane to ester over modified sulfated SnO<sub>2</sub> catalysts under mild conditions

Xue Cui, Hongzhu Ma, Bo Wang\*, Hongwei Chen

*Institute of Energy-Chemistry, College of Chemistry and Materials Science, Shaanxi Normal University, 710062 Xi'an, PR China*

Received 8 November 2006; received in revised form 1 December 2006; accepted 2 January 2007

Available online 2 February 2007

## Abstract

The direct oxidation of *n*-heptane to ester using air as the oxidant under mild conditions assisted by sulfated tin oxide (SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub>) and Co modified sulfated tin oxide (SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub>-Co<sub>2</sub>O<sub>3</sub>) prepared by chemical co-precipitation method and characterized by means of SEM, XRD, FT-IR and XPS techniques was studied. From the results it was found that the catalytic activity of SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub>-Co<sub>2</sub>O<sub>3</sub> is higher than that of SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub> in this target reaction, and two asymmetric esters: diisobutyl phthalate and cyclohexylmethyl tridecyl oxalate that have not been reported in the directly oxidation of *n*-heptane by traditional method have been obtained. The possible mechanism was also discussed.  
© 2007 Elsevier B.V. All rights reserved.

**Keywords:** Sulfated tin oxide catalysts; Modified; *n*-Heptane; Catalytic oxidation

## 1. Introduction

It is well known that sulfated metal oxide (SO<sub>4</sub><sup>2-</sup>/MxOy) have been used in isomerization, alkylation, acylation, polymerization, oligomerization, esterification, oxidation, etc. for their high strength of acidity, non-toxicity and high activity at low temperatures. It can be said that sulfated metal oxides are the most important heterogeneous catalysts used today [1,2].

Sulfated tin oxide, one of the most used sulfated metal oxides, has been proved to be a useful catalyst in isomerization reactions [2]. Tin oxides were usually obtained as fine particles, and a large part of the precipitates were passed through a conventional filter paper, resulting in their diminished yields.

Octane numbers (RON) provide a sensitive indication of the anti-knocking behavior of the fuel. The higher the octane number the better the gasoline resists detonation and the smoother the engine runs. The research octane number (RON) of a gasoline may range from that equivalent of *n*-heptane (RON=0) to greater than that of isooctane (RON=100) [3]. By this method the knock proneness of gasoline with different compositions became measurable by their comparison to corresponding standard mixtures with the same knock resistance.

Different additives were applied to achieve the required specifications of the highly knock resisting super grade gasoline used today. The so-called oxygenates, such as methyl *tert*-butyl ether (MTBE), diisopropyl ether (DIPE) and dimethoxymethane (DMM), are often used as octane-boosters [3,4]. Oxalates have attracted much attention as octane boosters, due to their pollution reduction and excellent blending capabilities. In its traditional synthesized method, sulfuric acid was used as catalyst, this conventional industrial acid catalyst has unavoidable drawbacks because of their severe corrosion and high susceptibility to water. Thus, the search for environmentally benign heterogeneous catalysts has driven the worldwide research of new materials as a substitute for current liquid acids and halogen-based solid acids.

Oxidation and isomerization are general process in refineries worldwide. Catalytic oxidations of hydrocarbons using oxygen or air as oxidant are significant and economical to the chemical industry. Their function is to upgrade low-octane straight run naphthas to higher-octane motor fuel blending components by catalytically promoting specific groups of chemical reactions, typically those leading to aromatic groups, cycloalkanes and oxygenous compounds.

Diisobutyl phthalate, its production amount over two million tons each year worldwide, are widely used as the plasticizer ingredients and have been identified as parts of the major outgassing compounds from wafer storage boxes. It was synthesized by esterification of phthalic anhydride and isobutanol

\* Corresponding author. Tel.: +86 29 85308442; fax: +86 29 85307774.  
E-mail address: [wangbo@snnu.edu.cn](mailto:wangbo@snnu.edu.cn) (B. Wang).

catalyzed by sulfated metal oxides operating in an autoclave at 423 K.

The promotion of sulfated metal oxides by metals can increase its catalytic activity for most reactions, so Co was selected to modified sulfated tin oxide and the effects of the modification on the catalytic activity of  $\text{SO}_4^{2-}/\text{SnO}_2\text{-Co}_2\text{O}_3$  binary oxides prepared by the chemical co-precipitation method was investigated. The directly oxidation of *n*-heptane under mild conditions was selected as the target reaction to investigate the catalytic activity of the prepared catalysts. Two asymmetric esters: diisobutyl phthalate and cyclohexylmethyl tridecyl oxalate which have not reported were obtained with high yield. All the products are octane boosters. And the possible mechanism was also proposed.

## 2. Experimental

### 2.1. Reagent

All chemicals used in the experiment were analytically grade and used without any further purification.  $\text{SnCl}_4$ ,  $\text{CoCl}_3$ ,  $\text{H}_2\text{SO}_4$  (98%) and *n*-heptane were obtained from Xi'an Reagent Co.

### 2.2. Catalyst preparation

$\text{SO}_4^{2-}/\text{SnO}_2$  catalyst was prepared by adopting a two-step route. In the first stage,  $\text{Sn}(\text{OH})_4$  is obtained by adding aqueous ammonia slowly into an aqueous solution of  $\text{SnCl}_4 \cdot x\text{H}_2\text{O}$  and the final pH of the solution is adjusted to 8. The precipitates are filtered, washed and then dried at 378 K for 12 h. Secondly, the obtained fix oxide powder (10 g) was placed in a glass flask with 150 mL of  $1 \text{ mol L}^{-1} \text{H}_2\text{SO}_4$ , stirred for 1 h, filtered by suction, dried at 378 K for 2 h, and finally calcined in air at 823 K for 3 h for obtaining  $\text{SO}_4^{2-}/\text{SnO}_2$  [5].

Sulfated tin oxide was modified by addition of Co to study the effects of the modification on the catalytic activity of sulfated metal oxides.  $\text{SO}_4^{2-}/\text{SnO}_2\text{-Co}_2\text{O}_3$  binary oxides were prepared by chemical co-precipitation method [6]. In the first stage,  $\text{Sn}(\text{OH})_4\text{-Co}(\text{OH})_3$  is obtained by adding aqueous ammonia slowly into an aqueous solution of  $\text{SnCl}_4 \cdot x\text{H}_2\text{O}$  and  $\text{CoCl}_2 \cdot x\text{H}_2\text{O}$ . The second stage was the same as the  $\text{SO}_4^{2-}/\text{SnO}_2$  catalyst. The concentration of Co was 2.0 wt.%.

### 2.3. Catalyst characterization

Scanning electron micrographs (SEM) were obtained with a scanning electron microscope (Quanta 2000, Philips-FEI Corporation, Holland). Powder X-ray diffraction (XRD) patterns were recorded on a D/Max-3c, Rigalco (Japan). Crystalline phases were identified with the help of JCPDS data files. IR-spectra were recorded on a Eouinx55 (Germany). XPS were recorded using a Perkin-Elmer PHI-5400 analyzing instrument (where Mg K $\alpha$  was the radiation source). UV-vis spectra of the samples were monitored using a double beam UV-vis spectrophotometer (UV-7504, China). The component and its distribution of the products were analyzed by GC/MS QP2010 (Japan).

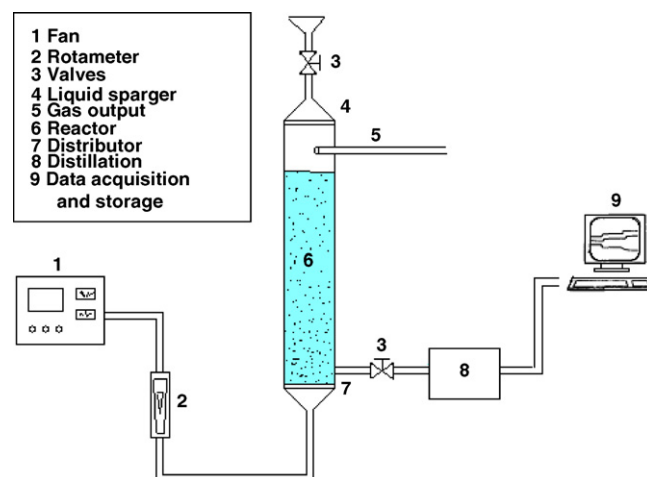


Fig. 1. Schematic set-up for the experimental.

### 2.4. Catalytic reaction

Fig. 1 shows schematic diagram of experimental set-up for catalytic reaction. The oxidation of *n*-heptane was carried out at room temperature in a micro-reactor connected to a gas chromatograph. The catalyst was pretreated at 573 K for 1 h in a nitrogen atmosphere before each term. Diethyleneglycol succinate on shimalite was used as packing material of GC column and its temperature for analyzing the product maintain at 423 K.

Typically, 5 g of catalyst and 100 ml *n*-heptane was used for each experiment, unless stated otherwise. The finely ground catalyst particles were placed on a porous frit. The reaction experiments were carried out at atmospheric pressure and room temperature. The total volumetric flow rate of air was  $1 \text{ m}^3 \text{ min}^{-1}$ . Products were analyzed with an on-line gas chromatograph-mass spectrometry.

## 3. Results and discussion

### 3.1. SEM

The SEM images of modified sulfated tin oxide ( $\text{SO}_4^{2-}/\text{SnO}_2\text{-Co}_2\text{O}_3$ ) supercritically after calcination at 823 K for 3 h given in Fig. 2 showing cubic particles are observed. It can be found that the surface of  $\text{SO}_4^{2-}/\text{SnO}_2\text{-Co}_2\text{O}_3$  is smooth and that ultrafine crystallites with average size around  $5 \mu\text{m}$  have been formed.

### 3.2. X-ray diffraction (XRD)

XRD patterns of the calcined samples for sulfated tin oxide and modified sulfated tin oxide are shown in Fig. 3 and it strongly suggested the presence of the sulfated tin oxide phase in the catalyst. There are little differences in XRD patterns between these two samples, maybe can concluded that a change in phase does not occur as a result of modified sulfated tin oxide by promotion of Co. While sulfated tin oxide samples show the presence of pure tetragonal phase only, which was consistent with the

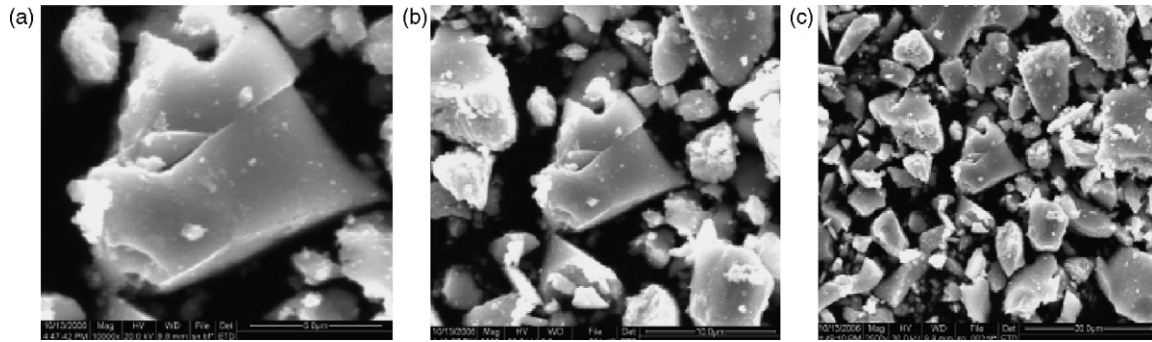


Fig. 2. SEM pictures of  $\text{SO}_4^{2-}/\text{SnO}_2\text{-Co}_2\text{O}_3$  crystals: (a) 10,000 $\times$ ; (b) 5000 $\times$ ; (c) 2500 $\times$ .

reference reported [7], that sulfate treatment can stabilize the tetragonal phase in tin oxide.

### 3.3. FT-IR

The IR spectra of modified sulfated tin oxide samples before reaction, after reaction and regeneration at 823 K show in Fig. 4.  $\text{SO}_4^{2-}/\text{SnO}_2\text{-Co}_2\text{O}_3$  calcined up to 823 K showed IR absorption bands at 1195, 1128, 1097 and 1050  $\text{cm}^{-1}$  which can be assigned to bidentate sulfate ion coordinated to the metal such as  $\text{Sn}^{4+}$  or  $\text{Co}^{3+}$ . These results are very similar to those reported by other authors [8,9]. In general, for the metal oxides modified with sulfate ion, a strong band assigned to S=O stretching frequency is observed at 1380–1370  $\text{cm}^{-1}$ . The band at 1625  $\text{cm}^{-1}$  can be assigned to the deformation vibration mode of the adsorbed water.

From Fig. 4 it can also be found that the intensity of acid features decreases with the reaction proceeded, compared with fresh catalyst. The deactivation of regenerated catalyst was less remarkable due to little differences even shown in IR spectra.

Therefore, it maybe proposed that the binding mode of Co-promoted sulfated tin oxide is  $\text{SO}_4/\text{SnO}_2$  coordinated to  $\text{Co}_2\text{O}_3$  as illustrated in Fig. 5, though several structures of the sulfated

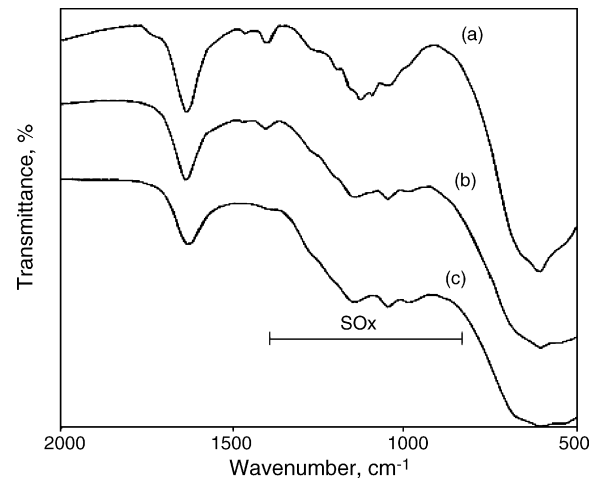


Fig. 4. Infrared spectra of  $\text{SO}_4^{2-}/\text{SnO}_2\text{-Co}_2\text{O}_3$ : (a) before reaction; (b) after reaction; (c) regeneration (823 K).

tin have been proposed. The  $\text{Co}_2\text{O}_3$  coordinated to S=O groups acts as electron withdrawing species followed by the inductive effect illustrated by the arrows; thus, the Lewis acid strength of  $\text{Sn}^{4+}$  becomes stronger.  $\text{Co}^{3+}$  is known to form sulfoxide complexes which are S-bonded, O-bonded, or a mixture of S and O-bonded ligands.

### 3.4. XPS analysis

The compositions and chemical states of sulfated  $\text{SnO}_2\text{-Co}_2\text{O}_3$  calcined at 823 K were investigated with XPS. Signals from S 2p photoelectrons were clearly observed

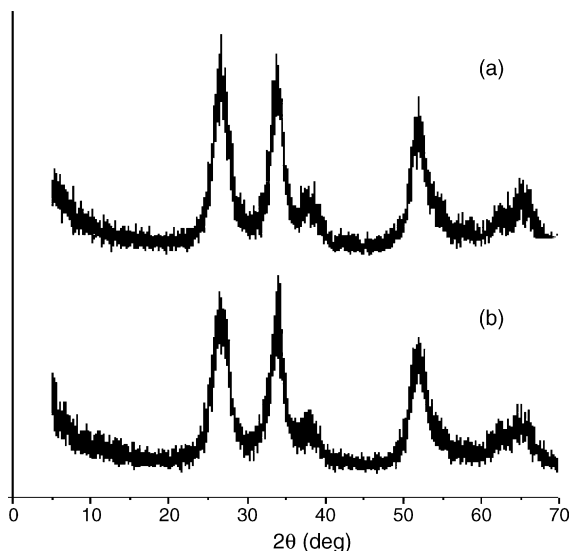


Fig. 3. XRD patterns of different samples: (a)  $\text{SO}_4^{2-}/\text{SnO}_2\text{-Co}_2\text{O}_3$ ; (b)  $\text{SO}_4^{2-}/\text{SnO}_2$ .

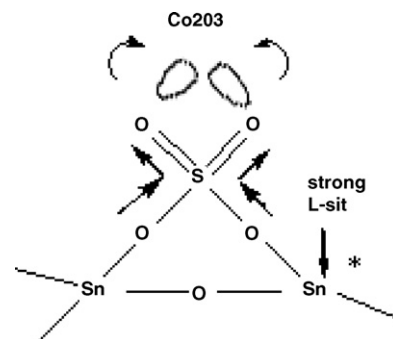
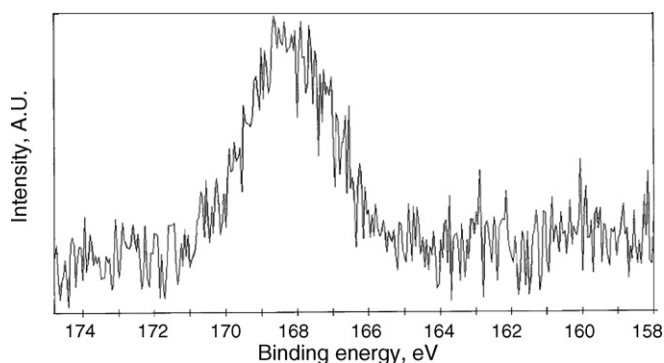
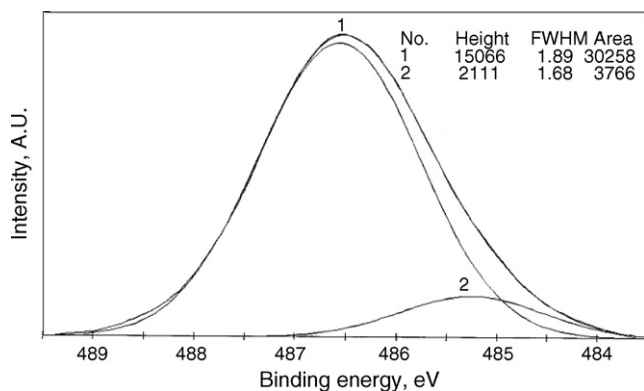
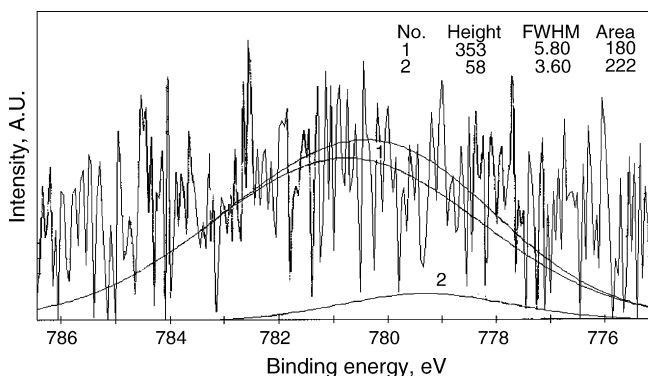
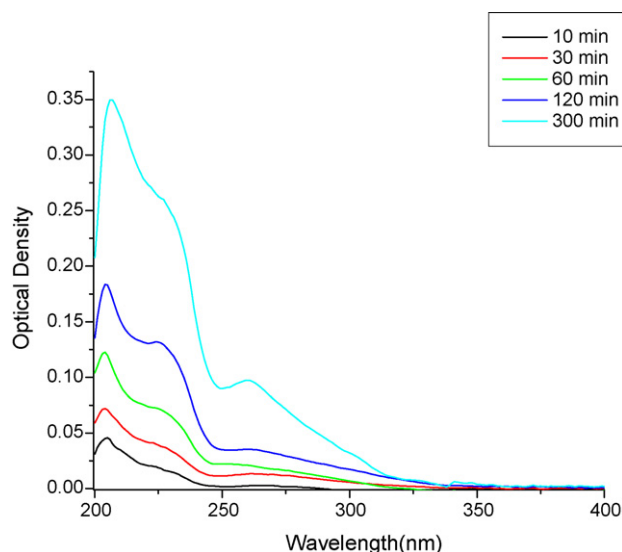


Fig. 5. Modes of sulfate binding.

Fig. 6. S 2p<sup>3/2</sup> XPS spectrum of SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub>-Co<sub>2</sub>O<sub>3</sub>.Fig. 7. Sn 3d XPS spectrum of SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub>-Co<sub>2</sub>O<sub>3</sub>.

[10,11] and shown in Fig. 6. It can be found that data from S 2p<sup>3/2</sup> was fitted by a Gaussian function centered at 169.2 eV, in agreement with the binding energies of S 2p<sup>3/2</sup> in SO<sub>4</sub><sup>2-</sup>. Hence, it can be concluded that SO<sub>4</sub><sup>2-</sup> exists in the sulfated catalyst, this is also consistent with the results of FT-IR.

In Fig. 7, the spin-orbit doublet, Sn 3d<sup>3/2</sup> and Sn 3d<sup>5/2</sup>, are located at 485.25 and 486.58 eV, respectively, with a separation of 1.33 eV, indicating the formation of SnO<sub>2</sub>. Fig. 8 show the binding energy of the Co 2p peaks are at 780.77 and 779.30 eV assignable to Co 2p<sup>1/2</sup> and Co 2p<sup>3/2</sup>, respectively, indicating the existence of Co element in SnO<sub>2</sub>-Co<sub>2</sub>O<sub>3</sub> catalyst. The peak has been deconvoluted to two different valent components and the ratio of two atoms is 90:10 (molar ratio). Compared to that Co<sup>3+</sup> occupied 100% of the total cobalt element before the oxidation

Fig. 8. Co 2p XPS spectrum of SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub>-Co<sub>2</sub>O<sub>3</sub>.Fig. 9. Effect of time on the reaction system catalyzed by SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub>-Co<sub>2</sub>O<sub>3</sub>.

reaction, it can be illuminated that Co<sup>3+</sup> was reduced to Co<sup>2+</sup> during the oxidation process.

### 3.5. UV spectra

UV-vis spectroscopy was used to investigate the whole process of the reaction and the results were shown in Fig. 9. With the time prolong, various peaks observed at 205, 226 and 266 nm, characteristic peaks of benzene ring, ascended gradually, moreover the peak becoming more pronounced and causing the shoulder to shift to slightly lower energy [12,13], indicating the formation of the benzene ring.

Although precise molecular structure information cannot be extracted from these electronic absorption spectra, the results are qualitatively in accord with GC-MS results. The evolution of the intensity of the peak shows that the concentration of benzene ring increases rapidly at the reaction, this result was also proved by GC-MS (Table 1).

### 3.6. GC-MS

Alternatively, gas chromatography in conjunction with mass spectrometry (GC-MS) has been known for its superior separation of complex organic compounds, greater sensitivity, and shorter measuring time, hence is better suited for detection and identification of volatile organic compounds [14]. The aromatic hydrocarbon and oxide fraction was analyzed by GC-MS. The results show that the main products of catalytic

Table 1  
Surface concentrations of sulfated SnO<sub>2</sub>-Co<sub>2</sub>O<sub>3</sub>

Element	Height (cts/s)	Sensitivity factor	Concentration (at.%)
O 1s	10,977	0.711	76.86
S 2p	658	0.604	5.42
Co 2p	494	2.362	1.04
Sn 3d <sup>5</sup>	15,824	4.725	16.67

Table 2  
Main product distribution

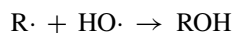
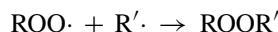
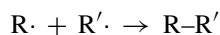
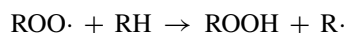
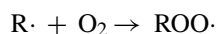
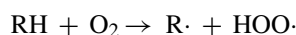
No.	Compounds	Structure	Product percentage (%)
1	2-Isopropyl-cyclohexanol		5.501
2	Hexadecane		12.057
3	Cyclohexylmethyl tridecyl oxalate		13.446
4	Heptadecane		14.784
5	Diisobutyl phthalate		5.406
6	Nonadecane		14.153
7	Icosane		12.578
8	Henicosane		11.543
9	Decosane		10.531

oxidation of *n*-heptane were esters (products 3 and 5) and long chain alkanes (products 2, 4, 6, 7, 8 and 9) as Fig. 10 and Table 2 show. It was also found that the yield of the asymmetric esters (products 3 and 5) were higher (18.852%) when  $\text{SO}_4^{2-}/\text{SnO}_2\text{-Co}_2\text{O}_3$  were used than that of  $\text{SO}_4^{2-}/\text{SnO}_2$  catalyst, indicating that the catalytic activities of  $\text{SO}_4^{2-}/\text{SnO}_2$  catalyst were promoted by the introduction of cobalt and the direct synthesis of the asymmetric esters from alkane can be accomplished by one step under mild condition.

### 3.7. Assumed mechanism

Oxidations of hydrocarbons with  $\text{O}_2$  are most likely to involve classical free radical autoxidation pathways with intermediate

formation of  $\text{RO}_2\text{H}$  [15]. The latter may subsequently undergo heterolytic oxygen transfer processes. Similar mechanisms are usually reported as follows [16–18]:



The mechanism of these reactions is not clear at this stage.  $\text{SO}_4^{2-}/\text{SnO}_2\text{-Co}_2\text{O}_3$  catalyzed oxidations can involve homolytic pathways via free radical ( $\text{HO}\cdot$ ,  $\text{HO}_2\cdot$ ,  $\text{RO}\cdot$ ,  $\text{RO}_2\cdot$ ) intermediates and/or heterolytic oxygen transfer processes. The reaction probably involves in situ formation of persulphonic acid by the reaction of sulphonic acid group of  $\text{SO}_4^{2-}/\text{SnO}_2\text{-Co}_2\text{O}_3$ , followed by the oxygen transfer to organic substrate.

XPS of Sn 3d and Co 2p peaks deconvoluted to two different valent, respectively, was observed, demonstrating that  $\text{Sn}^{4+}$  and  $\text{Co}^{3+}$  were reduced and related to the catalytic reaction.

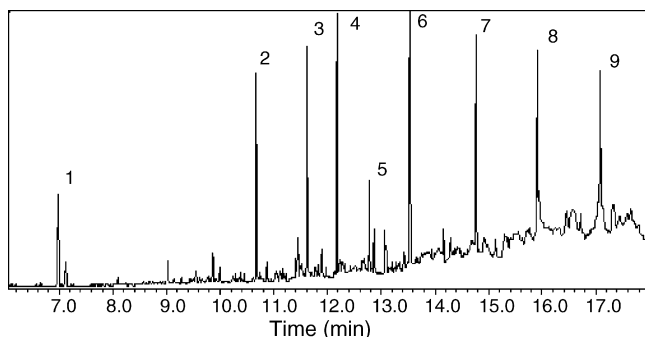


Fig. 10. GC of the products.

#### 4. Conclusions

Sulfated tin oxide ( $\text{SO}_4^{2-}/\text{SnO}_2$ ) and Co modified sulfated tin oxide ( $\text{SO}_4^{2-}/\text{SnO}_2\text{--Co}_2\text{O}_3$ ) prepared by chemical co-precipitation method and characterized by means of SEM, XRD, FT-IR and XPS techniques. The modified sulfated tin oxide catalyst shows activities for *n*-heptane oxidation with air as the oxidant. Two asymmetric esters: diisobutyl phthalate and cyclohexylmethyl tridecyl oxalate that have not reported were obtained. Simple work up procedure, milder reaction conditions and shorter reaction times are the advantages associated with the  $\text{SO}_4^{2-}/\text{SnO}_2\text{--Co}_2\text{O}_3$  catalytic process.

#### References

- [1] M. Hino, K. Aratab, Superacids by metal oxides, X: reaction of butane catalyzed by sulfated metal oxides, zeolites, or silica aluminas mixed with Pt–ZrO<sub>2</sub>, Appl. Catal. A: Gen. 173 (1998) 121–124.
- [2] H. Matsuhashi, H. Miyazaki, Y. Kawamura, H. Nakamura, K. Arata, Preparation of a solid superacid of sulfated tin oxide with acidity higher than that of sulfated zirconia and its applications to aldol condensation and benzoylation, Chem. Mater. 13 (2001) 3038–3042.
- [3] N. Pasadakis, V. Gaganis, C. Foteinopoulos, Octane number prediction for gasoline blends, Fuel Process. Technol. 87 (2006) 505–509.
- [4] K. Moljord, H.G. Hellenes, A. Hoff, I. Tanem, Effect of reaction pressure on octane number and reformat and hydrogen yields in catalytic reforming, Ind. Eng. Chem. Res. 35 (1996) 99–105.
- [5] K. Arata, H. Nakamura, M. Shouji, Friedel–Crafts acylation of toluene catalyzed by solid superacids, Appl. Catal. A: Gen. 197 (2000) 213–219.
- [6] G. Lu, Catalytic properties of  $\text{SO}_4^{2-}/\text{Ti–M–O}$  superacids in esterification, Appl. Catal. A: Gen. 133 (1995) 11–18.
- [7] P. Salas, J.G. Hernandez, J.A. Montoya, J. Navarrete, J. Salmones, Effect of tin content on silica mixed oxides: sulfated and unsulfated catalysts, J. Mol. Catal. A: Chem. 123 (1997) 149–154.
- [8] M.A. Ecomier, K. Wilson, A.F. Lee, Structure–reactivity correlations in sulphated-zirconia catalysts for the isomerisation of  $\alpha$ -pinene, J. Catal. 215 (2003) 57–65.
- [9] J.R. Sohn, S.H. Lee, J.S. Lim, New solid superacid catalyst prepared by doping ZrO<sub>2</sub> with Ce and modifying with sulfate and its catalytic activity for acid catalysis, Catal. Today 116 (2006) 143–150.
- [10] B.M. Reddy, P.M. Sreekanth, Y. Yamada, Q. Xub, T. Kobayashi, Surface characterization of sulfate, molybdate, and tungstate promoted TiO<sub>2</sub>–ZrO<sub>2</sub> solid acid catalysts by XPS and other techniques, Appl. Catal. A: Gen. 228 (2002) 269–278.
- [11] B.M. Reddy, P.M. Sreekanth, Y. Yamada, T. Kobayashi, Surface characterization and catalytic activity of sulfate-, molybdate- and tungstate-promoted Al<sub>2</sub>O<sub>3</sub>–ZrO<sub>2</sub> solid acid catalysts, J. Mol. Catal. A: Chem. 227 (2005) 81–89.
- [12] M. Kaminski, E. Gilgenast, A. Przyjazny, G. Romanik, Procedure for and results of simultaneous determination of aromatic hydrocarbons and fatty acid methyl esters in diesel fuels by high performance liquid chromatography, J. Chromatogr. A 1122 (2006) 153–160.
- [13] T. Nakato, M. Kimura, S. Nakata, T. Okuhara, Changes of surface properties and water-tolerant catalytic activity of solid acid Cs<sub>2.5</sub>H<sub>0.5</sub>PW<sub>12</sub>O<sub>40</sub> in water, Langmuir 14 (1998) 319–325.
- [14] A.G. Giumanini, G. Verardo, Identification of mononitro and dinitro isomers of diphenylmethane by GC–FT–IR and GC–MS techniques, Ind. Eng. Chem. Res. 40 (2001) 1449–1453.
- [15] R.A. Sheldon, I.W.C.E. Arends, H.E.B. Lempers, Liquid phase oxidation at metal ions and complexes in constrained environments, Catal. Today 41 (1998) 387–407.
- [16] F. Gugumus, Thermolysis of polyethylene hydroperoxides in the melt 5: mechanisms and formal kinetics of product formation, Polym. Degrad. Stab. 76 (2002) 381–391.
- [17] A. Marquez, J. Raul, A. Lvarez, A possible mechanism for furan formation in the tropospheric oxidation of dienes, Environ. Sci. Technol. 39 (2005) 8797–8802.
- [18] K. Arata, H. Matsuhashi, M. Hino, H. Nakamura, Synthesis of solid superacids and their activities for reactions of alkanes, Catal. Today 81 (2003) 17–30.