

Catalytic Dehydrogenation of Tetradecanol over Copper/Barium Oxide Catalysts

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The liquid phase dehydrogenation of tetradecanol to tetradecanal has been studied over a series of CuO/BaO catalysts. Catalytic activity and selectivity to tetradecanal was found to depend on the ratio of easily reducible copper sites to less easily reducible copper sites. The catalysts have been characterized by X-ray diffraction, temperature programmed reduction, and thermo-gravimetric analysis. TPR results have shown that there were at least two types of copper oxides with varying reducibility. The relationship between the activity and area ratio of various copper oxide sites and a scheme for the conversion of tetradecanol were discussed.

Key words:

Dehydrogenation, CuO/BaO catalyst, catalyst characterization, XRD, TPR

Introduction

Catalytic dehydrogenation of alcohols is an important research area since aldehydes have a variety of uses in industry. Although there are numerous studies¹ in catalytic dehydrogenation of light alcohols, regarding the high molecular mass alcohols (fatty alcohols), number of heterogeneous catalytic dehydrogenation studies decreases sharply. From these limited studies, it is understood that heterogeneous catalytic selectivity and activity in the formation of fatty aldehydes over oxide type catalysts was comparatively inferior to those obtained from low molecular mass alcohols. Activities of the copper-based catalysts were found to decrease within a few hours, thus attention was focused on the influence of promoters to improve the stability of the catalysts.

Catalysts for the dehydrogenation of alcohols can be divided into two groups; metal oxide and metal catalysts.¹ Within the metal oxides, basic oxides, ZnO, CuO, MgO²⁻⁴ etc. and catalysts with acid character, such as chromium containing copper,⁵ were good catalysts among many others. Copper-based metal oxides were particularly appropriate for this purpose. Although copper received much attention, its activity was reported to decline within a few hours of time-on-stream.⁵

The dehydrogenation activity was affected by the acid-base properties of the catalyst.³ When copper-based catalysts were used for dehydrogenation of alcohols, an additive to copper must be used. Al-

kaline additives were the most popular one. Additives,³ such as Ba, Mg, increased the yield and selectivity of aldehydes and similarly Cr was found to enhance copper surface area,⁵ thus it increased the stability.

In this study, catalytic dehydrogenation of tetradecanol into tetradecanal in the presence of copper oxide/barium oxide catalysts was investigated in liquid phase and under inert atmosphere. The catalytic reaction was studied under mild conditions. XRD, TPR and TGA characterization of copper oxide/barium oxide catalysts were discussed and a scheme for fatty alcohol conversion over copper oxide/barium oxide catalysts was elucidated.

Experimental

Materials

Tetradecanol (Merck, 98 %), tetradecanal (Fluka, 98 %), tetradecanoic acid (Merck, 98 %) were employed without further purification. High purity nitrogen gas (BOC Turkey, 99.998 %) was used as inert atmosphere. Copper acetate, barium hydroxide and $w = 25\%$ NH₃ solutions were used in catalyst preparation. They were all synthesis grades and obtained from Merck.

Reaction procedure

Liquid phase dehydrogenation of 1-tetradecanol was carried out in a glass reactor at a constant stirring speed of $n_s = 250 \text{ min}^{-1}$. The reaction vessel ($V = 100 \text{ ml}$) was placed in a temperature-controlled bath. A proportional and integral controller within an accuracy of $\pm 1^\circ\text{C}$ controlled the reaction temperature. The reactor was equipped with a ther-

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mocouple port, a reflux condenser and side sampling port. $m = 40$ g of tetradecanol and $m = 0.4$ g of catalyst were reacted under a nitrogen pressure of $p = 1$ bar and at reaction temperatures between $T = 150$ and 300 °C. The reaction vessel was loaded with $m = 40$ g of tetradecanol and temperature was stabilized at the reaction temperature. The catalyst was then added to the vessel while stirring the content under flowing nitrogen. The reaction was then timed.

Reaction products were analyzed by taking aliquots of products with intervals of fifteen to sixty minutes. Samples were frozen in an ice bath to stop further reaction. Approximately 0.1 g of frozen samples were dissolved in n-propanol and analyzed in a HP 6890+ gas chromatograph fitted with a $l = 30$ m long, $d = 320$ μ m internal diameter, and $\delta = 10$ μ m film thick HP Innowax fused silica capillary column attached to a FID detector. All the reaction products were qualitatively identified by a HP 5973a mass spectrometer using NIST98 library and products were quantified by using measured response factors of the known chemicals.

Blank tests, aimed to ascertain that the reaction did not occur thermally in the absence of catalysts, were done without catalyst. No indication of reaction occurring without catalyst was observed after 6 h of reaction time at the highest reaction temperature of $T = 300$ °C.

The absence of intraparticle and interparticle diffusion was also checked at the highest reaction temperature. The particle diameter of catalysts was changed from $d_p = 0.05$ mm up to 0.4 mm. No measurable change in the initial reaction rate of tetradecanol was observed. Therefore, this test assured us that there was no intraparticle diffusion limitation. Initial rates of reaction were also found not to depend on mixing speeds above $n_s = 100$ min^{-1} .

Initial reaction rates were found to be linearly dependent on the amount of catalyst used between $w = 0.1$ and 2 % loading of tetradecanol. Goodness of linearity was better than 0.95. This high linearity suggested that the initial rate of dehydrogenation of tetradecanol was kinetically controlled over the catalyst loadings used in the tests.

Some selected experiments were repeated four times to check the level of the experimental error. It was found that the error in the calculation of initial reaction rate was less than ± 10 %. The conversion of tetradecanol, $X_{\text{tetradecanol}}$, was defined as

$$X_{\text{tetradecanol}} = 100 \cdot \frac{n_{\text{tetradecanol in}} - n_{\text{tetradecanol out}}}{n_{\text{tetradecanol in}}}$$

$n_{\text{tetradecanol in}}$ = amount of tetradecanol fed into the reactor, and $n_{\text{tetradecanol out}}$ = amount of tetradecanol in the reactor after certain time of run. The selectivity for specific products, for example, to tetradecanal, $S_{\text{tetradecanal}}$, was calculated as

$$S_{\text{tetradecanal}} = 100 \cdot \frac{n_{\text{tetradecanal out}}}{n_{\text{tetradecanol in}} - n_{\text{tetradecanol out}}}$$

$n_{\text{tetradecanal}}$ = amount of tetradecanal in the reactor after certain time of run. The yields of various fractions were obtained by multiplying tetradecanol conversion by the corresponding selectivity.

Catalysts preparation

Copper-based catalysts with various copper oxide and barium oxide mole ratios, i.e. $r_{\text{CuO/BaO}} = 1.35 : 1$, $r_{\text{CuO/BaO}} = 1 : 1.75$, $r_{\text{CuO/BaO}} = 1 : 4.33$, $r_{\text{CuO/BaO}} = 1 : 7.42$, were used in screening tests. The numbers on right side are the amounts of the corresponding oxides, namely, CuO and BaO. For example, $r_{\text{CuO/BaO}} = 1.75 : 1$ indicates that 63.64 % CuO and 36.36 % BaO is present and in other words, for every 1.75 mole of CuO there is 1 mole of BaO in CuO/BaO catalyst. Catalyst preparation conditions, such as, precipitation temperature, precipitation pH, calcination time and temperature, drying time and temperature were all kept constant.

The catalysts were prepared by co-precipitation. Appropriate amounts of $\text{Cu}(\text{CH}_3\text{CO}_2)_2$ and $\text{Ba}(\text{OH})_2$ were dissolved in deionized hot water and the resulting solution was heated up to $T = 65$ °C. This mixture was precipitated by gradually adding $w = 25$ % NH_3 solution until pH value reached to 8.5–9. The resultant solution was slowly stirred for 2 h at 65 °C. The precipitate was filtered at 20 °C and dried at 105 °C for 2 h and then calcined at 400 °C for 5 h in a tubular furnace under the flowing air. The calcined catalysts were sieved and only the particles between 0.05–0.1 mm were used in experiments.

Catalyst characterization techniques

Thermogravimetric (TG) measurements were performed using a Shimadzu Thermal Analyzer (TG-50A). Thermogravimetric analysis was carried out with $T = 10$ °C min^{-1} heating rate of temperature change to 800 °C using $m = 15$ mg of samples under flowing air.

X-ray powder diffraction patterns were obtained using a Philips (PW 1140) diffractometer with nickel filtered Cu $K\alpha$ ($\lambda = 1.5405$) radiation. Spectra were obtained from 5 to 65° at a rate of 1° min^{-1} (in 2 Θ). The crystallite sizes were calculated from XRD line broadening analysis using Scherrer equation $t = C \cdot \lambda / (B \cdot \cos \theta)$, where λ is the X-ray wavelength (\AA), B is the full width at half maximum, θ is Bragg angle,

C is a factor depending on crystallite shape and C is taken to be 0.9, and t is the crystallite size (Å).

TPR profiles were obtained by using Quantachrome ChemBET 3000 flow type equipment. In TPR experiments, 60 mg of calcined catalyst was dried at 105 °C for 2 h, and 10.3 % H₂ + N₂ was used as reducing gas mixture. Temperature ramp rate was $T = 10\text{ °C min}^{-1}$ and flow rate was $Q = 70\text{ ml min}^{-1}$ in TPR analyses. The effluent was passed through cold liquid N₂ trap to remove water and CO₂, and then through TCD. The changes in H₂ flow were followed using a thermal conductivity detector.

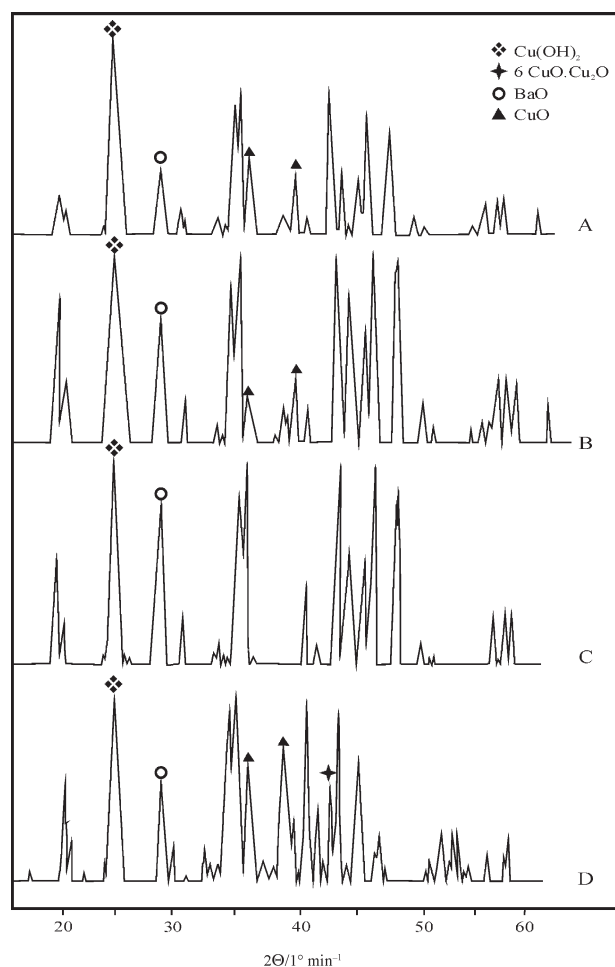
Result and discussion

Catalyst characterization

Thermogravimetric analysis of copper/barium oxide catalyst precursors showed a broad peak between 30 and 170 °C. The first mass loss occurred in the temperature range of $T = 30\text{--}170\text{ °C}$ was due to the dehydration of precursors. There was almost no mass change occurred after dehydration completed. Noticeable mass change was only seen in $r_{\text{CuO}/\text{BaO}} = 1 : 7.42$ catalyst. An overall 3 % mass loss in $r_{\text{CuO}/\text{BaO}}$ physical mixture was observed after 450 °C. A very low mass loss (less than 5 %) in BaO was observed up to 600 °C.

It is noteworthy to remind that calcination temperature was 400 °C. Since the thermal dehydration of Cu(OH)₂⁶ into CuO could be realized at higher temperatures (750–850 °C). The decomposition of Cu(OH)₂, which was the only decomposable catalyst ingredient, under calcinations temperatures used in this study could not complete at all. Therefore, the catalysts containing Cu(OH)₂ phase remained intact after the calcination at 400 °C.

Fig. 1 shows the XRD patterns of calcined $r_{\text{CuO}/\text{BaO}} = 1.35 : 1$, $r_{\text{CuO}/\text{BaO}} = 1 : 1.75$, $r_{\text{CuO}/\text{BaO}} = 1 : 4.33$ and $r_{\text{CuO}/\text{BaO}} = 1 : 7.42$ catalysts with increasing BaO content. In X-ray diffractograms, the most intense peaks of identifiable phases were labelled. In the catalysts with $r_{\text{CuO}/\text{BaO}} = 1.35 : 1$, $r_{\text{CuO}/\text{BaO}} = 1 : 1.75$, $r_{\text{CuO}/\text{BaO}} = 1 : 4.33$ compositions, Cu(OH)₂, CuO, and BaO phases were found in major quantities and in $r_{\text{CuO}/\text{BaO}} = 1.35 : 1$ catalyst, in addition to above phases, a mixed copper oxide, 6CuO·Cu₂O, was also detected in minor quantities. At the lower CuO containing catalysts, such as $r_{\text{CuO}/\text{BaO}} = 1 : 7.42$, there were no peaks due to the CuO. As the copper oxide content increased, CuO and especially Cu(OH)₂ peaks became more apparent. The phases and crystallite sizes calculated from XRD line-broadening calculations were summarized in Ta-



A: $r_{\text{CuO}/\text{BaO}} = 1 : 1.75$, B: $r_{\text{CuO}/\text{BaO}} = 1 : 4.33$, C: $r_{\text{CuO}/\text{BaO}} = 1 : 7.42$, D: $r_{\text{CuO}/\text{BaO}} = 1.35 : 1$

Fig. 1 – X-ray diffractograms of catalysts

Table 1 – Phases detected and crystallite sizes of CuO/BaO catalysts with different mole ratios

Mole ratio, $r_{\text{CuO}/\text{BaO}}$	1.35 : 1	1 : 1.75	1 : 4.33	1 : 7.42
major phases detected in the calcined catalysts	BaO CuO Cu(OH) ₂ 6CuO·Cu ₂ O	BaO CuO Cu(OH) ₂ ND	BaO CuO Cu(OH) ₂ ND	BaO ND Cu(OH) ₂ ND
crystallite size, nm				
Cu(OH) ₂	11.2	11.2	11.3	11.3
CuO	18.5	16.2	16.2	ND
BaO	30.3	30.3	45.5	45.5

ND – Not detected

ble 1. It was observed that CuO crystallite size decreased as barium oxide content increased.

Catalysts with different mole ratios of $r_{\text{CuO}/\text{BaO}}$ have been characterized by temperatures programmed reduction (TPR) and the TPR profiles

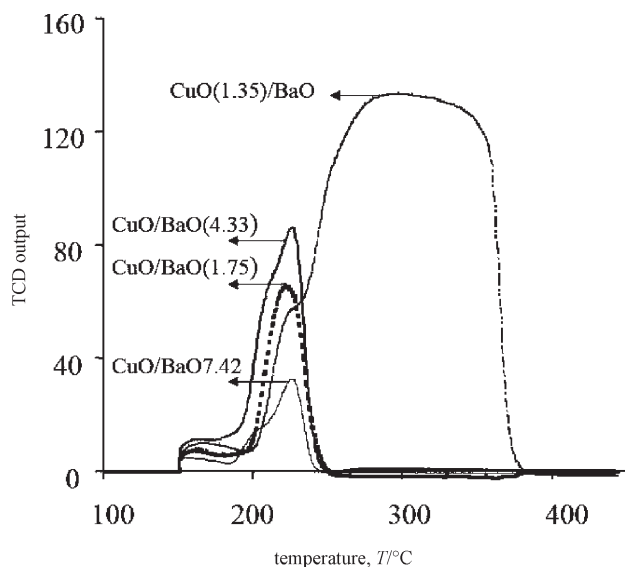


Fig. 2 – TPR profiles of the CuO and BaO alone and physical mixture of CuO/BaO

were shown in Fig. 2. Two groups of peaks were observed at distinctly separate temperature ranges. One group of reduction peaks appearing at approximately 210 °C was labelled as low temperature peaks (I) or easily reducible copper oxides. Peaks appearing at 290 °C were labelled as high temperature peaks (II) or less easily reducible copper oxides. Barium oxide was not reduced at temperatures below 800 °C as was shown in Fig. 3. In line with our findings, it was reported in the literature³ that barium oxide was not reduced at temperatures below 800 °C.

In this study, deconvolution of TPR peak groups revealed that the high and low tempera-

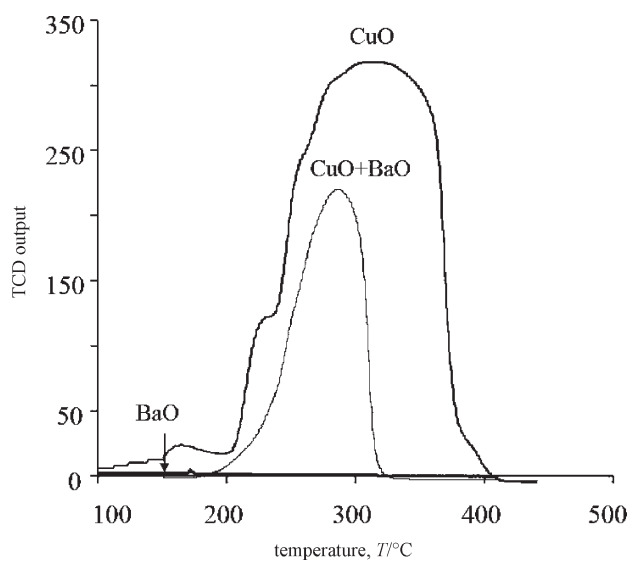


Fig. 3 – TPR profiles of the catalysts ($r_{\text{CuO}/\text{BaO}} = 1 : 7.42$, $r_{\text{CuO}/\text{BaO}} = 1 : 4.33$, $r_{\text{CuO}/\text{BaO}} = 1 : 1.75$, $r_{\text{CuO}/\text{BaO}} = 1.35 : 1$ calcined at 400 °C

ture copper reduction peaks of $r_{\text{CuO}/\text{BaO}} = 1.35 : 1$, $r_{\text{CuO}/\text{BaO}} = 1 : 1.75$, $r_{\text{CuO}/\text{BaO}} = 1 : 4.33$ and $r_{\text{CuO}/\text{BaO}} = 1 : 7.42$ catalysts appeared nearly at the expected temperatures, namely 210 and 290 °C. These selected temperature ranges were also in line with the literature values.⁷

For the single CuO, only one high temperature peak appeared at 290 °C. The overlapping TPR peaks were deconvoluted with a Fortran 90 program using a Gaussian response function and areas were labelled as A_I and A_{II} respectively at 210 and 290 °C. The changes in $A_I/(A_I + A_{II})$ area ratios were shown in Fig. 4. Results show that A_I over $(A_I + A_{II})$ ratio first increases up to $r_{\text{CuO}/\text{BaO}}$ ratio of 1 : 1.75 and then decreases in parallel to decreasing copper oxide content. From the integration of deconvoluted TPR peaks, it was found that changing BaO content does not only change the proportions of type I and type II copper oxides but also change the total area of reducible copper oxides ($A_I + A_{II}$). Over $r_{\text{CuO}/\text{BaO}} = 1 : 1.75$ catalyst, areas of low temperature peaks (I) reach a maximum and then as BaO content increased, the amount of easily reducible copper species decreased sharply. It seems to have a saturation phenomenon at $r_{\text{CuO}/\text{BaO}} = 1 : 1.75$ catalyst.

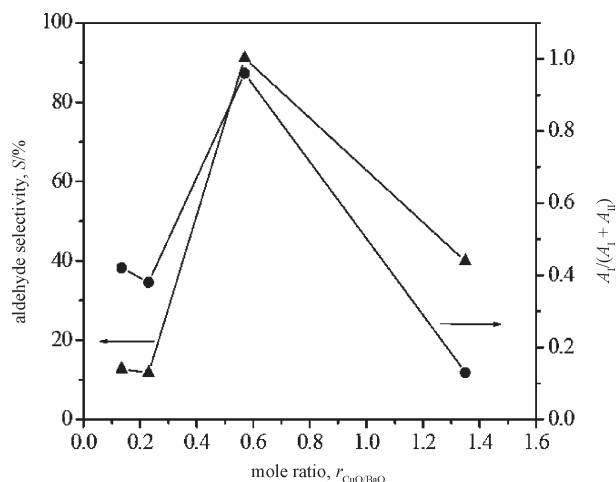


Fig. 4 – Changes in the selectivity and in the ratios of A_I to $A_I + A_{II}$ as a factor of $r_{\text{CuO}/\text{BaO}}$ mole ratio

It was reported⁸ that, area under the low temperature peak (I) reached a maximum value around 10 % CuO catalyst and peak maximum was reported to be 265 °C. The peak maximum of unmodified catalyst was found to be around 290 °C. The low temperature peaks (I) were reported to be due to the highly dispersed Cu^{2+} ions.⁸ Robertson et al.,⁸ and Van der Grift et al.,⁹ studied CuO/SiO₂ catalysts and concluded that the highly dispersed copper ions were more easily reduced than the bulk oxides. High temperature reduction peaks are considered to be due to bulk copper oxide and low temperature peaks were ascribed to those of surface CuO.

Conversion of tetradecanol

Effect of reaction temperature was studied at the temperatures of $T = 150, 200, 250$ and 300 °C. Tetradecanal selectivity was seen to rise from $S = 11$ % to 91.1 % with the increase of reaction temperature. Upper limit was bound to be 300 °C because above this temperature, tetradecanol started to boil and decompose, therefore 300 °C was chosen as the highest temperature to run the dehydrogenation reactions in liquid phase.

In order to determine the effect of a reductive activation of the catalyst, $r_{\text{CuO}/\text{BaO}} = 1 : 1.75$ catalyst was first reduced with $x = 10.3$ % H_2 in nitrogen at 300 °C for four hours and then reduced catalyst was tested under a typical reaction condition at 300 °C. It was interesting to note that there was no meaningful difference in product distribution as was shown in Table 2.

Table 2 – Composition comparison over reduced and unreduced catalysts after 90 min of run

Catalyst	Composition in mass fraction, w/%				
	aldehyde	alcohol	acid	aldol	others
$r_{\text{CuO}/\text{BaO}} = 1.35 : 1$	7.76	80.56	0.32	1.37	10
Reduced $r_{\text{CuO}/\text{BaO}} = 1.35 : 1$	5.46	81.70	0	0.76	12

Fig. 4 shows the relationship between the $r_{\text{CuO}/\text{BaO}}$ ratio and ratio of $A_I/(A_I + A_{II})$ and the changes in the selectivity to tetradecanal as the $r_{\text{CuO}/\text{BaO}}$ mole ratio changes. Tetradecanal selectivity was found to depend on the ratio of areas of low temperature peak (A_I) to total area ($A_I + A_{II}$) of peaks I and II. It was noteworthy that as ratio of $A_I/(A_I + A_{II})$ approached maximum at around $r_{\text{CuO}/\text{BaO}} = 1 : 1.75$ ratio, the selectivity reached to a maximum of 91.1 % as was shown in Fig. 4. Below this copper loading, the catalytic selectivity and area ratio decreased sharply. Similarly, above this peak turning point, the catalytic selectivity and area ratio decreased too. There was a correlation between the ratio of $A_I/(A_I + A_{II})$ and the catalytic selectivity with varying $r_{\text{CuO}/\text{BaO}}$ ratios as shown in Fig. 4. This concluded that predominant factors in the activity and selectivity of $r_{\text{CuO}/\text{BaO}}$ type catalysts should be the highly dispersed copper oxide species, while bulk CuO contributed to the selectivity little to none.

Screening tests were conducted with $r_{\text{CuO}/\text{BaO}} = 1.35 : 1$, $r_{\text{CuO}/\text{BaO}} = 1 : 1.75$, $r_{\text{CuO}/\text{BaO}} = 1 : 4.33$, $r_{\text{CuO}/\text{BaO}} = 1 : 7.42$ catalysts at 300 °C. Among the catalysts tested, $r_{\text{CuO}/\text{BaO}} = 1 : 1.75$ catalyst was

found to be the most active and selective towards tetradecanal. $r_{\text{CuO}/\text{BaO}} = 1 : 1.75$ catalyst showed the highest tetradecanal selectivity, $S = 91.1$ %, and total conversion of tetradecanol was $X = 60.1$ % at ninetieth minutes of reaction. After ninety minutes of reaction time, tetradecanal selectivity was seen to have markedly decreased down to 8.9 % and levelled at around 8 %. As the reaction progressed, an increase in 3-hydroxy-2-dodecanyl-hexadecanal concentration was also noted. The typical changes in the products spectrum over $r_{\text{CuO}/\text{BaO}} = 1 : 1.75$ catalyst were depicted in Fig. 5.

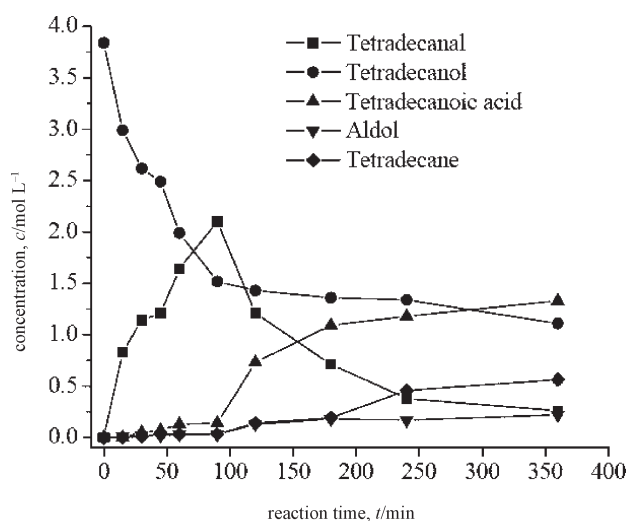


Fig. 5 – Reaction profile of tetradecanol conversion over a $r_{\text{CuO}/\text{BaO}} = 1 : 1.75$ catalyst

A study in the reaction of n-butanol in the presence of SiO_2 supported $r_{\text{BaO}/\text{CuO}} = 3 : 15$, $r_{\text{BaO}/\text{CuO}} = 5 : 1$, $r_{\text{BaO}/\text{CuO}} = 1 : 15$ and Cu catalysts at 270 °C showed that barium had beneficial effect on copper catalysts.¹⁰ Oxidative and direct dehydrogenation of n-butanol over copper-barium oxide catalyst was investigated between 210 – 270 °C. Conversion was in excess of 80 % and selectivity to butyraldehyde was over 99 %. With $r_{\text{BaO}/\text{CuO}} = 3 : 15$ catalyst, catalyst stability did not show an appreciable change in a continuous run of 8 h at operating temperatures up to 270 °C. Dehydrogenation of n-hexanol was also studied using various copper and barium catalysts supported on silica gel.¹¹ The dehydrogenation was conducted using 15 % copper and 5 % barium catalysts supported on silica gel at 280 °C and the maximum conversion of n-hexanol to hexaldehyde was only $X = 66.5$ %.¹¹ In another study, dehydrogenation of 2-octanol was carried out in the vapor phase using 10 % copper and 1 % barium catalyst supported on silica gel. The selectivity to 2-octanone¹² was found to be less than 1 %. As can be seen from these catalytic dehydrogenation studies, and although the list is not exhaustive and not

complete, it is apparent that as the carbon number of alcohols increased, selectivity towards aldehydes as well as conversion decreased in parallel over copper barium based catalysts. The conversion and selectivity levels attained in this study are unusually high.

All the reactions of tetradecanol dehydrogenation occurred in liquid phase. The selectivities for dehydrogenation, dehydration, and esterification depended on the type of the catalysts and the reaction temperature. Intermediate product, which was identified and labelled as an aldol condensation product between tetradecanal and tetradecanol, could well be a tetradecanal dimer since mass spectra for tetradecanal dimer and aldol products look quite similar. On the other hand, the sequential appearance of aldehyde and ever-increasing aldol product indicated that aldol structure was more likely to exist in the products rather than a dimer of tetradecanal. No significant formation of other products rather than tetradecane in minor quantities was detected. Only when almost all tetradecanal was converted, intermediate compounds were further dehydrogenated and dehydrated to the final products, such as tetradecanoic acid and tetradecane, respectively. Selectivities to tetradecanal, i.e. $S = 91.1\%$, and conversion of tetradecanal, i.e. $X = 60\%$, observed in this study were exceptionally higher than those reported in open literature.

The major reaction intermediates were tetradecanal, tetradecanoic acid, and tetradecane was the minor by-product. To make the scheme simpler, the main course of dehydrogenation of tetradecanol was described to proceed through the two main steps and two sequences in parallel. From the product distribution and sequence of formation of products and by-products, a simplified tentative reaction scheme was presented in Fig. 6.

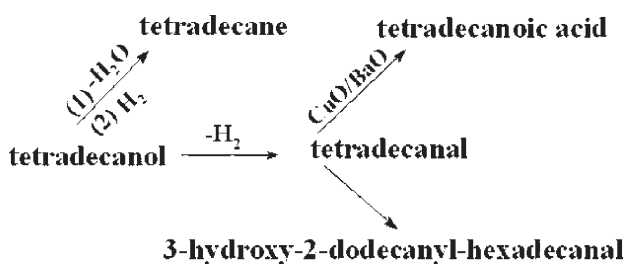


Fig. 6 – Simplified reaction scheme of tetradecanol dehydrogenation

In conclusion, the synergy of copper and barium oxide appears to be effective for the liquid phase dehydrogenation of tetradecanol. In this work, $r_{\text{CuO/BaO}} = 1 : 1.75$ catalyst has shown to be very good activity and selectivity in the catalytic conversion of tetradecanol into tetradecanal. Earth alkaline oxides might play a significant role in directing the

selectivity to aldehydes. It was found that the selectivity to tetradecanal was directly proportional to the ratio of easily reducible copper oxide area to total area of reducible copper oxide. An overall scheme for the conversion of tetradecanol was presented.

ACKNOWLEDGEMENT

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List of symbols

c	– concentration, mol L ⁻¹
d	– diameter, μm
l	– length, m
m	– mass, g
n	– amount of substance, mol
n_s	– stirring speed, min ⁻¹
p	– pressure, bar
r	– mole ratio, $n_{\text{CuO}}/n_{\text{BaO}}$
S	– selectivity, %
T	– temperature, °C
T	– rate of temperature change, °C min ⁻¹
V	– volume, mL
w	– mass fraction, %
X	– conversion, %
x	– mole fraction, %
δ	– film thick, μm
Θ	– Bragg angle, °
λ	– wavelength, nm

References

- Besson, M., Gallezot, P., *Catal. Today* **57** (2000) 127.
- Raizada, V. K., Tripathi V. S., Lal, D., Singh, G. S., Dwivedi, C. D., Sen, A. K., *J. Chem. Tech. Biotechnol.* **56** (1993) 265.
- Tu, Y. J., Chen, Y. W., *Ind. Eng. Chem. Res.* **37** (1998) 2618.
- Halawy, S. A., Mohamed, M. A., Abd El-Hafez, S. F., *J. Mol. Catal.* **94** (1994) 191.
- Tu, Y. J., Li, C., Chen, Y. W., *J. Chem. Technol. Biotechnol.* **59** (1994) 141.
- Kato, H., Hosimija, H., Nakazima, S., *J. Chem. Soc. Japan* **60** (1939) 1115.
- Zhou, R., Yu, T., Jiang, X., Chen, F., Zheng, X., *Appl. Surf. Sci.* **148** (1999) 263.
- Robertson, S. D., Mcnicol, B. D., Debaos, J. H., Kloet, S. C., Jenkins, J., *J. Catal.* **37** (1975) 424.
- Van der Grift, C. J. G., Mulder, A., Geus, J. W., *Appl. Catal.* **60** (1990) 181.
- Shiau, C. Y., Liaw, S. T., *J. Chem. Tech. Biotechnol.* **53** (1992) 13.
- Venkateshwar, S., Sridharan, S. S., Bhagwanth Rao, M., *Indian Journal of Tech.* **23** (1985) 305.
- Chokkaram, S., Srinivasan, R., Milburn, D. R., Davis, B. H., *J. Mol. Catal. A: Chemical* **121** (1997) 157.