

1 **Copper(II) complex of ( $\pm$ )*trans*-1,2-cyclohexanediamine azo-linked Schiff**  
2 **base ligand encapsulated in nanocavity of zeolite–Y for the catalytic**  
3 **oxidation of olefins**

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7  
8 **Abstract**

9 A Schiff base ligand derived from 4-(benzeneazo) salicylaldehyde and ( $\pm$ )*trans*-1,2-  
10 cyclohexanediamine (H<sub>2</sub>L) and its corresponding Cu(II) complex (CuL) has been  
11 synthesized and characterized by FT-IR, UV-VIS and <sup>1</sup>H NMR. The copper Schiff base  
12 complex encapsulated in the nanopores of zeolite-Y (CuL-Y) by flexible ligand method and  
13 its encapsulation has been ensured by different studies. These heterogeneous and  
14 homogeneous catalysts have been used for oxidation of different alkenes with *tert*-butyl  
15 hydroperoxide. Under the optimized reaction conditions, the oxidation of cyclooctene,  
16 cyclohexene, styrene and norbornene catalyzed by CuL gave 89, 63, 46 and 13% conversion,  
17 respectively. These olefins were oxidized efficiently with 50, 96, 96 and 92% conversion in  
18 the presence of CuL-Y, respectively. Comparison of the catalytic behavior of CuL and CuL-  
19 Y showed the higher catalytic activity and selectivity of the heterogeneous catalyst with  
20 respect to the homogenous one.

21  
22 **Keywords:** Catalyst, 4-(benzeneazo) salicylaldehyde, Styrene, Homogenous,  
23 Heterogeneous

24 **RUNNING TITLE: COPPER(II) COMPLEX OF ( $\pm$ )*TRANS*-1,2-**  
25 **CYLCLOHEXANEDIAMINE AZO-LINKE**

26 **INTRODUCTION**

27 Various transition metal complexes have been used in the catalytic oxidation of  
28 organic substrates.<sup>1</sup> In particular, the catalysis of alkene oxidation by transition metal  
29 complexes is an area of current interest.<sup>2,3</sup> Schiff base ligands are easily synthesized by  
30 the condensation between amines and aldehydes.<sup>4</sup> Schiff bases have both azo and  
31 azomethine groups are called azo Schiff bases. These compounds are used in the textile,  
32 leather and plastic industries<sup>5-7</sup> and have the potential for use in electronic and drug  
33 delivery applications.<sup>8,9</sup> Azo compounds are useful in analytical applications such as  
34 complexometric and pH indicators.<sup>10</sup> Also, these derivatives show biological activities.<sup>11,</sup>  
35 <sup>12</sup> A few azo Schiff base complexes are reported to be catalytically active towards  
36 oxidation.<sup>13</sup> Therefore, it is interesting to study azo linked compounds as catalysts.

37 Immobilization of homogeneous catalysts onto or into an insoluble solid, which can be either  
38 an inorganic solid or an organic polymer, provide higher activity, selectivity, and reusability  
39 of the catalysts.<sup>14-17</sup> Several examples of heterogenization of homogeneous catalysts onto  
40 some inorganic supports, such as MCM-41,<sup>18,19</sup> SBA-15<sup>20,21</sup> and zeolites<sup>22-24</sup> have been  
41 reported.

42 Among the different metal complexes, Cu(II) Schiff base complexes known for oxygenation  
43 reactions. Various copper complexes catalyzed olefin oxidation reactions in homogeneous<sup>25,</sup>  
44 <sup>26</sup> and heterogeneous<sup>27,28</sup> media and the mechanism of these reactions are well established.

45 In this study, we have encapsulated the copper(II) complex of a azo-linked Schiff base ligand  
46 in the nanocavity of zeolite-Y and the catalytic activity of the homogeneous and  
47 heterogeneous catalysts in the oxidation of various olefins with *tert*-butyl hydroperoxide has  
48 been investigated.

## 49 **EXPERIMENTALS**

### 50 *Materials*

51 All starting materials and solvents were purchased from Merck and were used without  
52 further purification.

### 53 *Physical measurements*

54 IR spectra (KBr discs, 500-4000 cm<sup>-1</sup>) were recorded using a Bruker FTIR model Tensor 27  
55 spectrometer. UV-VIS absorption spectra were made with a Perkin-Elmer Lambda 35  
56 spectrophotometer. <sup>1</sup>H NMR spectra were performed on a Bruker FT-NMR 250 MHz

57 spectrometer in  $\text{CDCl}_3$  with TMS as the internal reference. X-ray diffractograms were  
58 recorded using XRD, Seifect, 3003 PTS diffractometer with a  $\text{Cu-K}\alpha$  target. The reaction  
59 products of oxidation were determined and analyzed by GC-MS Quadrupole Agilent 5973  
60 MSD spectrometer.

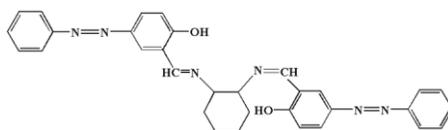
61 *Preparation of 4-(benzeneazo) salicylaldehyde*

62 4-(benzeneazo) salicylaldehyde was prepared using standard procedure.<sup>29</sup>

63 *Preparation of Ligand ( $\text{H}_2\text{L}$ )*

64 ( $\pm$ )*trans*-1,2-cyclohexanediamine (0.5 mmol, 0.06 g) in 5 mL ethanol was added to a solution  
65 of 4-(benzeneazo) salicylaldehyde (1 mmol, 0.23 g) in 10 ml ethanol and chloroform with  
66 the ratio of 2 to 1. The resulting mixture was refluxed for 4 h. Finally, the precipitate of  
67 ligand ( $\text{H}_2\text{L}$ ) was recovered by filtration and washed with ethanol and dried. Ligand was  
68 recrystallized from ethanol to give pure product (Figure 1). Yield: 57% ; M.p. 156 °C;  $^1\text{H}$   
69 NMR (250 MHz,  $\text{CDCl}_3$ ,  $\delta$  / ppm): 1.49–2.11 (8H, m,  $\text{CH}_2$ ), 3.43–3.46 (2H, m, CH), 8.23-8.41  
70 (2H, s,  $\text{HC}=\text{N}$ ), 7.00-7.94 (m, 16H, Ar-H), 10.05-11.35 (s, 2H, OH); IR (KBr,  $\text{cm}^{-1}$ ): 1281 (C-  
71 O), 1488 (C=C), 1630 (CH=N), 3449 (OH); UV-Vis ( $\text{CH}_3\text{CN}$ ) ( $\lambda_{\text{max}}$  / nm): 242, 280 (sh),  
72 377.

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Fig. 1. Structure of ligand ( $\text{H}_2\text{L}$ )

76 *Preparation of  $\text{CuL}$*

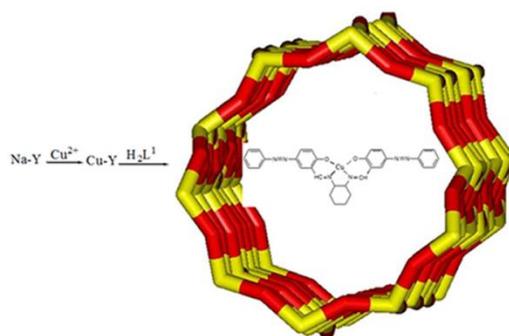
77 The  $\text{CuL}$  complex was prepared by adding a chloroform solution of ligand ( $\text{H}_2\text{L}$ ) (1.5 mmol,  
78 0.29 g) to an ethanolic solution of  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  (1.5 mmol, 0.79 g). The resulting  
79 mixture was refluxed around 2 h and a brown precipitate of copper complex was obtained.  
80 Finally, the precipitate of complex was recovered by filtration, washed with ethanol and  
81 dried at room temperature. Yield: 85%; M.p. 291°C, IR (KBr,  $\text{cm}^{-1}$ ): 1110 (C-O), 1463  
82 (C=C), 1608 (CH=N); UV-Vis ( $\text{CH}_3\text{CN}$ ) ( $\lambda_{\text{max}}$  / nm): 243, 329, 524.

83 *Incorporation of copper(II) in Na-Y (metal exchanged Y-zeolite)*

84 The Cu-Y was prepared using the standard procedure.<sup>30</sup> 4 g Na-Y zeolite was suspended in  
85 100 mL distilled water which contained copper(II) nitrate (4 mmol). The mixture was then  
86 stirred for 24 h. The solid was filtered and washed with deionized water and dried at room  
87 temperature to give a light blue powder of Cu-Y.

88 *Immobilization of H<sub>2</sub>L in Cu-Y*

89 An amount of 0.6 g Cu-Y and 0.1 g of ligand H<sub>2</sub>L were mixed in 50 mL of acetonitrile and  
90 the reaction mixture was refluxed for 7 h in an oil bath with constant stirring. The resulting  
91 material was taken out and extracted with acetonitrile using soxhlet extractor to remove  
92 unreacted ligand from the cavities of the zeolite as well as those located on the surface of  
93 the zeolite along with neat complexes, if any. The non-complexed metal ions present in the  
94 zeolite were removed by exchanging with aqueous 0.01 M NaCl solution. The resulting solid  
95 was finally washed with hot distilled water till no precipitation of AgCl was observed in  
96 reacting filtrate with AgNO<sub>3</sub> solution. This was then dried at 150 °C for several hours till  
97 constant weight was achieved (Fig. 2).



98  
99 Fig. 2. Preparation of encapsulated complex in the supercages of zeolite Y  
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101  
102 *Homogeneous oxidation*

103 To a solution of cyclooctene (10 mmol) and CuL (10 mg, 0.02 mmol) in CH<sub>3</sub>CN (5 mL),  
104 TBHP (25 mmol) was added. The resulting mixture was refluxed and the products were

105 collected at different time intervals, identified and quantified by GC and verified by GC–  
106 MS.

### 107 *Heterogeneous oxidation*

108 Catalyst (20 mg), cyclooctene (10 mmol) and TBHP (25 mmol) were mixed in 5 mL of  
109 CH<sub>3</sub>CN and the reaction mixture was refluxed with continuous stirring in an oil bath for 8  
110 h. The products were collected at different time intervals and identified and quantified by  
111 GC and verified by GC–MS.

## 112 **RESULTS AND DISCUSSION**

### 113 *Spectral studies*

114 In the IR spectrum of the ligand (H<sub>2</sub>L), a sharp band due to the azomethine  $\nu(\text{C}=\text{N})$  appears  
115 at 1630 cm<sup>-1</sup>. The bands at 2853 and 2919 cm<sup>-1</sup> are indicative of the presence of 1,2-  
116 cyclohexanediamine.<sup>31, 32</sup> The band due to  $\nu(\text{C}=\text{N})$  in the H<sub>2</sub>L shifts to lower wave numbers  
117 and appears at 1608 cm<sup>-1</sup> in the CuL. This indicates the involvement of azomethine nitrogen  
118 in coordination to the copper center. Also,  $\nu(\text{C}=\text{N})$  of CuL-Y appears at 1633 cm<sup>-1</sup>. IR  
119 spectra of the hybrid material showed an intense band at 1022 cm<sup>-1</sup> attributable to the  
120 asymmetric stretching of Al–O–Si chain of zeolite. The symmetric stretching and bending  
121 frequency bands of Al–O–Si framework of zeolite appear at 789 and 458 cm<sup>-1</sup>,  
122 respectively.<sup>33</sup>

123 The X-ray powder diffraction patterns of CuL-Y and Na-Y are essentially similar except the  
124 intensities are weaker in the immobilized complex (Fig. 3). This observation indicates that  
125 the framework of the zeolite has not structurally changed during immobilization.

126 The <sup>1</sup>H NMR spectrum of the ligand (H<sub>2</sub>L) was recorded using CDCl<sub>3</sub> solvent. Hydrogen  
127 atoms of the azomethine groups of H<sub>2</sub>L appeared at  $\delta$  8.23–8.41 ppm. The hydrogen atoms  
128 of the CH<sub>2</sub>/CH groups in the cyclohexane ring are observed in the  $\delta$  1.49–3.46 ppm range.  
129 The phenolic OH protons are shown at 10.05 and 11.35 ppm. The aromatic protons are found  
130 in the range  $\delta$  7.00–7.94 ppm as a multiplet.<sup>31, 32, 34</sup>

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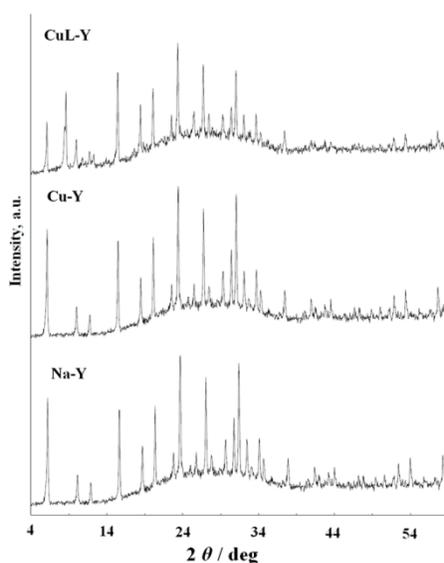


Fig. 3. XRD patterns of Na-Y, Cu-Y and CuL-Y

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135 The electronic spectrum of complex consists of one broad d–d transition band at 524 nm, as  
 136 is usual for square planar geometry Cu(II). The higher energy bands are due to  $\pi$ – $\pi^*$  or n–  
 137  $\pi^*$  transition.<sup>35</sup>

138 *The catalytic oxidation of alkenes*

139 The catalytic performance of CuL in the oxidation of cyclooctene, as a model substrate, with  
 140 H<sub>2</sub>O<sub>2</sub> and *tert*-butyl hydroperoxide as oxidizing agents was investigated. A series of blank  
 141 experiments (Table 1) show that the presence of catalyst is essential for an effective catalytic  
 142 reaction.

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148 TABLE I. Blank experiments

Entry	Alkene	Conversion, %	Selectivity, %
1	cyclooctene	5	50

2	cyclohexene	7	64
3	styrene	5	72
4	norbornene	9	58

149 Reaction conditions: substrate (10 mmol), TBHP (25 mmol), acetonitrile (5 ml); the reactions were run for 8 h  
 150 under reflux.

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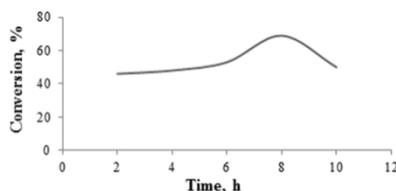
152 Different reaction parameters such as reaction time, reaction solvent, catalyst concentration,  
 153 the nature and the concentration of oxidant that may affect the conversion and selectivity of  
 154 the reaction has been optimized.

155 Fig. 4 illustrates the influence of reaction time in the catalytic oxidation of cyclooctene by  
 156 CuL. It was observed that oxidation of cyclooctene required 8 h for maximum conversion.

157 The effect of the solvent nature in the catalytic activity of the CuL for oxidation of  
 158 cyclooctene has been studied. Therefore, acetonitrile, ethanol, dichloromethane and  
 159 chloroform were used and the highest conversion was obtained in acetonitrile (Fig. 5). The  
 160 higher conversions in acetonitrile (89 %) relative to the others possibly may be due to the  
 161 polarity, hydrophilicity, size of the solvent molecule and higher boiling point of  
 162 acetonitrile.<sup>36</sup>

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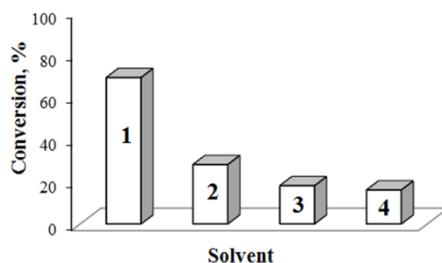
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166 Fig. 4. The effect of reaction time on the oxidation of cyclooctene. Reaction condition: cyclooctene (10 mmol),  
 167 catalyst (0.02 mmol), TBHP (25 mmol), solvent (CH<sub>3</sub>CN, 5 mL) and reflux.

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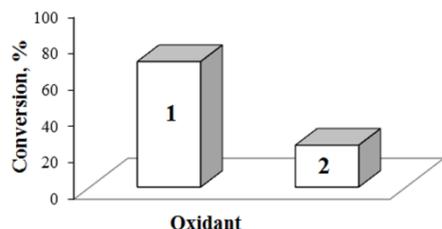
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171 Fig. 5. The influence of various solvents on the oxidation of cyclooctene. Reaction condition: cyclooctene (10  
172 mmol), catalyst (0.02 mmol), TBHP (25 mmol) and solvent (5 mL; 1: acetonitrile, 2: ethanol, 3: chloroform,  
173 4: dichloromethane); the reactions were run for 8 h under reflux.

174

175 In order to investigate the effect of the oxidizing agent in the oxidation reaction, H<sub>2</sub>O<sub>2</sub> and  
176 TBHP were used (Fig. 6). In the presence of TBHP, higher conversion (89%) and selectivity  
177 (53%) was obtained.

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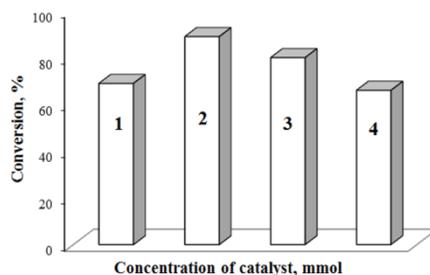
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180 Fig. 6. The influence of kind of oxidant on the oxidation of cyclooctene. Reaction condition: cyclooctene (10  
181 mmol), catalyst (0.04mmol), CH<sub>3</sub>CN (5 mL), oxidant (25 mmol; 1: TBHP, 2: H<sub>2</sub>O<sub>2</sub>); the reactions were run  
182 for 8 h under reflux.

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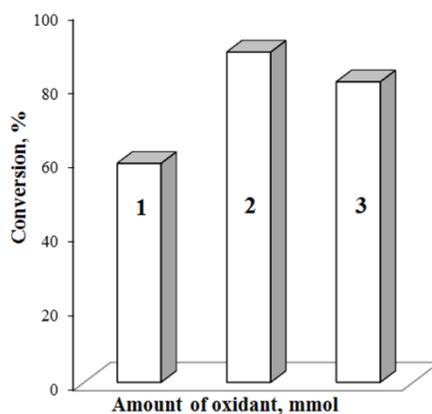
184 The influence of catalyst concentrations have been used in the oxidation of cyclooctene. As  
185 seen in Fig. 7, the highest conversion was obtained with 0.04 mmol (0.02 g) of catalyst.

186 Different oxidant (TBHP) concentrations have been studied in the oxidation of cyclooctene  
187 (Fig. 8). The results indicate that the highest conversion (89%) was obtained at 1:2.5 molar  
188 ratio of cyclooctene to TBHP.



189

190 Fig. 7. The effect of catalyst concentration on the oxidation of cyclooctene. Reaction condition: cyclooctene  
 191 (10 mmol), CH<sub>3</sub>CN (5 mL) and TBHP (25 mmol), concentration of catalyst (1: 0.02 mmol, 2: 0.04 mmol, 3:  
 192 0.06 mmol, 4: 0.08 mmol); the reactions were run for 8 h under reflux.



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194 Fig. 8. The effect of amount of oxidant on the oxidation of cyclooctene. Reaction condition: cyclooctene (10  
 195 mmol), catalyst (0.04 mmol) and CH<sub>3</sub>CN (5 mL), oxidant (TBHP; 1: 20 mmol, 2: 25 mmol, 3: 30 mmol); the  
 196 reactions were run for 8 h under reflux.

197 To establish the general applicability of the method, under the optimized conditions,  
 198 oxidation of different olefins was subjected in the presence of the catalytic amount of CuL  
 199 and CuL-Y, the results are given in Table 2 and 3.

200 Comparison of the catalytic behavior of the copper Schiff base complex encapsulated in the  
 201 super cages of zeolite-Y and free CuL showed the higher catalytic activity and selectivity of  
 202 the heterogeneous catalyst with respect to the homogenous one.

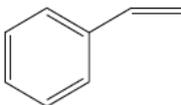
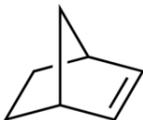
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207 TABLE II. Oxidation of olefins using TBHP catalyzed by CuL.

Alkene	Conversion, %	Selectivity, %		
		Main product	Others	
	89	<sup>a</sup> 53	<sup>b</sup> 38	9
	63	<sup>c</sup> 60	<sup>d</sup> 40	0
	46	<sup>e</sup> 60	<sup>f</sup> 25	9
	13	<sup>g</sup> 100	0	0

208 Reaction conditions: catalyst (0.040 mmol), substrate (10 mmol), TBHP (25 mmol),

209 acetonitrile (5 ml); the reactions were run for 8 h under reflux. .

210 <sup>a</sup> cyclooctene oxide211 <sup>b</sup> cyclooctenone212 <sup>c</sup> cyclohexene oxide213 <sup>d</sup> 2-cyclohexen-1-ol214 <sup>e</sup> benzaldehyde215 <sup>f</sup> benzoic acid216 <sup>g</sup> norbornene epoxide

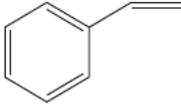
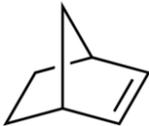
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221 TABLE III. Oxidation of olefins using TBHP catalyzed by CuL-Y

Alkene	Conversion, %	Selectivity, %	
		Main product	Others
	50	<sup>a</sup> 68	<sup>b</sup> 32
	96	<sup>c</sup> 80	<sup>d</sup> 20
	95	<sup>e</sup> 80	<sup>f</sup> 20
	92	<sup>g</sup> 100	0

222 Reaction conditions: catalyst (20 mg), substrate (10 mmol), TBHP (25 mmol), acetonitrile (5 ml); the

223 reactions were run for 8 h under reflux.

224 <sup>a</sup> cyclooctene oxide225 <sup>b</sup> cyclooctenone226 <sup>c</sup> cyclohexene oxide227 <sup>d</sup> 2-cyclohexen-1-ol228 <sup>e</sup> benzaldehyde229 <sup>f</sup> benzoic acid230 <sup>g</sup> norbornene epoxide

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233

## 234 CONCLUSIONS

235 In summary, azo Schiff base ligand (H<sub>2</sub>L) derivative of ( $\pm$ )*trans*-1,2-cyclohexanediamine  
236 and 4-(benzeneazo) salicylaldehyde was prepared. The copper Schiff base complex (CuL)  
237 encapsulated in the nanopores of zeolite-Y (CuL-Y). Also, these heterogeneous and  
238 homogeneous catalysts have been used for oxidation of different alkenes with *tert*-butyl  
239 hydroperoxide. Various reaction parameters were investigated and optimized in the  
240 oxidation reaction. The oxidation of cyclooctene, cyclohexene, styrene and norbornene  
241 catalyzed by CuL gave 89, 63, 46 and 13% conversion, respectively. Under the  
242 heterogeneous condition, the oxidation of these olefins with 50, 96, 96 and 92% conversion  
243 was obtained, respectively. It has been observed that CuL-Y has higher catalytic activity and  
244 selectivity than CuL. This change was specially seen for norbornene.

## 245 Acknowledgement

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## 247 REFERENCES

- 248 1. R. G. Sheldon, B. J. Kochi, *Metal-Catalyzed Oxidations of Organic Compounds*,  
249 Academic Press, New York, 1981, p. 1
- 250 2. X. Cai, H. Wang, Q. Zhang, J. Tong, Z. Lei, *J. Mol. Catal. A: Chem.* **383–384** (2014) 217
- 251 3. M. Lashanizadegan, Z. Zareian, *Catal. Lett.* **141** (2011) 1698
- 252 4. H. Schiff, *Ann. Suppl.* **3** (1864) 343
- 253 5. S. C. Catino, E. Farris, *Concise Encyclopedia of Chemical Technology*, John Wiley, New  
254 York, 1985, p. 142
- 255 6. K. Venkataraman, *The Chemistry of Synthetic Dyes*, Academic press, New York and  
256 London, 1974, p. 46
- 257 7. K. Hunger, *Industrial Dyes: Chemistry, Properties, Applications*, Wiley–vch vertag,  
258 Germany, 2003, p. 375
- 259
- 260 8. Y. S. Zhou, L. J. Zhung, X. R. Zeng, J. J. Vital, X. Z. You, *J. Mol. Struct.* **553** (2000) 25
- 261 9. R. Walker, *Food Cosmet. Toxicol.* **8** (1970) 659

- 262 10. S. Patai, *The Chemistry of the Hydrazo, Azo and Azoxy Groups*, John Wiley, London,  
263 1997, p. 234
- 264 11. P. Pathak, V. S. Jolly, K. P. Sharma, *Orient. J. Chem.* **15** (2000) 161
- 265 12. H. Xu, X. Zeng, *Bioorg. Med. Chem. Lett.* **20** (2010) 4193
- 266 13. E. Ispir, *Dyes. Pigments.* **82** (2009) 13
- 267 14. Y. Chang, Y. Lv, F. Lu, F. Zha, Z. Lei, *J. Mol. Catal. A:* **320** (2010) 56
- 268 15. Y. Chang, X. L. Shi, D. M. Zhu, Y. Liu, *Polym. Adv. Technol.* **19** (2008) 877
- 269 16. S. Sharma, S. Sinha, *Chand, Ind. Eng. Chem. Res.* **51** (2012) 8806
- 270 17. Z. Li, R. Tang, G. Liu, *Catal. Lett.* **143** (2013) 592
- 271 18. J. Adhikary, A. Guha, T. Chattopadhyay, D. Das, *Inorg. Chim. Acta* **406** (2013) 1
- 272 19. S. Jana, B. Dutta, R. Bera, S. Koner, *Langmuir* **23** (2007) 2492
- 273 20. X. Wang, G. Wu, W. Wei, Y. Sun, *Catal. Lett.* **136** (2010) 96
- 274 21. Y. Yang, S. Hao, P. Qiu, F. Shang, W. Ding, Q. Kan, *Reac. Kinet. Mech. Cat.* **100** (2010)  
275 363
- 276 22. M. Ghorbanloo, S. Rahmani, H. Yahiro, *Transition Met. Chem.* **38** (2013) 725
- 277 23. G. Willingh, H. S. Abbo, S. J. J. Titinchi, *Catal. Today* **227** (2014) 96
- 278 24. H. S. Abbo, S. J. J. Titinchi, *Appl. Catal. A: Gen.* **356** (2009) 167
- 279 27. S. M. Islam, A. S. Roy, P. Mondal, M. Mubarak, S. Mondal, D. Hossain, S. Banerjee, S.  
280 C. Santra, *J. Mol. Catal. A: Chem.* **336** (2011) 106
- 281 26. F. Heshmatpour, S. Rayati, M. Afghan-Hajiabbas, P. Abdolalian, B. Neumüller,  
282 *Polyhedron* **31** (2012) 443
- 283 25. H. Hosseini-Monfared, E. Pousaneh, S. Sadighian, S. W. Ng, E. R. T. Tiekink, Z. Anorg,  
284 *Allg. Chem.* **639** (2013) 435
- 285 28. A. Bezaatpour, M. Behzad, V. Jahed, M. Amiri, Y. Mansoori, Z. Rajabalizadeh, S. Sarvi,  
286 *Reac. Kinet. Mech. Cat.* **107** (2012) 367
- 287 29. A. Vogel, *A Text-Book of Practical Organic Chemistry*, Longman, New York, 1956, p.  
288 620
- 289 30. S. Koner, *Inorg. Chem. Commun.* (1998) 593
- 290 31. M. Aslantas, E. Kendi, N. Demir, A. E. S. Abik, M. Tumer, M. Kertmen, *Spectrochim.*  
291 *Acta, Part A* **74** (2009) 617

- 292 32. M. Lashanizadegan, M. Sarkheil, *Main Group Chem.* **12** (2013) 15
- 293 33. R. M. Barrer, *Hydrothermal Chemistry of Zeolite*, Academic Press, New York, 1982
- 294 34. M. Lashanizadegan, M. Sarkheil, *J. Serb. Chem. Soc.* **77** (2012) 1589
- 295 35. C. M. Liu, R. G. Xiong, X.Z. You, *Polyhedron* **16** (1997) 119
- 296 36. R. Neumann, C. Abu-Gnim, *J. Am. Chem. Soc.* **112** (1990) 6025
- 297
- 298