Catal Lett (2009) 128:323–330
DOI 10.1007/s10562-008-9735-7

The Influence of Thermal Treatment and Noble Metal Addition on Hopcalite Activity in Oxidation of Thiophene

M. I. Szynkowska · A. Węglińska · E. Wojciechowska · T. Paryjczak

Received: 4 August 2008 / Accepted: 15 October 2008 / Published online: 14 November 2008

Abstract In this paper the comparison of activity of hopcalite (Mn–Cu mixed oxides) modified with noble metals (Pd, Pt and Au) calcined at 300, 400 and 500 °C in oxidation of thiophene was presented. Hopcalite modified with Pd demonstrated the highest activity among the studied samples, thus the results of a more detailed study of the most promising palladium catalyst were also shown. Surface and bulk properties of catalyst were studied with BET, XRD, TPR_{H2} and TG-DTA-MS. The redox properties and distribution of active components on the catalyst surface seem to be important factors influencing the modified hopcalite performance in the oxidation reactions. It was found that irreversible changes occurred during thermal treatment in the Pd-modified hopcalite structure, however they have no marked influence on activity of modified catalysts.

Keywords Catalytic oxidation · Hopcalite · Thiophene

1 Introduction

Agricultural odors present an increasingly difficult and pressing problem. Odor complaints have risen dramatically during the last decade with the increase in the number of concentrated animal feeding operations. Microbiological degradation of biosolids including animal manure and feed leads to the production of many malodours compounds such as hydrogen sulfide, organic sulfur compounds, carboxylic acid, amonnia, cresol or indoles [1]. Volatile sulphur compounds are considered a major constituent of odour gases [2]. Their emission has received a particular attention because they can not only affect human sensory irritation but also have potential health effects. Therefore, a proper control of their emission is a crucial task for the protection of environment. Recently a lot of research has focused on the development of strategies to eliminate emissions of odours. The most commonly used include combustion, catalytic combustion, absorption, adsorption or condensation [1, 3]. The catalytic combustion attracts more attention because it is not energy intensive.

Noble metal catalysts, such as Pt and Pd dispersed on alumina supports are typically used for volatile organic compounds (VOCs) elimination and many catalytic processes have been commercialised and have successfully operated by using the noble metals [4–8].

In general, metal catalysts show higher activity than the oxide catalysts contributing to the reduction of operating costs despite their higher manufacturing cost, however, it was demonstrated that metal oxides can sometimes exhibit higher activity than noble metals catalysts [9, 10].

Among the base metals, copper and manganese catalysts were extensively studied due to their promising activity in oxidation reactions [11–17]. In recent research copper and manganese systems were found to be the most active in oxidation of organic compounds among the base catalysts. According to Wang et al. [18] activity of catalysts in oxidation of toluene decreased in the order Cu > Fe > Mn > Cr > Co > Mo > Ni. Similar results were presented by Kim [19] who reported that copper and manganese catalysts were the most effective in oxidation of aromatic hydrocarbons. The catalyst activity with respect to metal followed the sequence: Cu > Mn > Fe > V > Mo > Co > Ni > Zn. Moreover, copper and manganese based

M. I. Szynkowska (✉) · A. Węglińska · E. Wojciechowska · T. Paryjczak
Institute of General and Ecological Chemistry, Technical University of Lodz, Żeromskiego 116, 90-924 Lodz, Poland
e-mail: miszynk@p.lodz.pl

catalysts showed a promising activity in oxidation of odour compounds such as dimethyl disulphide, methanethiol or ammonia [20–25].

Morales et al. [26, 27] have reported that total oxidation of VOCs over Mn–Cu mixed oxide was more efficient in comparison with Mn and Cu pure oxides. Mixed copper manganese oxide catalyst—$CuMn_2O_4$ (hopcalite), first examined in the 1920s, has been widely studied in oxidation reactions because of its high activity at low temperatures [28, 29]. The results showed that the formation of the spinel $Cu_xMn_{3-x}O_4$ in the oxidized catalyst is responsible for its high activity [30–32].

Moreover, studies concerning an application of the mixtures of noble metals and copper or manganese oxides indicate that they can display higher activity in oxidation processes than monometallic catalysts [33–36]. Furthermore, they can be also more resistant in the presence of sulphur compounds such as SO_x, which are produced in oxidative atmosphere from VOCs containing sulphur, and have a very strong deactivation effect on the catalysts [34].

Our previous studies showed that commercial hopcalite calcined at different temperatures (300, 400, 500 °C) displayed a higher activity in oxidation of thiophene in comparison with commercial untreated hopcalite [37]. Catalyst calcined at 300 °C characterized by amorphous structure, the highest surface area and the best reducibility indicated the most promising performance among studied samples, however, a decrease of its activity above amorphous to crystalline phase transition was observed under reaction conditions applied. Moreover, the beneficial effect of an addition of Pd, Pt and Au was also observed, nevertheless noble metals doped hopcalite catalyst calcined at 400 and 500 °C exhibited similar catalytic behaviour independently of calcination temperature [37–39]. It was also shown that commercial hopcalite modified with Pd demonstrated the highest activity among studied samples [39]. A higher activity of hopcalite containing Pd can be accompanied by better reducibility of the catalysts comparing to hopcalite modified with Pt or Au [37]. On the other hand, nonhomogenous distribution of Au atoms observed on the catalyst surface could have an influence on the lowest oxidation activity of Au modified systems.

The present work was undertaken with the aim of expanding our previous studies concerning application of commercial hopcalite modified with noble metals (Pt, Pd, and Au) [37–39] in oxidation of sulphur compounds. The results of a more detailed study of the most promising catalyst (modified with palladium) used in oxidation of thiophene are also shown. An influence of Pd addition to hopcalite on its sulphur resistance will be the subject of our future work.

2 Experimental

Commercial hopcalite (70% MnO_2 and 30% CuO) supplied by Chemical Company Inowrocław Soda (Poland) was tested in oxidation of thiophene without thermal treatment or after calcination at 500 °C (denoted as *CuMn*, *CuMn500*). The noble metals modified catalysts were prepared by the wet impregnation method of commercial hopcalite with aqueous solutions of H_2PtCl_6 (Mennica, Poland), $PdCl_2$ (POCh Gliwice) and $HAuCl_4 \cdot 4H_2O$ (POCh Gliwice). Metals loadings in the obtained catalysts were 1 wt.% or 0.5 and 0.2% in the case of palladium catalyst and 1% in the case of catalysts modified with Au or Pt. After impregnation the samples were dried at 130 °C for 0.5 h and then calcined in static air at 300, 400 or 500 °C for 4 h (denoted as *CuMn500-Pdx*, 500—temperature of calcination, Pd—noble metals used, x = 0.2, 0.5, 1 wt.%).

BET surface area measurments of catalyst sample were determined by Sorptomatic 1900 Carlo-Erba using the low temperature nitrogen adsorption-desorption method.

X-ray diffraction patterns were recorded by a Simens D 5000 diffractometer using the Cu Kα radiation. Data were collected in the range of 10–80° 2θ with the scanning step 0.02°.

Thermogravimetic analysis (TG), differential thermal analysis (DTA) and mass spectrometry analysis (MS) were carried out using SETSYS—16/18 (Setaram) instrument. Temperature programmed decomposition of the samples (about 10 mg) was carried out in the platinum crucible in He atmosphere with a linear heating rate 10 °C/min in the temperature range 20–1000 °C.

Temperature programmed reduction (TPR) measurements were carried out using an Altamira AMI-1 instrument equipped with a TDC detector. The mixture of $5\%H_2/95\%Ar$ with a flow rate 50 cm^3/min was used. The process was carried out up to 900 °C with a linear increase in temperature 10 °C/min. After reaching the maximum temperature, the reduction was continued isothermally for 30 min.

Subsequent reoxidation-reduction cycles were performed by using the mixtures of $5\%H_2/95\%Ar$ and $5\%O_2/95\%Ar$. The process was carried out up to 400 °C with a linear increase in temperature 10 °C/min. After reaching the maximum temperature, the reduction was continued isothermally for 30 min. After reduction the sample was cooled down to ambient temperature and then reoxidation in $5\%O_2/95\%Ar$ was carried out up to temperature corresponding with temperature of calcination of the sample. Two subsequent reoxidation-reduction cycles were performed.

Catalytic activity measurements were carried out in a quartz flow reactor using 200 mg of catalyst. The reactant mixtures 1.5% C_4H_4S and 20% O_2 in He were passed through the reactor with the flow rate of 40 cm^3/min. The analyses of the reactor effluent were performed with on-line gas chromatograph equipped with TDC detector and HayeSep Q column. The thiophene conversion and selectivity to CO_2 were calculated as follows:

$$\% \ C_4H_4S \text{ conversion} = \frac{(C_4H_4S)_{in} - (C_4H_4S)_{out}}{(C_4H_4S)_{in}} \times 100\%$$

$$\text{Selectivity to } CO_2 = \frac{P_{CO_2}}{4 \times P_{tot}} \times 100\%$$

where:

$(C_4H_4S)_{in}$—inlet C_4H_4S concentration,
$(C_4H_4S)_{out}$—outlet C_4H_4S concentration,
4—stoichiometric factor,
P_{co_2}—number of C_4H_4S moles transformed to CO_2,
P_{tot}—number of C_4H_4S moles transformed during reaction.

Table 1 Comparison of activity of hopcalite modified with noble metals (Pd, Pt, Au) calcined at 300, 400 and 500 °C

Temperature of reaction (°C)	Conversion of thiophene at various temperatures (%)		
	CuMn300–Pd1	CuMn300–Pt1	CuMn300–Au1
310	41	11	25
340	100	96	39
370	100	100	70
400	100	100	93
	CuMn400–Pd1	CuMn400–Pt1	CuMn400–Au1
310	87	20	15
340	96	100	26
370	94	100	63
400	96	100	91
	CuMn500–Pd1	CuMn500–Pt1	CuMn500–Au1
310	93	7	8
340	95	100	24
370	94	100	51
400	93	100	69

3 Results and Discussion

Activity data of hopcalite modified with Pd, Pt and Au treated with different temperatures (300, 400, 500 °C) are summarised in Table 1. According to the presented results the best promoting effect in oxidation of thiophene is obtained with Pd as additive, because of higher conversion of thiophene at 310 °C for hopcalite modified with Pd in comparison with hopcalite containing Pt or Au. Selectivity to total oxidation product CO_2 increases with reaction temperature over all studied catalysts (results not shown) and high conversion results in high selectivity to CO_2.

The essential differences in catalytic activity of modified catalyst treated with different temperatures (300, 400, 500 °C) are found for samples containing Au. For *CuMn–Au1* calcined at 300 and 400 °C approximately 90% conversion is achieved at 400 °C, contrary to that only 70% of thiophene is removed over *CuMn500–Au1* in the same conditions. To find an explanation of these differences in activity both surface and bulk properties of catalysts were studied with ToF-SIMS and TPR_{H2}.

The exemplary results of TPR experiments of *CuMn300* and *CuMn300* modified with noble metals (*CuMn300–Pd1*, *CuMn300–Pt* and *CuMn300–Au1*) are given in Fig. 1.

TPR profile of *CuMn300* consists of two well-defined reduction peaks located at 213 and 272 °C and additionally, a small-unresolved peak in the low temperature region is observed. It was early suggested that Cu^+ and Cu^{2+} ions present in hopcalite spinel lattice are reduced at low temperatures (150–350 °C) while Mn^{4+} and Mn^{3+} ions are reduced at higher temperature region (300–550 °C) [27, 40]. Therefore, in the case of *CuMn300* two main maxima can be attributed to the reduction of Mn^{4+} and Mn^{3+}, whereas the first broad shoulder to the reduction of Cu^+ and Cu^{2+} present in the spinel lattice. The TPR profiles of Pd and Au modified catalysts exhibit two reduction effects whereas *CuMn300–Pt1* only one hydrogen consumption region thus there is a possibility of overlapping the reduction peaks due to Cu and Mn species.

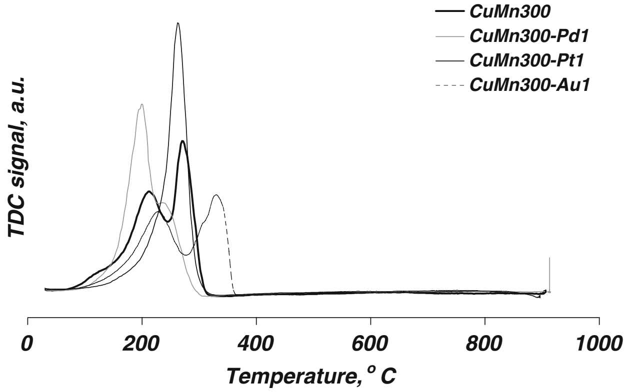


Fig. 1 Temperature-programmed reduction profiles of hopcalite modified with noble metals calcined at 300 °C

Furthermore the reduction peaks of *CuMn300–Pd1* and *CuMn300–Pt1* are shifted towards lower temperatures in comparison with *CuMn300*, indicating the influence of Pd and Pt addition on reducibility of base catalyst. Moreover

Pd has a greater influence on the reduction of hopcalite than Pt. These observations are in line with previous activity results [34]. For hopcalite modified with gold a shift of the reduction peaks towards higher temperatures in relation to *CuMn300* was obtained that is in accordance with results reported by Solsona et al. [41] concerning manganese catalysts modified with Au. Considering above modification of redox behaviour of the samples doped with noble metals it seems to be one of the factors influencing the catalyst performance.

In order to determine the influence of surface distribution of atoms and molecues on catalyst activity SEM-EDS studies were carried out. Figure 2 shows that Pd atoms are evenly distributed in micrometer range on the catalyst surface regardless of the reaction temperature. In the case of Au areas of its enhanced surface concentration can be observed after calcination at 400 and 500 °C (Fig. 3). These results indicate that the highest activity of hopcalite calcined at 300 °C is accompanied by homogenous distribution of Au atoms on the catalyst surface. SEM-EDS results for catalysts containing Pt (not shown) are similar as obtained for samples doped with Pd.

On the bases of these results hopcalite modified palladium catalysts was selected for detailed investigations as the most promising system in oxidation of thiophene.

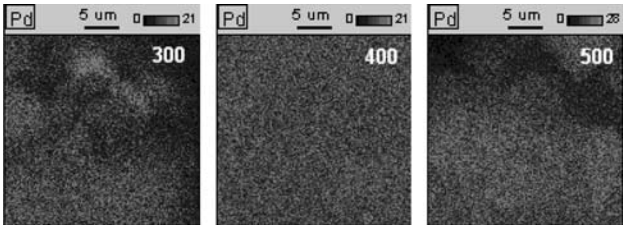


Fig. 2 EDS map of Pd distribution on the surface of *CuMn–Pd1* calcined at 300, 400 and 500 °C

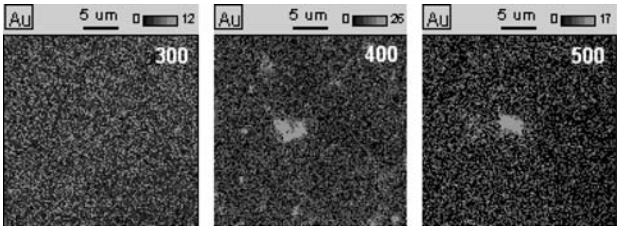


Fig. 3 EDS map of Pd distribution on the surface of *CuMn–Au1* calcined at 300, 400 and 500 °C

Table 2 Chemical composition and textural characteristics of hopcalite modified with Pd calcined at 300, 400, 500 °C

Catalyst	$S_{BET}/m^2/g$	Crystalline phase
CuMn300–Pd1	86	Amorphous
CuMn400–Pd1	45	$CuMn_2O_4$
CuMn500–Pd1	28	$CuMn_2O_4$, PdO, PdO_2
CuMn500–Pd0.5	22	$CuMn_2O_4$, PdO
CuMn500–Pd0.2	20	$CuMn_2O_4$

The main characteristics of hopcalite modified with Pd are reported in Table 2. Catalysts calcined at 300 °C (*CuMn300–Pd1*) are characterised by an amorphous form. Contrary to that, catalysts calcined at 400 and 500 °C are found to be crystalline $CuMn_2O_4$ spinel. This observation is in agreement with the former studies [28]. It has been shown that the crystallised form of hopcalite can be observed in samples aged at 350 °C and crystallisation is completed at 500 °C. Additionally, the XRD analysis of the hopcalite modified with 0.5 and 1% Pd indicates the presence of crystalline palladium oxides. For the catalyst with the lowest palladium content (0.2%) the diffraction lines of palladium oxides are not detected. This observation indicates that the palladium oxide structures are highly dispersed or remain in an amorphous state. Crystallization of amorphous catalyst is known to induce extensive sintering, thus BET measurements confirm a logical decrease in the surface area with the increase in the calcination temperature. Surprisingly, values of BET areas of the catalysts increase slightly with the increasing noble metal content (Table 2).

Figures 4 and 5 display the conversion of thiophene and selectivity to CO_2 as a function of the reaction temperature for commercial hopcalite, hopcalite calcined at 500 °C and hopcalite calcined at 500 °C modified with different amount of Pd (0.2, 0.5, 1%).

It is evident that commercial hopcalite shows very low oxidative performance in oxidation of thiophene. It can be seen from light-off curve of *CuMn* that conversion grows to 30% at 340 °C and decrease upon further increase of temperature in accordance with reported thermal deactivation of hopcalite [28]. *CuMn500* presents higher activity than commercial sample because the hopcalite catalyst is usually activated at temperatures above which the loss of water occurs. In the case of hopcalite modified with noble metals significant increase of activity for oxidation of thiophene can be seen (Fig. 4). The higher metal loading results in increase of conversion of thiophene. It is clearly observed than even small addition of Pd causes significant improvement in the catalytic performance of the base system. Accordingly, the highest activity of hopcalite modified with Pd can be accompanied by the presence of PdO and PdO_2 crystallites on the catalyst surface.

Although hopcalite has proved to be an excellent system in total oxidation of CO [30–32] as well as in combustion of VOCs [27] it has been shown that hopcalite is thermally deactivated. Therefore, TG-DTA-MS analysis was applied

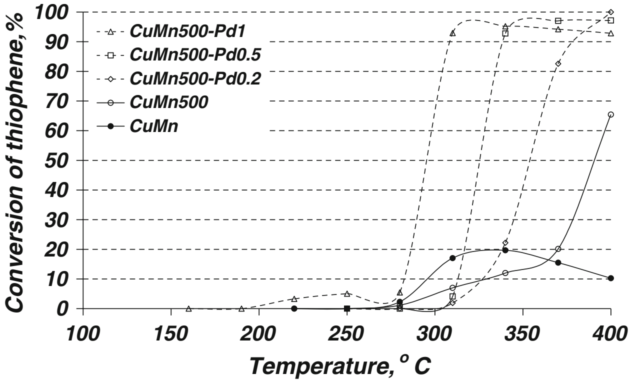


Fig. 4 Thiophene conversion as a function of temperature over *CuMn*, *CuMn500*, *CuMn500–Pdx*

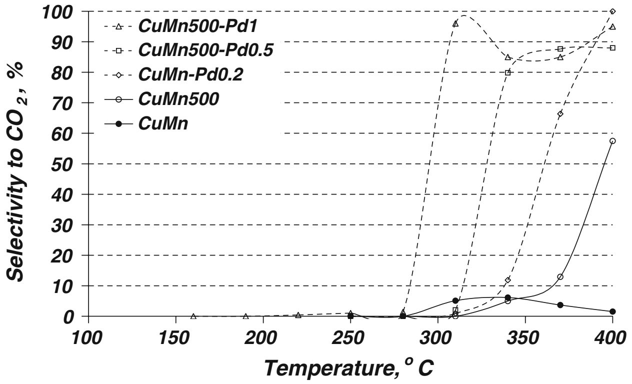
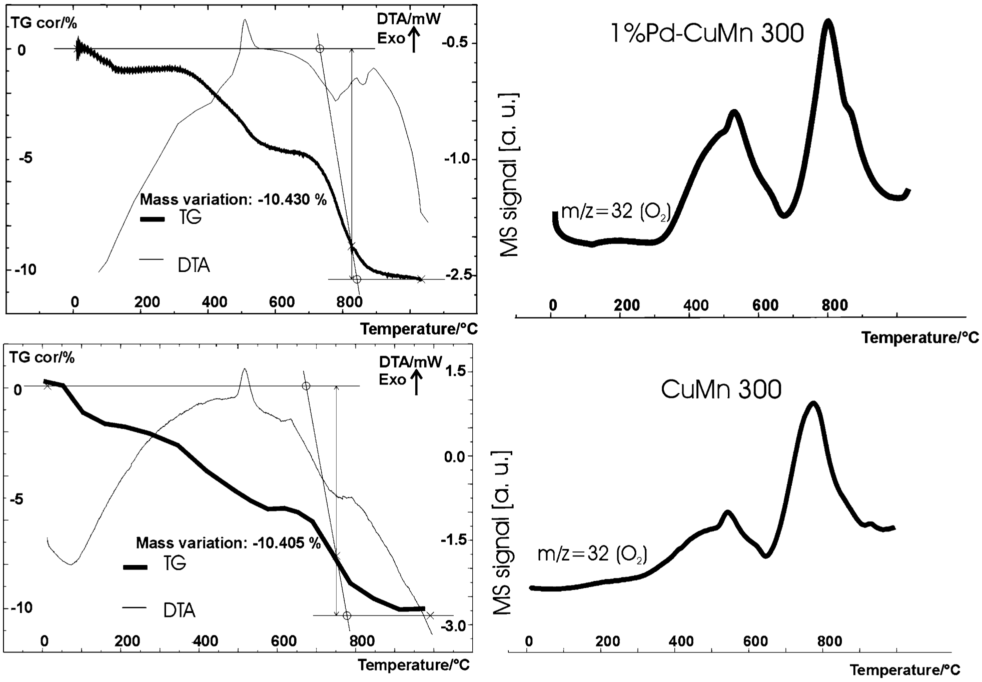


Fig. 5 Selectivity to CO_2 as a function of temperature over *CuMn*, *CuMn500*, *CuMn500–Pdx*

to examine the influence of Pd addition on thermal stability of modified samples. Exemplary, TG-DTA characterization of thermal decomposition of hopcalite calcined at 300 °C and hopcalite modified with Pd is presented in Fig. 6. Both DTG curves of *CuMn300* and *CuMn300–Pd1* show three decomposition steps. They are attributed to the removal of physically adsorbed water and oxygen as it is evidenced by the endothermic peaks on the DTA curve and MS signal profile. The removal of water is observed below 200 °C, on the other hand the release of oxygen from catalyst occurs in two steps in the temperature ranges 350–700 and 700–1000 °C. It is a general rule that oxidative performance of the catalyst appears to be dependent on the amount of available oxygen and the metal–oxygen bond strength [17, 36]. According to the previous results oxygen adsorbed on the catalyst surface (α-oxygen) and oxygen released from catalyst bulk (*β*-oxygen) can participate in the oxidation process. The surface oxygen is released at temperatures below 400 °C and participates in the superficial reaction mechanism. Contrary to that oxygen coming from the catalyst bulk is observed at temperatures above 400 °C and is relevant when oxygen mobility in the catalyst lattice is necessary to complete a Mars-van Krevelen redox cycle. Morales et al. [27] have concluded that the better performance of Mn–Cu mixed oxides in total oxidation of ethanol results from the presence of α-oxygen adsorbed on anion vacancies on the $CuMn_x$ surface and released in the low temperature region. Our results indicate that mobility of bulk oxygen can also have an influence on catalytic performance of hopcalite.

Fig. 6 TG-DTA-MS analysis of hopcalite calcined at 300 °C and hopcalite modified with Pd calcined at 300 °C



In DTA curves of *CuMn300* and *CuMn300–Pd1* the exothermic effect at 500 °C corresponding to the crystallization of the $CuMn_2O_4$ spinel phase is observed. These results show that the modification of the base hopcalite with Pd does not prevent amorphous spinel from reaching a crystalline structure.

The results of thermal analysis of other studied samples (not shown), compiled in Table 1, are essentially similar to these presented in this work. Desorption of water and two-step releasing of oxygen from catalyst bulk is observed. For samples modified with Pd and calcined at 500 °C the exotermic effect because of $CuMn_2O_4$ phase transition is not seen indicating complete spinel crystallization after calcinations at 500 °C. It is in line with XRD results (Table 2).

With the objective of studying the effect of modification on the catalyst reducibility and stability, subsequent reduction-reoxidation TPR/TPO cycles were additionally applied. The results of the analysis of selected *CuMn300*, *CuMn500* and *CuMn300–Pd1* samples are presented in Figs. 7, 8, and 9. The samples reduced after the first and the second processes of reoxidation are denoted as *CuMn I* and *CuMn II*, respectively. As it was mentioned earlier, the reduction of *CuMn300* starts at about 70 °C giving three hydrogen consumption regions. Reduction of catalyst calcined at 500 °C appears above 230 °C and the maximum of the hydrogen consumption is observed at 350 °C (Fig. 8). Lower reducibility of *CuMn500* in relation to *CuMn300* can result from higher crystallinity of the former as was evidenced in the previous works [37]. TPR profiles of hopcalite modified with Pd calcined at 500 °C (Fig. 9) are completely different with respect to non-modified sample calcined at the same temperature. The spectra exhibit two main peaks indicating two reduction steps. One assigned at 147 °C and the other located at 243 °C. At about 320 °C the reduction process of catalyst containing Pd is nearly complete, showing a great influence of Pd addition on the catalyst reducibility.

Reoxidation steps significantly change the reduction profiles of all presented samples. In the case of *CuMn300* after the first and second reoxidation procedure the smaller amount of hydrogen is consumed (Fig. 7; Table 3). Moreover, the reduction starts at a higher temperature in comparison with *CuMn300* indicating lower reducibility of reoxidized sample. However, the reduction profiles of *CuMn300 I* and *CuMn300 II* are essentially similar.

Subsequent temperature-programmed reduction and reoxidation processes of *CuMn500* do not lead to an increase in the reduction temperature and the significant changes of the consumption of hydrogen (Fig. 8; Table 3).

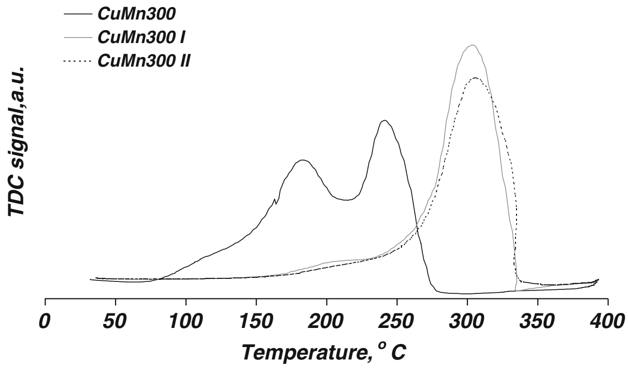


Fig. 7 TPR_{H2} profile of base hopcalite calcined at 300 °C and after the first (*CuMn300 I*) and the second reoxidation (*CuMn300 II*)

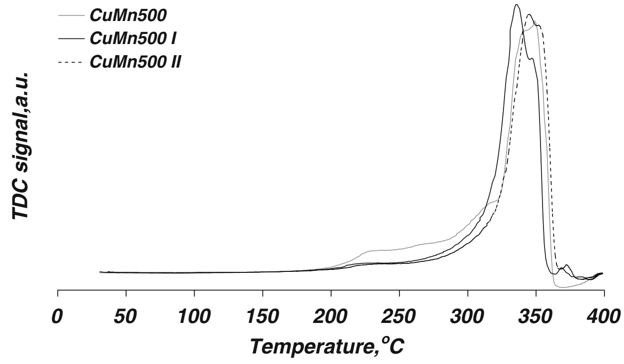


Fig. 8 TPR_{H2} profile of base hopcalite calcined at 500 °C and after the first (*CuMn500 I*) and the second reoxidation (*CuMn 500 II*)

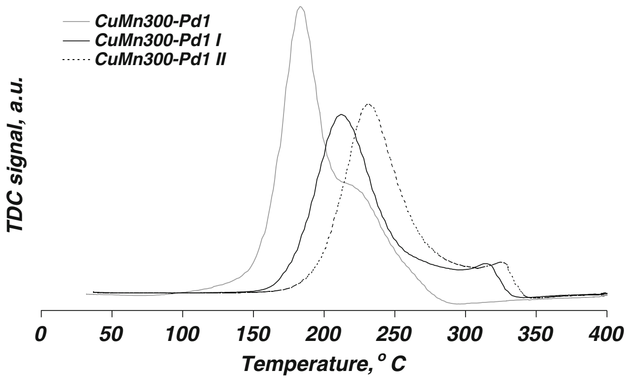


Fig. 9 TPR_{H2} profile of hopcalite modified with Pd calcined at 500 °C and after the first (*CuMn500–Pd1 I*) and the second reoxidation (*CuMn500–Pd1 II*)

Table 3 H_2 uptake (μmol H_2/g) of hopcalite calcined at 300 and 500 °C and hopcalite modified with Pd calcined at 300 °C

Catalyst	H_2 uptake (μmol H_2/g)		
		Reoxidation I	Reoxidation II
CuMn300	10,492	9,279	8,495
CuMn500	8,464	9,039	8,632
CuMn300–Pd1	11,918	8,802	8,592

Considering above results it can be state that the higher reduction temperatures of *CuMn300* after regeneration must be due to a higher crystallinity of the sample.

Furthermore, in order to determine the influence of Pd addition on stability on base hopcalite the multiple reduction-reoxidation cycles of *CuMn300–Pd1* were also performed. The results of the investigations are shown in Fig. 9. After the introduction of Pd into hopcalite matrix stabilization of the catalyst is not achieved. Both shift of reduction signals towards higher temperatures and lower hydrogen consumption of reoxidized *CuMn300–Pd1 I* and *CuMn300–Pd1 II* is observed relative to *CuMn300–Pd1* (Fig. 9; Table 3). Considering the observations it can be found that the decrease in reducibility of base catalyst and sample modified with Pd shows irreversible changes in the spinel lattice occurring during thermal treatment. These observations are also supported by XRD data.

Our previous results indicate that temperature of calcination significantly influences unmodified hopcalite performance and that the decrease of its activity can be observed because of amorphous to crystalline phase transition. In this work it was evidenced that in spite the fact that Pd does not prevent amorphous spinel from reaching a crystalline structure, the decrease in catalyst activity of modified system was not observed. It suggests that different active centers can be responsible for catalytic activity of base and modified system. In the case of hopcalite modified with Pd, noble metal atoms are responsible for the presence of additional metallic active centers.

4 Conclusions

The catalytic performance of hopcalite catalyst in oxidation of thiophene was studied in this work. Some specific conclusions derived from this study are summarized as follows:

(I). Hopcalite modified with Pd displays the most promising activity in oxidation of thiophene. Its higher activity is accompanied by better reducibility in comparison with catalysts modified with Pt and Au.

(II). The redox properties and distribution of active components on the catalyst surface seems to be very important factors influencing the modified hopcalite performance in oxidation reactions.

(III). Temperature of calcination has the most significant influence on activity in the case of Au modified samples. Lower temperature of calcination results in homogenous distribution of Au and higher activity of catalyst.

(IV). Finally, modification of base hopcalite with Pd does not prevent transformation of amorphous spinel into a crystalline structure, however this phenomenon has not marked an influence on activity of Pd containing catalyst.

Acknowledgment The financial support of this work by the Polish Scientific Research Council (grant G 006/T02/2007) is gratefully acknowledged.

References

1. Kośmider J, Mazur-Chrzanowska B, Wyszyński B (2002) Odory. PWN, Warsaw
2. Schiffman SS, Bennett JL, Raymer JHJH (2001) Agric For Metorol 108:213
3. Mills B (1995) Filltr Separat 2:147
4. Peng J, Wang S (2007) Appl Catal B Environ 73:282
5. Avgouropoulos G, Oikonomopoulos E, Kanistras D, Ioannides T (2006) Appl Catal B Environ 65:62
6. Garetto TF, Rincón E, Apesteguía CR (2004) Appl Catal B Environ 48:167
7. Garetto TF, Apesteguía CR (2000) Catal Today 62:189
8. Okumura K, Kobayashi T, Tanaka H, Niwa M (2003) Appl Catal B Environ 44:325
9. Watanabe N, Yamashita H, Miyadera H, Tominaga S (1996) Appl Catal B Environ 8:405
10. Lahousse C, Bernier A, Grange P, Delmon B, Papaefthimiou P, Ioannides T, Verykios X (1998) J Catal 178:214
11. Kim SC, Shim WG (2008) Appl Catal B Environ 79:149
12. Águila G, Garcia F, Cortesés J, Araya P (2008) Appl Catal B Environ 77:325
13. Ali N, Lu C, Masel R (2000) Catal Today 62:347
14. Cellier C, Lambert S, Gaigneaux EM, Poleunis C, Ruaux V, Eloy P, Lahousse C, Bertrand P, Pirard J-P, Grange P (2007) Appl Catal B Environ 70:406
15. Álvarez-Galván MC, de la Peña O'Shea VA, Fierro JLG, Arias PL (2003) Catal Commun 4:223
16. Álvarez-Galván MC, Pawelec B, de la Peña O'Shea VA, Fierro JLG, Arias PL (2004) Appl Catal B Environ 51:83
17. de la Peña O'Shea VA, Álvarez-Galván MC, Fierro JLG, Arias PL (2005) Appl Catal B Environ 57:191
18. Wang C-H, Lin S-S, Chen C-L, Weng H-S (2006) Chemosphere 64:503
19. Kim S-C (2002) J Hazard Mater B91:285
20. Wang C-H, Weng H-S (1997) Ind Eng Chem Res 36:2537
21. Wang C-H, Lee C-N, Weng H-S (1998) Ind Eng Chem Res 37:1774
22. Wang C-H, Weng H-S (1998) Appl Catal A Gen 170:73
23. Wang C-H, Lin S-S, Liou S-B, Weng H-S (2002) Chemosphere 49:389
24. Cellier CM, Vromman V, Ruaux V, Gaigneaux EM, Grange P (2004) J Phys Chem B 108:9989
25. Kušar HMJ, Ersson AG, Vosecký M, Järås SG (2005) Appl Catal B Environ 58:25
26. Morales MR, Barbero BP, Cadús LE (2008) Fuel 87:1177
27. Morales MR, Barbero BP, Cadús LE (2006) Appl Catal B Environ 67:229
28. Vepřek S, Cocke DL, Kehl S, Oswald HR (1986) J Catal 100:250
29. Kanungo SB (1979) J Catal 58:419
30. Krämer M, Schmid T, Stöwe K, Maier WF (2006) Appl Catal A Gen 302:257
31. Larsson P-O, Andersson A (2000) Appl Catal B Environ 24:175
32. Solsona B, Hutchings GJ, Garcia T, Taylor SH (2004) New J Chem 28:708

33. Ayastuy JL, González-Marcos MP, González-Velasco JR, Gutiérrez-Ortiz MA (2007) Appl Catal B Environ 70:532
34. Ferrandon M, Carnö J, Järås S, Björnbom E (1999) Appl Catal A 180:153
35. Carnö J, Ferrandon M, Björnbom E, Järås S (1997) Appl Catal A 155:265
36. de la Peña O'Shea VA, Álvarez-Galván MC, Requies J, Barrio VL, Arias PL, Cambra JF, Gümez MB, Fierro JLG (2007) Catal Com 8:1287
37. Szynkowska MI, Węglińska A, Wojciechowska E, Paryjczak T (in review) Chem Lett
38. Rogowski J, Szynkowska MI, Węglińska A, Wojciechowska E, Paryjczak T (in press) Pol J Chem
39. Szynkowska MI, Wojciechowska E, Węglińska A, Paryjczak T (2008) Przem Chem 8:87
40. Tanaka Y, Utaka T, Kikuchi R, Takeguchi T, Sasaki K, Eguchi K (2003) J Catal 215:271
41. Solsona BE, Garcia T, Jones C, Taylor SH, Carley AF, Hutchings GJ (2006) Appl Catal A 312:67