Role of Mn in supported Au-Mn/TOS catalysts

A. M. Ali[1], M. A. Daous[1], L. A. Petrov[2]*

[1] Department of Chemical and Materials Engineering, Faculty of Engineering, King Abdulaziz University, P.O. Box 80204, Jeddah 21589, Saudi Arabia
[2] SABIC Chair of Catalysis, King Abdulaziz University, P.O. Box 80204, Jeddah 21589, Saudi Arabia

In this study, a complete catalytic propane oxidation was investigated by using four different supported Au-Mn catalytic systems. Results showed that addition of manganese to a supported gold catalyst promoted lattice oxygen activity in metal oxides, such as ceria, zirconia, and titania, which resulted in an enhanced catalytic activity of an Au-Mn catalyst because of formation of a dinuclear compound, either Au5Mn2 or Au2Mn. A competition between Au and Mn to capture free lattice oxygen, dominated by manganese, was observed. In general, Ce 3d3/2, Au 4f7/2, and Mn 2p1/2 orbitals are related to dominant elemental species that are responsible for the enhanced catalytic activity of the Au-Mn catalyst in the complete oxidation of propane.

Keywords: gold catalysts, gold-manganese catalysts, XPS, propane oxidation

INTRODUCTION

Since the discovery of the high catalytic ability of Au nanoparticles, supported on a high surface area metal oxide support, gold has been extensively studied as a heterogeneous catalyst in both liquid and gaseous phases. In the last two decades, much attention is paid to the treatment, management, and ultimate elimination of toxic and hazardous materials [1] and effluent gases [2] from various toxic sources. Volatile organic compounds (VOCs), such as propane, are one of the main concerned pollutants [3]. For its abatement, direct combustion, a least efficient and high cost method, was used [4].

In recent decade, most scientists [5–12] had preferred catalytic oxidation to eliminate VOCs emissions and to meet stringent environmental quality standards (EQS). Various combinations of metal oxides and metals (both precious and nonprecious metals) were investigated for their potential as efficient oxidation catalysts. Among them, ceria-supported catalysts [5, 13–16] were mostly used for the catalytic oxidation of VOCs. Combinations between mixed ceria- and zirconia-based catalyst carriers were also tested and were found to be catalytically efficient because of possible changes of catalyst surface area [17]. Presence of each titania [18, 19], ceria, and zirconia [20] with an optimum amount of manganese oxide has shown an enhanced catalytic ability because of both enlarged surface area and redox qualities.

Supporting Au nanoparticles on ceria-titania [21] and ceria-zirconia [22] was found to be productive to eliminate VOC compounds owing to gold activity and influence of Au on the reduction of ceria-titania or ceria-zirconia supports. However, gold was not enough efficient as compared to platinum because of the very good dispersion of Pt on the ceria-zirconia support. It is generally believed that excellent dispersion of Au nanoparticles on a metal oxide(s) support play a key role for observed high catalytic activity of the prepared Au catalysts.

Potentially well-dispersed Au nanoparticles on the metal oxide(s) support could increase lattice oxygen mobility and cause weakening of Ce-O bonds. This may lead to the release of surface capping oxygen [23, 24] that could participate in a Mars-Van Krevelen type of oxidation reaction mechanism [23, 25–28].

Among many transition metal oxides, manganese oxide has a huge range of various types of liable oxygen sources, such as MnO, MnO_2, α-Mn_2O_3, Mn_2O_3, γ-Mn_2O_3, Mn_3O_4, MnO_2, and β-MnO_2 that may participate in an oxidation process in a competitive way. Lahousse *et al.* have summarised that γ-MnO_2 catalyst is favourable for abatement of volatile organic compounds [3]. Few studies were also conducted attempting to explain the importance of the presence of Mn on CeO_2 [29].

Based on own experimental data and published papers [7–23], it is fairly to presume that Au-Mn catalysts supported on mixed oxide carriers composed of CeO_2, ZrO_2, and TiO_2 could possibly have an increased catalytic activity in oxidation of VOCs, such as propane, the latter being one of the stringent and difficult organic compound to get oxidized. As

---

per authors' knowledge, so far none of the published studies has been reported on the possible role of Mn in supported Au-Mn catalysts especially through a detailed investigation carried out by XPS, which is a highly reliable way to identify possible orbital and/or suborbital overlapping to induce a synergistic effect of this system. This study was aimed at identifying how each elemental orbital does participate in such a catalytic system.
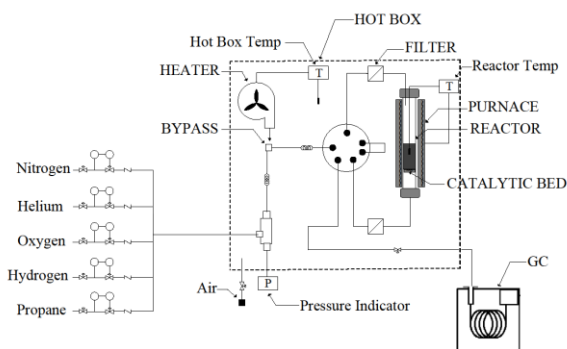
EXPERIMENTAL

Catalyst preparation and characterisation

An Au-Mn/TOS catalyst was prepared in three steps: (i) preparation of a triple oxide support (TOS) of $5.5CeO_2$:$2.5ZrO_2$:$2TiO_2$ composition, (ii) manganese impregnation of the triple oxide support (1%Mn/TOS), and (iii) gold deposition-precipitation on Mn/TOS (1%Au-1%Mn/TOS). For comparative purposes, a 1%Au/TOS catalyst was prepared by deposition-precipitation method. Both a list of all the chemicals used and detailed catalyst preparations as well as XPS and XRD analysis details can be found in a previously reported article [30].

Catalyst testing

Catalytic activity measurements in complete propane oxidation were carried out in a PID micro-activity reference reactor system. A schematic diagram of the experimental setup is shown in Figure 1. The experiments were exactly performed under the reaction conditions carried out by Ali *et al*. [30].

Fig. 1. Schematic diagram of the experimental setup.

The only components in the reaction mixture at the reactor exit in all experiments were propane, oxygen, carbon dioxide, and water. An Agilent 7890A GC system, equipped with a flame ionisation detector (FID) and a thermal conductivity detector (TCD), was used to identify and monitor the propane and the reaction products. Data processing was acquired by applying GC ChemStation®B.04.03 (54). 0.5-cm^3 gas samples, an Agilent DB1/122-1063 (1 μm, 60 m × 0.25 mm) column, an Hp-8ft

HAYSEP Q column, and He and N_2 carrier gases used for FID and TCD, respectively. Chromatographic oven temperature profiles are summarised in Table 1.

Table 1. Oven temperature profile

|	Rate, °C.min^{-1})	Temperature	Hold time
initial		40	3
ramp 1	30	130	0
ramp 2	20	220	0.5

RESULTS AND DISCUSSION

In order to investigate a possible association between gold and manganese in the presence of TOS support, freshly prepared catalyst samples were analysed for catalytic ability in the complete oxidation of propane.

Catalytic activity

Results of the catalytic tests are discussed and summarised in the following sections. Fig. 2 shows a detailed comparison of the catalytic activity of the Au-Mn, Au, and Mn catalysts and of the support (TOS).

The results showed that the triple oxide support itself exhibited a certain catalytic ability. Up to 300°C, less than 5% conversion of the propane took place. It reached 10% at 400°C and then shot up to nearly 90% at 450°C. As previously published [9, 31], we consider this conversion as being due mostly to cerium oxide.

The catalytic activity of the supported Mn catalyst at temperatures up to 350°C was practically the same as that of the catalyst carrier. At temperatures above 350°C, the Mn catalyst manifested a slightly higher catalytic activity than catalyst support. These results show that Mn is practically non-active in the reaction of propane oxidation at temperatures up to 500°C.
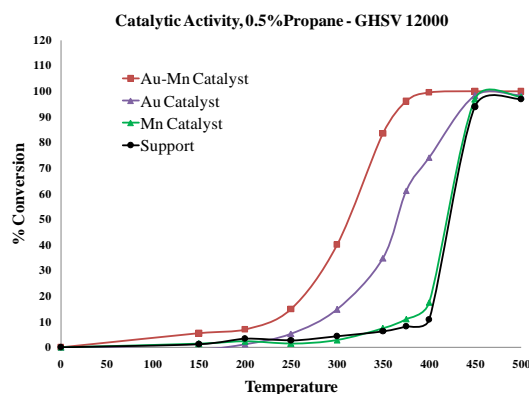
Fig. 2. Catalytic activity of the Au, Mn, and Au-Mn catalysts and the support in propane complete oxidation.

The Au catalyst had a moderate catalytic activity. Oxidation started after 200°C and a nearly 95% propane conversion was achieved at 400°C. The catalytic activity of the supported Au catalyst was substantially higher in comparison with Mn catalyst and triple oxide support in the temperature interval from 300 to 375°C. However, a 95%-conversion of propane was observed at the same temperature for the Mn catalyst. These results clearly indicate that the gold catalyst is relatively active in the reaction of propane total oxidation at moderate temperatures.

The catalytic conversion of propane over the Au-Mn catalyst started below 150°C and then strongly accelerated at temperatures above 225°C. A 95%-conversion was accomplished at 375°C. A complete conversion of propane over the Au-Mn catalyst was attained at 400°C. The catalytic activity of the Au-Mn catalyst was much higher than the activities of the rest studied samples. Obviously, it may be concluded from these results that manganese strongly enhanced the catalytic activity of the supported gold catalyst.

A synergism was observed due to interaction between Au and Mn in the presence of TOS and, as per authors' knowledge, so far no evidence is found in the literature. The nature and mechanism of such an interaction is yet to be studied and understood.

In order to investigate any interaction between Au and Mn and possible impacts of each of the metal oxides present in the support, a detailed XPS analysis was carried out before and after catalytic measurements.

XPS study

To study the possibility of any association between Au and Mn as well as their individual or collective role on enhanced catalytic activity, an XPS study was conducted in detail. Results are discussed and summarised below.

Impact of introduction of Au and/or Mn to the support

Before reaction

Figure 3 shows an overall comparison of survey XPS spectra of the triple oxide support, Au, Mn, and Au-Mn samples before catalytic reaction. In triple oxide support, oxygen (O 1s and O 2s), titanium (Ti 2s, Ti 2p, Ti 3s, and Ti 3p), cerium (Ce 4p, Ce 4d, Ce 3p, and Ce 3d), and zirconium (Zr 3d, Zr 3p, and Zr 3s) were found to be present. Among these peaks O 1s, Ti 2p, Ce 3d, and Zr3p are identified as the main peaks. Addition of either gold or manganese did not change much the spectra, however, bearing in mind the following three main differences:

(i) Au 4f and Mn 2p peaks were identified upon addition of gold and manganese, respectively.

(ii) Upon introduction of gold or manganese separately to the triple oxide support, a significant and clear peak of Ce 4s was found.

(iii) Addition of manganese to the gold catalyst (Au/TOS) gave rise to a significant and clear Mn 2s peak, which was not present when only manganese was added to the triple oxide support.

It is evident that Mn introduced to the Au catalyst has considerably affected the Ce component of the triple oxide support. This effect could be observed because of any possible synergism and/or any other interaction between gold and manganese that may have resulted in an enormous increase in catalytic activity of the gold catalyst.

In order to investigate any change in the results summarised in the previous section before and after catalytic reactions, a detailed XPS study of all the catalysts was also performed after the catalytic activity tests.

Figure 4 shows an overall comparison of survey overlaid XPS spectra before and after the catalytic reaction. Some of the key results are presented below.

(i) In triple oxide support (Fig. 4B), before and after the catalytic reaction, O 1s, Ti 2p and Zr 3p peaks were nearly the same in terms of intensity except for a significant change of binding energy (BE) in the range of 800–1200 eV. The Ce 3d peak was among those that seemed greatly affected. This change could be because of either partial reduction of Ce^{4+} to Ce^{3+} or due to its exposure to X-ray irradiation.

(ii) The surface scan spectra of the Mn catalyst (Fig. 4D) remained almost the same before and after reaction excepting negligible intensity variations after 800–1200 eV. Manganese presence did not cause any noticeable changes to the support except for a negligible change of the Ce ions. This could be explained as a possible reason that manganese alone on the support did not affect significantly the catalytic activity (see Fig. 2).

(iii) Considering the Au catalyst (Fig. 4B), a clear change can be seen after the binding energy range of 550–1200 eV. This variation is quite large as compared to the changes of the Mn catalyst and ceria. It might be because of the active role of gold for increasing the catalytic activity of the Au catalyst, as it was much higher than that of the Mn catalyst and ceria.

(iv) The highest variation was found in the overall survey laid XPS spectra of the Au-Mn catalyst (Fig. 4A), before and after the reaction, in the binding energy range of 200–1200 eV. This differ-

ence clearly indicates that the introduction of manganese to the Au catalyst is really affecting greatly in comparison with the Au and Mn catalysts. The highest catalytic activity of the Au-Mn catalyst might be associated with a possible interaction between gold and manganese.

The nature of this interaction can be a key aspect to better understanding of the enhanced catalytic activity and possible role of each of the mobile oxygen resources present in the catalysts. Further subsections describe possible reasons about this key aspect.
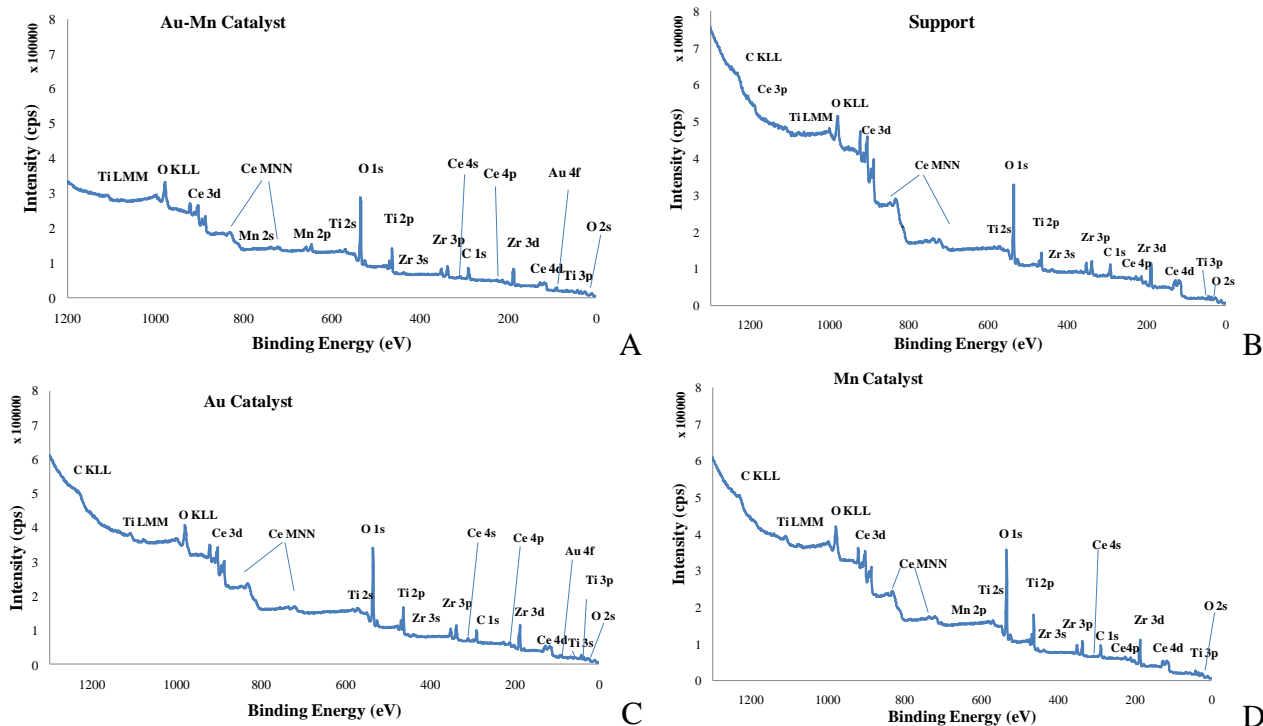

Fig. 3. Overall comparison of survey XPS spectra: A – Au-Mn catalyst, B – support, C – Au catalyst, D – Mn catalyst.
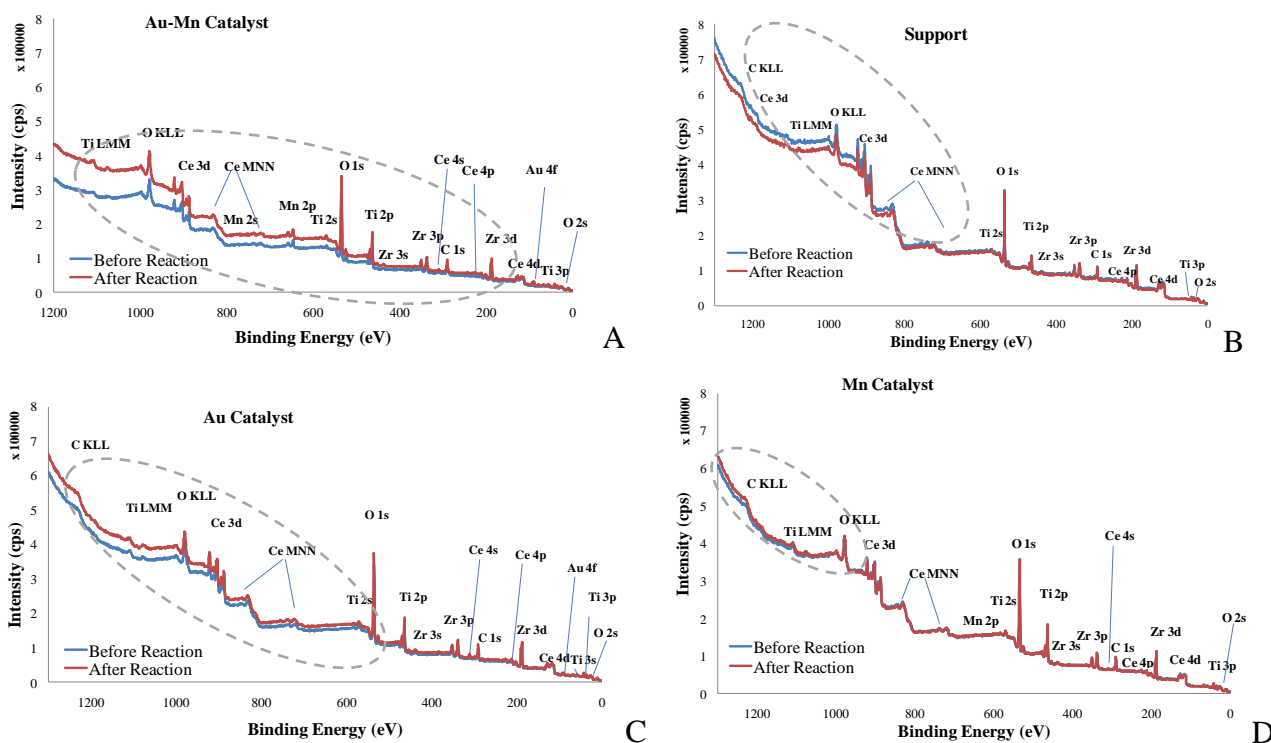

Fig. 4. Overall comparison of survey overlaid XPS spectra before and after catalytic reaction: A – Au-Mn catalyst, B – support, C – Au catalyst, D – Mn catalyst.

Role of Au, Mn, and triple oxide support in the catalytic reaction

It is seen (Fig. 4A) that titanium and zirconium regions are not changed much before and after the catalytic reaction for the highly active Au-Mn catalyst. This could be because the presence of manganese may affect cerium significantly and/or due to a possible interaction between gold and manganese. To investigate this interaction between Au and Mn as well as the role cerium, a deconvolution study of Ce, Au, and Mn was carried out before and after catalysis.

Role of ceria

Figure 5 shows a detailed comparison of deconvoluted XPS spectra of CeO_2, before and after the reaction, for each catalyst (Au-Mn/TOS, Au/TOS, Mn/TOS), support, and pure CeO_2.

Before reaction

Figure 5A shows an in-depth comparison of the cerium deconvoluted XPS spectra for all the catalysts before reaction. A most probable oxidation state of cerium (Ce^{4+}) in Au-Mn, Mn, and Au catalysts was observed [32]. Almost all the peaks, V, V″, V‴ of Ce $3d_{5/2}$ and U, U″, U‴ of Ce $3d_{3/2}$, remained nearly the same excepting V′-Ce $3d_{5/2}$ and U′-Ce $3d_{3/2}$. Table 2 shows a summary of the binding energies (eV) for the V′ and U′ peaks of all the catalysts and support.

Compared with the Au-Mn catalyst, the V′-Ce $3d_{5/2}$ peak of the support and of the Mn catalyst remained constant. A significant difference of 0.66 eV was observed between the V′-Ce $3d_{5/2}$ peaks of the Au-Mn and Au catalysts. A similar pattern was also detected for U′-Ce $3d_{3/2}$ where the difference was found to be 0.80 eV. This might be owing to a partial reduction of Ce^{4+} to Ce^{3+} in the ceria upon addition of manganese to the Au catalyst as well as due to a favourable variation in the activation energies.

After reaction

Figure 5B shows V′-Ce $3d_{5/2}$ and U′-Ce $3d_{3/2}$ peak positions of deconvoluted XPS spectra of Ce after the catalytic reaction. No changes in associated oxidation states of cerium were observed after the reaction. Also, a similar change in BE of 0.30 eV (see Table 3) for the V′-Ce $3d_{5/2}$ peak existed between the Au-Mn and Au catalysts, i.e. nearly half of the difference found before reaction. However, the difference between the U′-Ce $3d_{3/2}$ peak values of the Au-Mn and Au catalysts was much smaller, nearly by two thirds, as to that before reaction. This

may lead to a conclusion that U′-Ce $3d_{3/2}$ perhaps played a key role for the enhanced catalytic activity of the Au-Mn catalyst as to cerium belonging to the V′ peak of Ce $3d_{5/2}$.

Role of gold

Figure 6 shows deconvoluted XPS spectra of gold for the Au-Mn and Au catalysts before and after catalytic reaction.

Before reaction

Three peaks W, W′, W″ of Au $4f_{7/2}$ and two peaks X, X′ of Au $4f_{5/2}$ were identified with possible Au^{1+} oxidation state of the gold in the Au-Mn and Au catalysts (Fig. 6B). Each of the three peaks of Au $4f_{7/2}$ (W, W′, W″) and one of Au $4f_{5/2}$ (X) were found to be identical in terms of binding energy except for the X′ peak of Au $4f_{5/2}$ for the gold containing catalysts before reaction (0.33 eV, see Table 3). This perhaps could be because of non-metallic gold in the Au-Mn catalyst as compared to slightly higher metallic nature of gold in the Au catalyst.
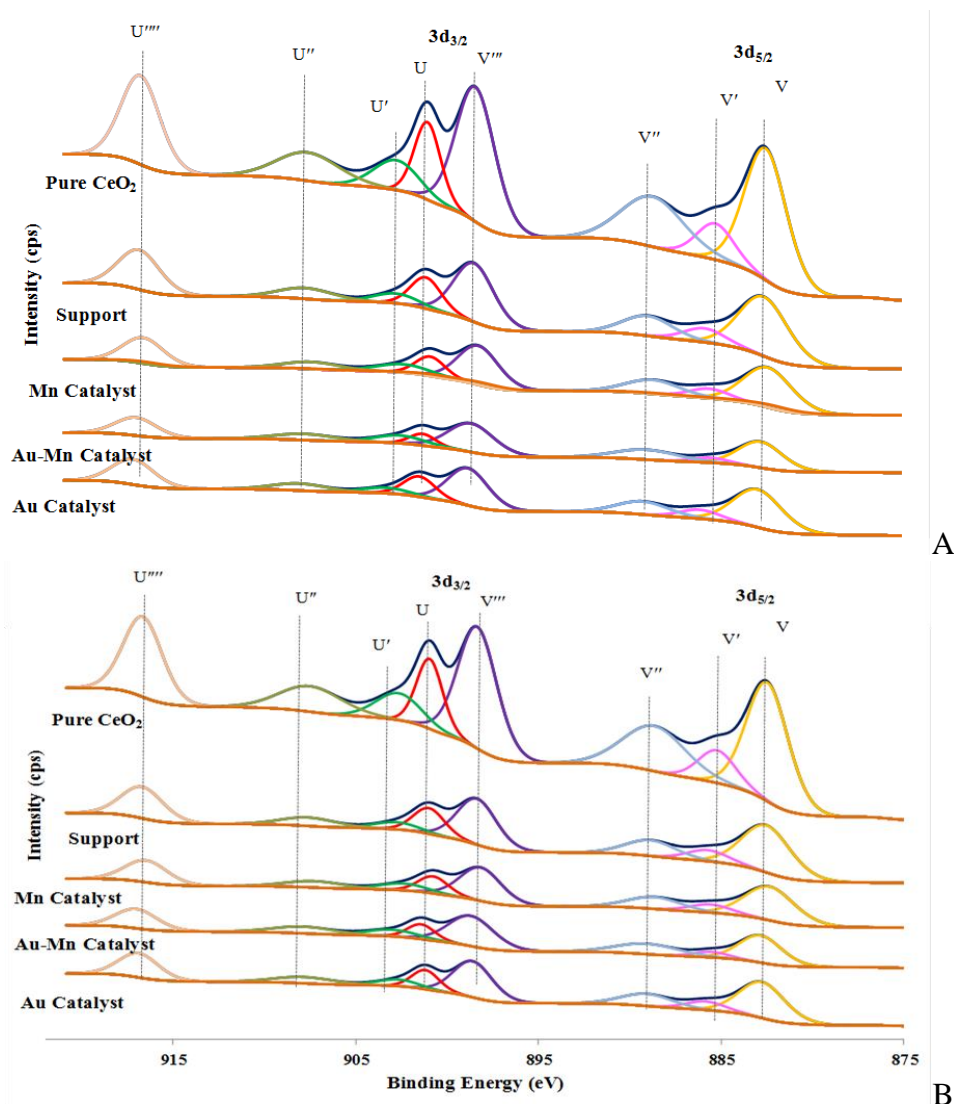
After reaction

After the catalytic reaction, two Au $4f_{7/2}$ peaks (W and W″) and one Au $4f_{5/2}$ peak (X′) were slightly changed (see Fig. 6B) for the Au-Mn and Au catalysts contrary to the change of only one Au $4f_{5/2}$ peak (X′) before reaction. This may further indicate that during the catalytic reaction gold existed in a higher oxidation state (1+) in the Au-Mn catalyst as compared to the Au catalyst. This can also be related to the presence of Mn that did promote the non-metallic nature of gold because of its higher number of available unpaired valence shell electrons.

Table 2. Binding energies of the V′-Ce $3d_{5/2}$ and U′-Ce $3d_{3/2}$ cerium peaks before and after catalytic reaction

| Catalyst | Binding energy, eV | | | |
| | before reaction | | after reaction | |
	V′-Ce $3d_{5/2}$	U′-Ce$3d_{3/2}$	V′-Ce $3d_{5/2}$	U′-Ce $3d_{3/2}$
Au-Mn	885.40	902.45	885.54	903.03
Au	886.06	903.25	885.84	902.70
Mn	885.50	902.30	885.60	902.40
support	885.50	902.70	885.70	902.80
CeO_2	885.20	902.70	885.20	902.70

Table 3. Binding energies of the W-Au$4f_{7/2}$, W″-Au$4f_{7/2}$, and X′-Au $4f_{5/2}$ gold peaks before and after catalytic reaction

| Catalyst | Binding energy, eV | | | |
| | before reaction | | after reaction | |
	X′-Au$4f_{5/2}$	W-Au$4f_{7/2}$	W″-Au$4f_{7/2}$	X′-Au$4f_{5/2}$
Au-Mn	89.50	82.15	85.94	89.25
Au	89.17	82.40	85.25	89.42

Fig. 5. Overall comparison of overlaid deconvoluted Ce XPS spectra: A – before reaction; B – after reaction.

Role of manganese

The catalytic activity of the Au catalyst was moderate, whereas the catalytic activity of the Mn catalyst did not differ from that of the triple oxide support, i.e. Mn is not active in propane oxidation reaction. However, the catalytic activity of the Au-Mn catalyst was substantially increased compared to other two catalyst compositions. Apparently, this increase in catalytic activity is mainly due to an occurring synergism between catalyst components. Both the Au and Mn catalysts exhibited a much lower activity in the complete propane oxidation than the Au-Mn catalyst. It might be an indication that there existed a synergism (promotion of Au activity by Mn).

Based on the catalytic activity of the Au-Mn catalyst in comparison with the catalytic activity of the Au and Mn catalysts it was assumed that it might be because of an efficient behaviour of Mn as promoter. Further, a detailed deconvoluted XPS study of manganese was also conducted. Fig. 7 shows an overall comparison of overlaid deconvoluted XPS spectra of the Mn catalyst before and after reaction.

Before reaction

Two peaks of Mn $2p_{3/2}$ (Y, Y′) and two peaks (Z, Z′) belonging to Mn $2p_{1/2}$ with possible oxidation states of Mn^{+3} and Mn^{+4} in the Au-Mn catalyst were observed (Fig. 7) in comparison with single Y and Z peaks, ascribed to Mn $2p_{3/2}$ and Mn $2p_{1/2}$, respectively, in the Mn catalyst [33].

This shows that the simultaneous presence of Au and Mn on the support gives rise to an entirely different behaviour of the Au-Mn catalyst in cata-

lysis in contrast to sole Mn on the support. The peaks Y′ and Z′ were identified as Au peaks within the main peaks Y and Z of the manganese. Possibly these sub-peaks (Y′ and Z′) within the main peaks of Mn belong to dinuclear (Au-Mn) compounds [34].

Table 4. Binding energies of the Y,Y′-Mn $2p_{3/2}$ and Z,Z′-Mn $2p_{1/2}$ manganese peaks before and after catalytic reaction

| Condition | Binding energy, eV | | | | | |
	Mn		Au-Mn			
	Mn $2p_{3/2}$	Mn $2p_{1/2}$	Mn $2p_{3/2}$		Mn $2p_{1/2}$	
	Y	Z	Y	Y′	Z	Z′
before reaction	641.20	653.3	641.64	644.84	653.20	655.66
after reaction	641.28	653.35	641.80	644.98	652.40	653.80

After reaction

The Mn $2p_{3/2}$ and Mn $2p_{1/2}$ peaks remained the same before and after the reaction (Table 4). Whereas, in the case of Au-Mn catalyst the Y and Y′ peaks of Mn$2p_{3/2}$ did not change at all as to those of Z and Z′ peaks of Mn$2p_{1/2}$, which showed the largest shift (Table 5). This clearly indicates that both the dinuclear (Au-Mn) peak (Z′) and the main peak (Z) of Mn$2p_{1/2}$ played an important role for the enhanced catalytic activity of the Au-Mn catalyst. Based on both XPS and catalytic activity results, it can be summarised that manganese is a key component for the increased catalytic activity of the gold catalyst. The presence of manganese as a promoter enhanced the catalytic activity by interacting with gold in the form of Au-Mn active system.

Identification of Au-Mn interaction

XPS studies have shown a unique association between Au and Mn that had caused an enhanced catalytic activity because of a dinuclear compound formation. In order to cross verify results, a thorough XRD study was conducted for all the catalysts before and after catalytic tests. Some results have already been reported by Ali *et al.* [30] showing that fresh and spent Au-Mn catalyst samples remained exactly the same, which is an indication that the Au-Mn catalyst was highly stable. Based on Au-Mn lattice parameters of Au solid solution *versus* composition, the expected structure contained more than 25% Mn but less than 35%. From the Au-Mn phase diagram, it was found that there could be two most probable structures: Au_5Mn_2 and Au_2Mn having a crystallite size of 7 nm.
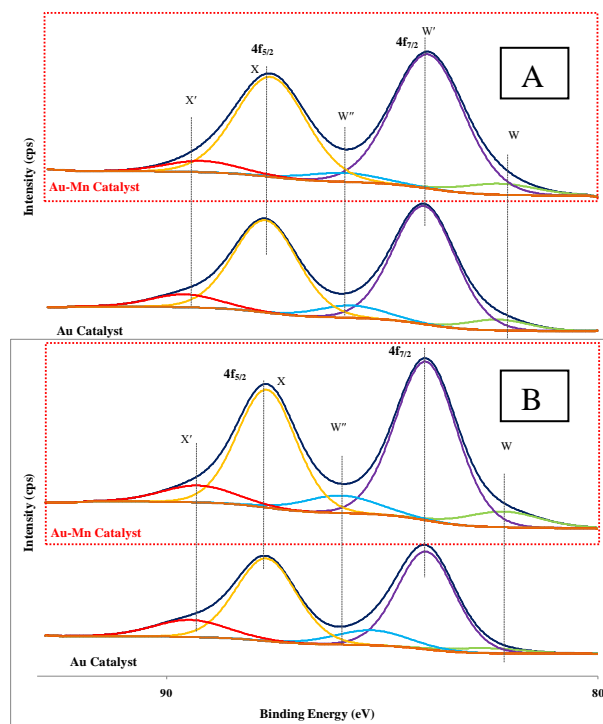
Fig. 6. Overall comparison of deconvoluted Au XPS spectra: A – before reaction, B – after reaction.
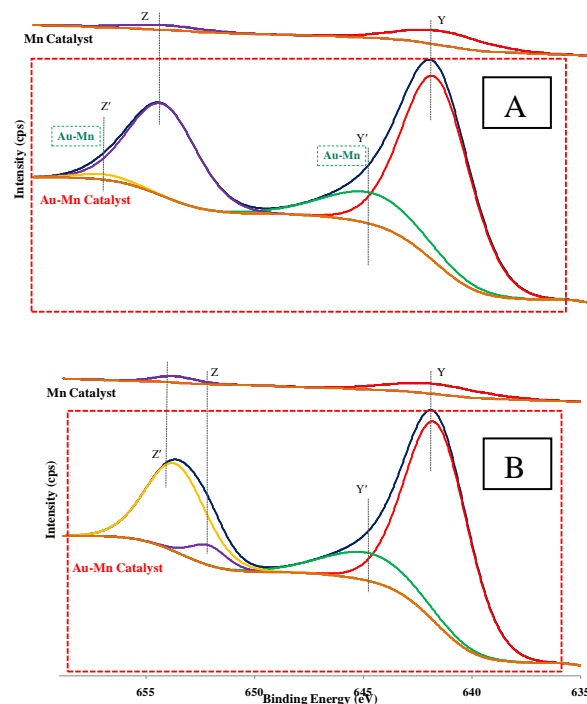
Fig. 7. Overall comparison of deconvoluted Mn XPS spectra: A – before reaction, B – after reaction.

Hence, based on XRD and XPS results the enhanced catalytic activity of Au-Mn could be due to the presence of dinuclear compound: Au_5Mn_2 or Au_2Mn.

CONCLUSIONS

In conclusion, a supported Au-Mn catalyst has shown the highest catalytic ability in the complete oxidation of propane in comparison with Au and Mn catalysts. Manganese introduction to a gold catalyst promoted mobilization of lattice oxygen species of metal oxides of cerium, zirconium, and titanium that resulted in an enhanced catalytic activity of the Au-Mn catalyst. Enhanced lattice oxygen or adsorbed oxygen mobility was attributed to formation of a dinuclear Au-Mn compound: Au_5Mn_2 or Au_2Mn. In the absence of manganese, a moderate catalytic activity of Au catalyst was due to participation of ceria and titania lattice oxygens only. A competition between Au and Mn for free lattice oxygen, dominated by manganese, was also observed. In general, Ce $3d_{3/2}$, Au $4f_{7/2}$, and Mn $2p_{1/2}$ orbitals were found to be related to dominating elemental species for enhanced catalytic activity of the Au-Mn catalyst in propane complete oxidation.

REFERENCES

1. U. I. Gaya, A. H. Abdullah, Z. Zainal, M. Z. Hussein, *J. Hazard. Mater.*, **168**, 57 (2009).
2. S. Deng, Z. Li, J. Huang, G. Yu, *J. Hazard. Mater.*, **179**, 1014 (2010).
3. C. Lahousse, C. Cellier, B. Delmon, P. Grange, in *Stud. Surf. Sci. Catal.*, Vol. 130, A. Corma, J. L. G. Fierro, Eds., Elsevier, 2000.
4. M. McGrath, *Appl. Catal. B-Environ.*, **5**, 25 (1995).
5. Z. Abbasi, M. Haghighi, E. Fatehifar, S. Saedy, *J. Hazard. Mater.*, **186**, 1445 (2011).
6. D. A. Aguilera, A. Perez, R. Molina, S. Moreno, *Appl. Catal. B-Environ.*, **104**, 144 (2011).
7. S. S. T. Bastos, S. A. C. Carabineiro, J. J. M. Órfão, M. F. R. Pereira, J. J. Delgado, J. L. Figueiredo, *Catal. Today*, **180**, 148 (2012).
8. M. Ousmane, L. F. Liotta, G. D. Carlo, G. Pantaleo, A. M. Venezia, G. Deganello, L. Retailleau, A. Boreave, A. Giroir-Fendler, *Appl. Catal. B-Environ.*, **101**, 629 (2011).
9. S. Scirè, L. F. Liotta, *Appl. Catal. B-Environ.*, **125**, 222 (2012).
10. T. Tabakova, D. Dimitrov, M. Manzoli, F. Vindigni, P. Petrova, L. Ilieva, R. Zanella, K. Ivanov, *Catal. Commun.*, **35**, 51 (2013).
11. Z.-X. Yu, W. Zheng, W.-L. Xu, P. Zhang, H.-Y. Fu, Y.-H. Zhang, *Trans. Nonferrous Met. Soc. China*, **21**, (Suppl 2) 405 (2011).
12. D. Vitry, J.-L. Dubois, W. Ueda, *J. Mol. Catal. A-Chem.*, **220**, 67 (2004).
13. X. Liu, Z. Zhan, X. Meng, W. Huang, S. Wang, T. Wen, *J. Power Sources*, **199**, 138 (2012).
14. J. Okal, M. Zawadzki, L. Krajczyk, *Catal. Today*, **176**, 173 (2011).
15. V. Balcaen, H. Poelman, D. Poelman, G. B. Marin, *J. Catal.*, **283**, 75 (2011).
16. D. B. Dadyburjor, T. K. Das, E. L. Kugler, *Appl. Catal. A-Gen.*, **392**, 127 (2011).
17. G. Picasso, M. Gutiérrez, M. P. Pina, J. Herguido, *Chem. Eng. J.*, **126**, 119 (2007).
18. G. Qi, R. T. Yang, *Appl. Catal. B-Environ.*, **44**, 217 (2003).
19. M. Baldi, F. Milella, J. M. Gallardo-Amores, G. Busca, *J. Mater. Chem.*, **8**, 2525 (1998).
20. B. Shen, X. Zhang, H. Ma, Y. Yao, T. Liu, *J. Environ. Sci.*, **25**, 791 (2013).
21. C. Gennequin, M. Lamallem, R. Cousin, S. Siffert, F. Aïssi, A. Aboukaïs, *Catal. Today*, **122**, 301 (2007).
22. J. Gaalova, P. Topka, L. Kaluza, O. Solcova, *Catal. Today*, **175**, 231 (2011).
23. S. Scirè, S. Minicò, C. Crisafulli, C. Satriano, A. Pistone, *Appl. Catal. B-Environ.*, **40**, 43 (2003).
24. G. C. Bond, C. Louis, D. T. Thompson, Catalysis by Gold, Imperial College Press, London, 2006.
25. A. M. Ali, E. A. C. Emanuelsson, D. A. Patterson, *Appl. Catal. B-Environ.*, **106**, 323 (2011).
26. A. M. Ali, E. A. C. Emanuelsson, D. A. Patterson, *Appl. Catal. B-Environ.*, **97**, 168 (2010).
27. S. Minicò, S. Sciré, C. Crisafulli, R. Maggiore, S. Galvagno, *Appl. Catal. B-Environ.*, **28**, 245 (2000).
28. C. Doornkamp, V. Ponec, *J. Mol. Catal. A-Chem.*, **162**, 19 (2000).
29. L. E. Gómez, E. E. Miró, A. V. Boix, *Int. J. Hydrogen Energy*, **38**, 5645 (2013).
30. A. M. Ali, M. A. Daous, A. A. M. Khamis, H. Driss, R. Burch, L. A. Petrov, *Appl. Catal. A-Gen.*, **489**, 24 2015.
31. L. Delannoy, K. Fajerwerg, P. Lakshmanan, C. Potvin, C. Méthivier, C. Louis, *Appl. Catal. B-Environ.*, **94**, 117 (2010).
32. B. Skårman, L. R. Wallenberg, P.-O. Larsson, A. Andersson, J.-O. Bovin, S. N. Jacobsen, U. Helmersson, *J. Catal.*, **181**, 6 (1999).
33. J. Papavasiliou, G. Avgouropoulos, T. Ioannides, *J. Catal.*, **251**, 7 (2007).
34. Modern Supramolecular Gold Chemistry: Gold-Metal Interactions and Applications, A. Laguna, Ed., Wiley-VCH, 2008.

РОЛЯ НА МАНГАНА В НАНЕСЕНИ Au-Mn/TOS КАТАЛИЗАТОРИ

А. М. Али[1], М. А. Даус[1], Л. А. Петров[2]*

[1] *Департамент по инженерна химия и материали, Факултет по инженерство, Университет Крал Абдулазис, п.к. 80204, Джеда 21589, Саудитска Арабия*
[2] *Катедра „Катализ" на Саудитската основна индустриална корпорация, Департамент по инженерна химия и материали, Факултет по инженерство, Университет Крал Абдулазис, п.к. 80204, Джеда 21589, Саудитска Арабия*

(Резюме)

Изследвано е пълното каталитично окисление на пропан върху четири каталитични системи. Получените резултати показват, че добавянето на манган към нанесен златен катализатор промотира подвижността на решетъчния кислород в носителя – смесени оксиди CeO_2, ZrO_2 и TiO_2 (TOS). В резултат на това се увеличава каталитичната активност на катализаторите. Установено е образуването на двуядрени съединения между златото и мангана със състав Au_5Mn_2 и Au_2Mn. Установено е, че свободният решетъчен кислород се захваща както от златото, така и предимно от мангана. Намерено е, че орбиталите $Ce\ 3d_{3/2}$, $Au\ 4f_{7/2}$ и $Mn\ 2p_{1/2}$ са свързани с преобладаващите активни форми на елементите на повърхността на Au-Mn катализатори.