Catalytic Combustion of Toluene over a Copper-Manganese-Silver Mixed-Oxide Catalyst Supported on a Washcoated Ceramic Monolith

Monolithic catalysts were prepared by washcoating an alumina sol and then impregnating Cu-Mn-Ag mixed oxides onto cordierite substrates. The effects of the preparation parameters including the Ag/Cu/Mn ratio, the total amount of active phase and the loading of washcoat, and the reaction conditions, e.g., the space velocity and the oxygen/toluene ratio on the catalytic performance for the combustion of toluene were investigated. It is shown that the Cu-Mn-Ag oxides are very active for the combustion of toluene and that the highest catalytic activity is achieved over a monolithic catalyst containing 14.7 wt % of washcoat and 21.2 wt % of active phase with a Ag/Cu/Mn molar ratio of 13.8/43.1/43.1. It is also seen that the optimum catalyst has a good catalytic stability and exhibits an excellent activity not only at a rather high space velocity but also within a wide range of oxygen/toluene ratios.

Keywords: Catalytic combustion, Mixed oxides, Monolithic catalysts, Toluene, Volatile organic compounds

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1 Introduction

Volatile organic compounds (VOCs) are recognized as increasing contributors to air pollution [1]. Catalytic combustion is one of the most attractive ways of controlling these emissions, since the oxidation of VOCs over a catalyst takes place at temperatures much lower than that required for thermal incineration [1–4].

The commercial catalysts widely used in the abatement of VOCs are generally noble metals dispersed on porous supports, e.g., platinum or palladium on alumina, silica, etc. [2–4]. Although noble metal catalysts are very active for catalytic combustion, they are rather expensive and susceptible to deactivation by poisoning, particularly in the presence of compounds containing chlorine, sulfur and phosphorus, or in the presence of water, one of the combustion products [3–5]. Therefore, there is a significant interest to replace noble metal catalysts with cheaper catalysts resistant to deactivation phenomena. Catalysts based on transition metal (Ni, Cu, Co, Cr, Mn, and Fe) oxides have been extensively studied and the combustion activity shown by these oxides is generally lower than that of noble metal catalysts [2–4, 6]. Among the metal oxide catalysts, manganese and copper oxides have been considered as the most active and promising catalysts for the combustion of VOCs [4, 6, 7]. Therefore, much effort has been undertaken to improve the catalytic performance of the two oxides as well as their mixed oxides [7–12], e.g., ceria promoted copper oxide was found to be more active than single copper oxide or Cu-Mn mixed oxides [8]. Titania supported Mn-Cu mixed oxide with a Mn/Cu atomic ratio of 1/1 showed significantly greater activity than single manganese or copper oxide, or mixed oxides with other compositions [7]. Similar results were also reported by Morales et al. [9], while Zimowska et al. [10] examined the catalytic activities of Cu-Mn mixed oxides prepared from the hydrotalcite-like precursors. Recently, silver has received much attention as a suitable catalyst for many redox reactions such as low temperature NOx reduction [13], CH4 oxidation [14, 15], CO oxidation [15, 16], and oxidation of VOCs [17–20]. Cordi and Falconer [17] observed that Ag/Al2O3 catalyst was very active for the complete oxidation of VOCs. They considered that adsorbed VOCs diffused along the alumina surface and reacted at the silver sites where oxygen was adsorbed and that as the oxidation occurred at high temperatures, VOCs reacted in parallel on silver and
alumina sites. Baek et al. [18] studied various transition metals, e.g., Mn, Fe, Co, Ni, Cu, Zn, and Ag for the catalytic oxidation of toluene and methyl ethyl ketone and found that silver showed the best activity among the tested catalysts. Wong et al. [19] reported that silver-loaded zeolite (HY and HZSM-5) catalysts exhibited high activities for the oxidation of butyl acetate. It was also shown that the addition of silver to LaMnO$_3\cdot$perovskite significantly improved the catalyst activity and selectivity for the combustion of VOCs [20].

Although a reasonable amount of information is already available concerning the catalytic combustion of VOCs, to the best of the authors’ knowledge, no effort has been made to examine the performance of the Cu-Mn mixed oxides with the addition of silver. Therefore, an interest in studying the Cu-Mn-Ag mixed oxide catalysts arises. Moreover, for practical applications, the catalysts should be supported on a structured support, e.g., ceramic or metallic monoliths, to treat large gas flows with low pressure drop [12, 21]. Therefore, for these purposes, a series of Cu-Mn-Ag mixed oxides supported on ceramic monolith were prepared in this work. The effects of the preparation parameters including the Ag/Cu/Mn ratio, the total amount of active phase and the loading of washcoat, as well as the reaction conditions, i.e., the space velocity and the oxygen/toluene ratio, on the catalytic performance for the combustion of toluene as a VOC model were investigated in detail. In addition, the catalytic stability of the catalyst with the optimum composition was also examined.

## 2 Experimental

### 2.1 Catalyst Preparation

All the monolithic structures used were cylindrical in shape, with a diameter of 8 mm and a length of 24 mm. They were obtained by cutting commercial cordierite straight-channel monoliths with a square cell density of 400 cpsi (cells per square inch) and a wall thickness of 0.21 mm. Before use, they were pretreated in an acetic acid solution for 1 h and then calcined at 600 °C in air for 2 h to remove absorbed impurities.

An alumina sol with a typical viscosity of 170 mPa·s at room temperature was prepared from a mixture of pseudo-boehmite and deionized water in a weight ratio of 2/5, vigorously stirred at 80 °C for 1 h at a pH of 2.5 adjusted with dilute nitric acid. A dried monolith was dipped in the sol for ca. 1 min. The excess liquid remaining in the monolith channels was then shaken out. The monolith was maintained horizontally at room temperature overnight and then dried at 120 °C in air for 1 h, followed by calcination at 600 °C in air for 3 h.

In this work, eleven monolithic catalysts were prepared, as listed in Tab. 1, where the loading of washcoat (γ-alumina) and the total amount of the deposited active phase (Cu-Mn-Ag mixed oxides) are both their actual values in relation to the initial weight of the monolithic substrate, and the Ag/Cu/Mn molar ratio is the material ratio of the impregnating solution used.

### 2.2 Catalytic Activity Measurements

Catalytic combustions of toluene on all the catalysts were carried out at atmospheric pressure in a fixed-bed quartz tubular reactor with an inner diameter of 10 mm. The reactor was placed inside an electric oven equipped with an automatic temperature controller. A monolithic catalyst wrapped with fiberglass layers was placed in the middle of the reactor, and a thermocouple was inserted near the outlet of the monolith. Prior to the reaction, the catalyst was activated under air flow at 450 °C for 1 h. After the catalyst bed was cooled to ca. 100 °C, a reactant mixture consisting of toluene (0.89 vol.-%), O$_2$ (14.8 vol.-%) and N$_2$ (balance gas) was fed to the reactor by bubbling air at a rate of 150 mL/min and N$_2$ at a rate of 50 mL/min through a saturator containing toluene at 0 °C, resulting in a gas hourly space velocity (GHSV) of ca. 10000 h$^{-1}$ based on the total monolith volume and an oxygen/toluene molar ratio of ca. 16.6/1 in the feed gas. Afterwards, the catalyst bed was heated to ca. 400 °C at a heating rate of 2.5 °C/min, and in this period the reaction exit gases were periodically sampled and analyzed using an online gas chromatograph.
equipped with a SE-30 column. The temperature ramp of 2.5 °C/min was considered to be sufficiently slow to reach a pseudo-steady state at every point. The conversion of toluene was calculated as a function of the reaction temperature from the amount of toluene at the inlet and outlet of the reactor, i.e., \(\frac{[\text{toluene}]_{\text{in}} - [\text{toluene}]_{\text{out}}}{[\text{toluene}]_{\text{in}}}\).

To examine the adaptability of the catalyst to the operating conditions, the toluene combustion on the catalyst with the optimum composition was also performed at different GHSV levels and different feed gas compositions, implemented by changing the two flow rates of air and \(\text{N}_2\). The two gas flows varied proportionately when studying the effect of the GHSV. However, when examining the effect of the oxygen/toluene ratio, one gas flow increased and the other decreased, while their total flow rate did not vary. The experimental process and the reaction conditions are identical with those mentioned above except for the operating parameter examined.

3 Results and Discussion

3.1 Effect of the Ag/Cu/Mn Ratio

In Tab. 1, the first six monolithic catalysts contain not only a similar washcoat loading but also a similar total amount of active phase. However, different Ag/Cu/Mn molar ratios exist in the active phases of these catalysts. It can be seen that for Cu-Mn mixed oxides or supported Cu-Mn mixed oxides, the Cu/Mn ratio = 1 usually led to the optimal catalytic activity for the combustion of VOCs [7, 9], and therefore, the atomic ratio of Cu to Mn was fixed at 1/1 for the overall study. The curves of toluene conversion versus the reaction temperature for the six samples are shown on Fig. 1. Three different temperature intervals are observed on these activity curves. At the beginning of the reaction, the catalytic activity increases very slowly, followed by a sharp increase and then a slow increase in the catalytic activity once again. To confirm these catalytic activities, a blank test was previously carried out with a bare monolith as an inert material placed in the reactor and resulted in no conversion of toluene at temperatures up to 524 °C. Therefore, it is clear from the light-off curves in Fig. 1 that all the tested catalysts are active for toluene combustion. In particular, the conversion of toluene on sample S3 starts at ca. 100 °C and it is completed below ca. 300 °C. For the convenience of making comparisons between these samples, the reaction temperatures, \(T_{10}\) and \(T_{90}\), corresponding to 10 % and 90 % conversions of toluene, respectively, were obtained for each sample and then plotted as a function of the sample number in Fig. 2. It can be seen that the catalytic performance varies with the sample number. Overall, the \(T_{10}\) or \(T_{90}\) temperature decreases at first, reaches a minimum, and then increases with increasing the sample number. Interestingly, it is sample S3 that reaches both the minimum \(T_{10}\) and \(T_{90}\) values. The sample with an Ag/Cu/Mn molar ratio of 13.8/43.1/43.1 in the active phase gives \(T_{10}\) and \(T_{90}\) temperatures of only 171 and 264 °C, respectively, and thus, shows a much better catalytic activity for toluene combustion.

Figure 1. Toluene conversion as a function of the reaction temperature over the first six monolithic catalysts in Tab. 1. ○: S1, □: S2, ▲: S3, Δ: S4, ○: S5, and ●: S6.

Figure 2. \(T_{10}\) (△) and \(T_{90}\) (□) temperatures of the catalyst samples with different Ag/Cu/Mn molar ratios.

It is known that the crystalline phases of mixed oxides are generally dependent on their compositions. Here, there is a significant possibility of different crystalline phases existing in the Cu-Mn-Ag mixed oxides with different Ag/Cu/Mn ratios, leading to a significant variation in the catalytic performance of the monolithic catalysts. Although XRD analysis can be used to identify these phases, it is difficult to examine the monolithic catalysts directly by this method. Moreover, from samples S1 to S6, the Ag content increases, but the Cu and Mn contents decrease, as shown in Tab. 1. Thus, it can also be seen that an appropriate Ag content in the catalyst examined is crucial for the catalytic performance for toluene combustion, probably due to the variation of oxidation state of Ag with its content. A similar result was also reported by Kucharczyk and Tylus [15] for the oxidation of methane and carbon oxide over La-Ag-Mn perovskite catalysts.
3.2 Effect of the Total Amount of Active Phase

In order to examine the effect of the total loading of active phase, another two monolithic catalysts with a similar washcoat loading and the same Ag/Cu/Mn ratio as sample S3 were prepared, i.e., samples S7 and S8 in Tab. 1. The light-off curves of the two samples, together with sample S3 are shown in Fig. 3. Clearly, the catalyst with 21.2 wt % of active phase, i.e., sample S3, possesses both the lowest $T_{10}$ and $T_{90}$ temperatures, indicating that a proper amount of active phase may lead to a high activity of the monolithic catalyst.

The low activity of the catalyst with a lower amount of active phase, i.e., 11.5 wt %, probably arises from the fact that there are not enough active sites for the combustion reaction with a high space velocity. Thus, it is seen that the catalytic activity generally increases with the amount of active phase deposited on the coated monolith. However, an abnormal example is also shown in Fig. 3, where a higher loading of active phase, i.e., 30.8 wt %, leads to a lower catalytic activity for sample S8, as compared with sample S3. In order to clarify this situation, a repeat of sample S8 was prepared and then cut along its radial direction into two parts before calcination. It was surprisingly obvious that the color is much darker at the two outlets of the monolith than at the center of the monolith. This shows that the metal precursor salts have moved significantly through the monolith during drying in static air, and thus, the active phase has accumulated at the outer part of the monolith where the water evaporates at the fastest rate, resulting in an inefficient monolith with only the outer part of the structure having significant catalytic activity. Nevertheless, for the repeats of the other samples in Tab. 1, the phenomenon of active phase migration was not observed and a homogeneous distribution of active phase was obtained. Thus, it can be seen that the active phase accumulation of sample S8 is possibly due to the use of a highly concentrated impregnating solution. Moreover, it is known that impregnation using a concentrated solution will lead to a large average crystalline size of the active phase, which might be another important reason for the low activity of sample S8.

In order to prevent the misdistribution of active phase occurring, e.g., in the case of the impregnation using a concentrated solution, a freeze-drying procedure has been highly recommended by several authors for the manufacture of impregnated monoliths [22, 23]. However, this technique is much more expensive than the conventional drying methods, leading to very few applications of the procedure in industry. Therefore, the deposition of a proper amount of active phase on the monolith is fairly significant not only for the commercial cost but also for the even active phase distribution and the resultant catalytic performance.

3.3 Effect of the Washcoat Loading

For the purpose of studying the effect of the washcoat loading, three additional monolithic catalysts with a similar amount of active phase and the same Ag/Cu/Mn ratio as sample S3 were prepared, i.e., samples S9, S10 and S11 in Tab. 1. The light-off curves of the three samples, as well as sample S3, are shown in Fig. 4. It can be seen that when there is no washcoat layer on the monolith, i.e., sample S9, the $T_{10}$ and $T_{90}$ temperatures are ca. 311 and 328 °C, respectively. Therefore, the catalyst is still active for the toluene combustion, as compared with the blank test sample mentioned above. However, a proper loading of washcoat, i.e., 14.7 wt %, leads to the highest catalytic activity for sample S3, similar to the effect of the amount of active phase observed earlier.

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hence, to a more significant catalytic activity, which has been verified by the light-off curves of samples S3, S9 and S10 in Fig. 4. However, it can also be seen from Fig. 4, that the catalyst with the highest loading of washcoat, accounting for 31.0 wt % of the monolithic substrate weight, is less active than sample S3. The main reason for the reduction of activity is that the extremely large loading of washcoat results in a significant decrease in the contact time between the reactants and the catalyst active phase. At the early stage, the washcoating using the sol method works mainly by means of pore-filling [22], i.e., most of the washcoat material is actually fixed inside the macropores of the monolithic substrate instead of only being attached to the external surface of the monolith channels. However, as the number of washcoats increases, the pores will be completely filled owing to the overfull loading of washcoat, and the washcoat material will become inaccessible. Therefore, the material has to stick on the channel walls of the monolithic substrate, resulting not only in a poor adherence of washcoat layer to the monolith but also in the reduction of the open frontal area of the monolith. For a given total flow rate of the reactant mixture, with the decrease of the open frontal area of the monolith, the pressure drop across the reactor increases, and the contact time between the reactant mixture and the catalyst active phase decreases, which possibly results in a lower catalytic activity for sample S11.

3.4 Effect of the Space Velocity

All of the above results show that sample S3 is the catalyst with the optimum composition for toluene combustion. In this and the next subsections, the catalytic performance of the optimum sample is examined at different operating conditions. The influence of the space velocity on the toluene combustion as a function of the reaction temperature is shown in Fig. 5. It can be seen that the light-off curve obtained at 5000 h⁻¹ is fairly close to that obtained at 10000 h⁻¹, indicating that the space velocity in its low range has no significant effect on the catalytic activity. However, as expected, the catalytic performance decreases on further increasing the space velocity to 15000 or 20000 h⁻¹, due to a significant decrease in the contact time between the reactants and the catalyst. Similar results were also reported for the combustion of dilute toluene and methyl ethyl ketone over transition metal-doped zirconia catalysts [24] and for the combustion of toluene over Cu-Mn/MCM-41 catalysts [11]. It is also clear from Fig. 5, that even at the highest space velocity examined, i.e., 20000 h⁻¹, the optimum catalyst gives \( T_{10} \) and \( T_{90} \) temperatures of only 275 and 328 °C, respectively. Therefore, the catalyst shows excellent activity for the combustion of toluene within a wide range of space velocities. It should be further mentioned that the definition of the space velocity is different from the one adopted for powdered catalysts often tested in laboratory studies. In this study, the space velocity was calculated based on the total monolith volume instead of only the volume of the active phase and support material (washcoat layer) loaded on the monolith. Clearly, the values of the space velocity will become larger if they are transformed into the latter form, e.g., the space velocity of 10000 h⁻¹ in this work corresponds to ca. 50000 h⁻¹ based on the volume of the active phase and support material of sample S3. Therefore, from a practical point of view, the optimum catalyst is a more useful catalyst for the abatement of toluene at a high space velocity.

3.5 Effect of the Oxygen/Toluene Ratio

Since the oxygen content is generally one of the key factors for combustion reactions, the effect of the oxygen/toluene ratio on the toluene conversion over the optimum catalyst was also studied. The experimental results are shown in Fig. 6. It can be seen that when the oxygen/toluene ratio has a low value of 6/1 or 9/1, the conversion of toluene amounts to only 70.0 or
89.4%, respectively, at the highest reaction temperature examined, i.e., 390 °C. It is also seen that the $T_{10}$ temperature decreases with an oxygen/toluene ratio up to 16.6/1 and then increases on further increasing the oxygen/toluene ratio to 20/1. These results indicate that a proper oxygen/toluene ratio of 16.6/1 results in the highest catalytic activity for the combustion of toluene.

It is known from the thermodynamic effect, that increasing the oxygen/toluene ratio promotes the conversion of toluene, resulting in a better catalytic activity for the combustion of toluene. On the other hand, with the increase of the oxygen/toluene ratio, a significant amount of excess oxygen covers the catalytically active sites, and thus, the adsorption of toluene molecules may be hindered on these sites, producing a negative effect on the toluene conversion. In particular, under a large oxygen/toluene ratio, the adsorption effect may become far more important than the thermodynamic effect, which possibly explains why the catalytic activity decreases on increasing the oxygen/toluene ratio from 16.6/1 to 20/1.

It should be noted that the light-off curves obtained at the oxygen/toluene ratios of 12/1–20/1 are close to each other, as shown in Fig. 6. In particular, there are only minor discrepancies existing among the $T_{10}$ temperatures. Consequently, the catalyst shows a good catalytic performance within a wide range of oxygen/toluene ratios, although only the oxygen/toluene ratio of 16.6/1 gives the highest catalytic activity for the combustion of toluene.

### 3.6 Catalytic Stability

As indicated above, the optimum catalyst obtained has a satisfactory activity for the combustion of toluene. However, for the commercial application of the catalyst, its catalytic stability should be further investigated. For this purpose, the catalytic performance of a new replicate of sample S3, following the activation mentioned above, was evaluated at a reaction temperature of 300 °C for 10 h. The temperature leading to ca. 96.3% conversion of toluene, as obtained from Fig. 1, was selected in order to allow for the easy detection of possible catalyst deactivation. The other reaction conditions are identical with those described for Figs. 1, 3 and 4.

The evolution of the toluene conversion with the reaction time for the replicate catalyst is shown in Fig. 7. It can be seen that a 98.1% conversion of toluene is reached at the beginning of the test, which is fairly close to that obtained at 300 °C by the temperature-programmed reaction, as shown in Fig. 1. This demonstrates that reliable light-off curves have been obtained by the temperature-programmed method and that the experimental results have a satisfactory reproducibility in this study. As can also be seen from Fig. 7, the toluene conversion shows a small increase at the early stage of the combustion reaction, and is then maintained at ca. 99.7% for the overall time duration examined. These results indicate that no catalyst deactivation occurs under the conditions examined. Therefore, the optimum catalyst has not only an excellent catalytic activity but also a good catalytic stability for the combustion of toluene.

![Figure 7. Toluene conversion versus the reaction time over a replicate of sample S3 at a given reaction temperature of 300 °C.](http://www.cet-journal.com)

### 4 Conclusions

In this study, a series of copper-manganese-silver mixed-oxide catalysts supported on a washcoated ceramic monolith were examined for the catalytic combustion of toluene. As shown by experimental results, the copper-manganese-silver mixed oxides are very active for the toluene combustion, and the highest catalytic activity is achieved over a monolithic catalyst containing 14.7 wt % of washcoat and 21.2 wt % of active phase with an Ag/Cu/Mn molar ratio of 13.8/43.1/43.1. Moreover, the effects of the reaction conditions on the catalytic performance were investigated. It is found that the optimum catalyst has a good catalytic stability and can exhibit an excellent activity not only at a high space velocity but also within a wide range of oxygen/toluene ratios. Therefore, from a practical point of view, it could be a more useful catalyst for the abatement of VOCs.

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### References


