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Catalytic oxidation of toluene on Mn–containing mixed oxides prepared in reverse microemulsions

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Abstract

Catalytic combustion of toluene over Mn–containing mixed oxides has been investigated. The catalysts have been prepared by reverse microemulsion method and characterized by XRD, SEM and TPR. It is found that catalytic conversion of toluene on the Mn–Zr mixed oxides prepared by reverse microemulsion method is much higher than that on the Mn–Zr mixed oxides prepared by conventional coprecipitation with the same chemical compositions. The catalytic activity gradually increases with an increase of Mn loading on ZrO_2 prepared by reverse microemulsion method. When Mn loading reaches 50 mol%, the total conversion temperature is lowered to 260 °C. Heat treatment of the catalysts leads to the decrease in the activity of toluene conversion, however the toluene conversion remains still high, i.e., 99% at 320 °C after calcination up to 750 °C, which implies the catalyst is highly thermally stable. In addition, Fe–Mn, Co–Mn and Cu–Mn mixed oxides have also been synthesized by reverse microemulsion method, and tested for catalytic oxidation of toluene. Among these metal oxides, the Cu–Mn catalyst is found to give the highest activity for complete oxidation of toluene. $Mn_{0.67}$–$Cu_{0.33}$ (Cu loading 33 mol%) shows the total oxidation of toluene at about 220 °C, which is very close to the activity of the widely investigated Pd catalyst for the reaction.

Keywords: Manganese oxide; Toluene oxidation; Catalytic combustion; VOC; Microemulsion; Mixed oxides

1. Introduction

Volatile organic compounds (VOCs) emitted from industrial processes and automobile exhaust emissions are recognized as major contributions to air pollution because of their toxic properties and their involving in the formation of photochemical smog. Catalytic combustion at a lower temperature is an alternative route to eliminate VOCs, which can significantly reduce energy costs and formation of harmful by-products such as dioxins from chlorinated compounds and nitrogen oxides in contrast to thermal incineration [1]. Supported noble metals [2], metal oxides [3–5] and perovskite oxides [6,7] have been widely investigated for the combustion of VOCs.

Among these non-noble metal oxide catalysts investigated, manganese-containing catalysts are low cost, environmentally friendly and relatively highly active for the combustion of volatile organic compounds (VOCs). However, deactivation of the Mn-based catalyst is still challenging. On the other hand, Zarur and Ying have reported that microemulsion method is very useful to prepare high-surface-area materials and therefore significantly improve the activity for catalytic combustion of methane [8]. Indeed it has been recently found in our laboratory that ZrO_2 and MnO_x–ZrO_2 mixed oxides prepared in reverse microemulsion shows higher specific surface areas, that is 464 m^2/g for ZrO_2 calcined at 450 °C [9] and 305 m^2/g MnO_x–ZrO_2 [10] calcined at 450 °C, respectively, as compared to the samples prepared with conventional precipitation method. Based on the experiences from the recent works in our laboratory with manganese-containing mixed oxides for the catalytic combustion of methane [11–13], we hope the Mn–containing mixed oxides are useful for developing a stable catalyst with low costs and high activity for catalytic oxidation of VOCs.

Therefore, in this presentation, a series of the mixture of MnO_x/ZrO_2, MnO_x/Fe_2O_3, MnO_x–CoO_x and MnO_x/CuO_x with high surface areas have been prepared in reverse microemulsions. Thereafter toluene, one of major volatile organic compounds in the atmosphere, was chosen for the catalytic combustion test on these above samples.

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2. Experimental

2.1. Synthesis of MnO_x/ZrO_2

Two aliquots of reverse microemulsions of H_2O/TritonX-100/*n*-octanol/cyclohexane with the identical molar ratio as 1:0.06:0.30:1.66 were first prepared, of which one contained an appropriate amount of 25 wt.% aqueous hydrous ammonia and the other contained a mixed aqueous solution of zirconyl chloride and manganese nitrate. They were thoroughly mixed and stirred for 1 h, thereafter the precipitates were obtained after distilling for 2 h, followed by filtering and washing with ethanol and water to eliminate excess organic species and chloride ions. The white powders were then obtained after drying at 100 °C in air and calcining at 450–1000 °C in oxygen. The sample was then crushed and sieved to 100–150 meshes and ready for the catalyst activity tests. The sample was denoted as Mn_xZr_{1-x}, where the subscript x corresponds to the Mn versus Zr atomic composition in the samples. For a reference, a mixed aqueous solution of zirconyl chloride and manganese nitrate were used to coprecipitate with a solution of 25 wt.% aqueous hydrous ammonia to obtain 40 mol% MnO_2 in the final Mn/ZrO_2 sample, which was denoted as $Mn_{0.4}Zr_{0.6}$–CP.

2.2. Synthesis of Mn–M (M = Fe, Co or Cu) mixed oxides

The similar synthesis procedure was used to prepare the Mn–Fe, Mn–Co and Mn–Cu mixed oxides except that an aqueous solution of $Fe(NO_3)_3$, $Co(NO_3)_2$ or $Cu(CH_3COO)_2$ was used to replace an aqueous solution of $Zr(NO_3)_4$ for the synthesis of MnO_x/ZrO_2 in Section 2.2. The post-treatment of the samples were the same with that for the Mn_xZr_{1-x} mixed oxides above. Each samples was denoted as Mn_xM_{1-x}, where the subscript x corresponds to the Mn versus M (M = Fe, Co or Cu) atomic composition in the samples.

2.3. Characterization of the catalysts

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/max RB X-ray diffractometer using nickel-filtered Cu Kα ($\lambda = 0.15404$ nm) radiation. The step scans were taken over the range of 2θ angels from 20° to 70° in steps of 0.02°, the intensity data for each step being collected for 5 s. Scanning electron microscope (SEM) combined with element detection (EDX) was taken on the JSM-6301F instrument with pre-coating samples with gold. Nitrogen adsorption and desorption isotherms were measured at −196 °C on Quantachrome Autosorb-1 Analyzer after the sample was outgassed at 450 °C for 12 h, and the specific surface area was calculated by the BET method.

The TPR experiments were collected in a conventional flow apparatus equipped with a TC-detector. The sample was pretreated at 200 °C for 1 h in 40 cm^3/min (STP) before reduction. A 45 ml min^{-1} (NTP) gas flow of 5% H_2 in N_2 passed over 35 mg samples in a quartz reactor to the detector. The reduction temperature was linearly raised at 10 °C min^{-1} from 20 to 800 °C, and then kept at 800 °C for 20 min. In order to calibrate the TPR peak areas, a known volume of H_2 were injected in a pure N_2 flow.

2.4. Catalytic activity measurements

Catalytic activities were measured in a 10 mm i.d. quartz tubular reactor. The reaction mixture consisting of toluene (0.35 vol.%), O_2 (9 vol.%) and argon (balance gas) was passed continuously through a 0.1 g catalyst sample bed with a total flow rate of 60 ml/min of argon. The inlet and outlet gas compositions were analyzed after stepwise changes in the reaction temperatures by on-line gas chromatograph (Shimatzu 14B) with an FID detector using a Porapak Q column.

3. Results and discussion

3.1. Catalytic activities on the Mn_xZr_y catalysts

Catalytic activities of toluene oxidation were measured as a function of reaction temperature on a series of Mn–Zr mixed oxides. In Fig. 1, it is shown that catalytic conversion of toluene on $Mn_{0.4}Zr_{0.6}$ prepared by microemulsion method after calcination at 450 °C is much higher than that on the $Mn_{0.4}Zr_{0.6}$–CP prepared by coprecipitation with the same chemical compositions, i.e., 99% of conversion of toluene was obtained at 270 °C on $Mn_{0.4}Zr_{0.6}$ as compared to 95% of the conversion at 290 °C on $Mn_{0.4}Zr_{0.6}$–CP. The BET specific surface areas are 250 and 130 m^2/g for $Mn_{0.4}Zr_{0.6}$ and $Mn_{0.4}Zr_{0.6}$–CP, respectively, after calcinations of the samples at 450 °C.

Fig. 2 shows SEM images of the $Mn_{0.4}Zr_{0.6}$ sample after calcinations at 450 °C and 900 °C. It is clear that a uniform morphology was observed on the sample after thermal treatment at 450 °C, further heating the sample up to 900 °C led to the spherical morphology with the uniform diameter at ca. 25 nm. Considering an apparent growth of $Mn_{0.4}Zr_{0.6}$ particles by a sintering process as shown later by

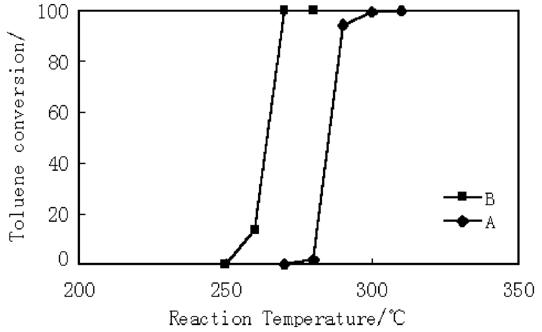

Fig. 1. Toluene conversion vs. reaction temperatures over $Mn_{0.4}Zr_{0.6}$–CP (A) and $Mn_{0.4}Zr_{0.6}$ (B).

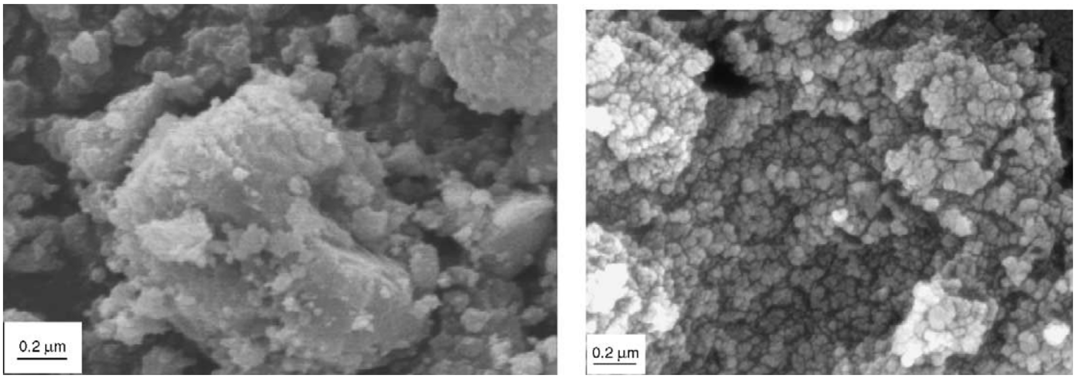

Fig. 2. SEM images of the $Mn_{0.4}Zr_{0.6}$ sample calcined at 450 °C (left) and 900 °C (right).

XRD analysis in Fig. 6, it is inferred that the samples calcined at a lower temperature of 450 °C composed of much smaller particles with more uniform particle sizes. That is in agreement with the high surface areas analyzed by nitrogen adsorption/desorption, and hence results in the high activity of toluene oxidation. In addition, EDX analysis revealed a good dispersion of the manganese on the zirconia (data not shown). It was difficult to detect any area with the significantly different Mn/Cu molar ratio. The uniform mixture of Mn and Cu species could be another reason responsible for the high activity of toluene conversion on the sample prepared by microemulsion method.

TPR analysis usually shows the degree of oxidation of the metal from calculation of the quantity of hydrogen consumed, and highlights the possible species produced during calcinations and thus shows the interaction of the different species on the metal oxides. TPR experiments were performed on $Mn_{0.4}Zr_{0.6}$ and $Mn_{0.4}Zr_{0.6}$–CP as shown in Fig. 3. Three H_2-consumption peaks at 330, 430 and 560 °C were observed on $Mn_{0.4}Zr_{0.6}$–CP, while other three peaks at 322, 400 and 560 °C were observed on $Mn_{0.4}Zr_{0.6}$. The differences in the TPR profiles between the two catalysts lie in the two lower temperature peaks of the two TPR profiles. In the case of $Mn_{0.4}Zr_{0.6}$–CP, the first two peaks are very similar to that exhibited by bulk manganese oxide prepared by either coprecipitation or microemulsion method, while the third peak that is almost same with that on $Mn_{0.4}Zr_{0.6}$ is associated with ziconia species; In the case of $Mn_{0.4}Zr_{0.6}$, the two lower temperature peaks shifted towards lower reduction temperatures as compared to that for $Mn_{0.4}Zr_{0.6}$–CP, suggesting that the easier reduction of manganese oxide for the sample prepared through incorporation of well dispersed Zr species into manganese species by the microemusion method.

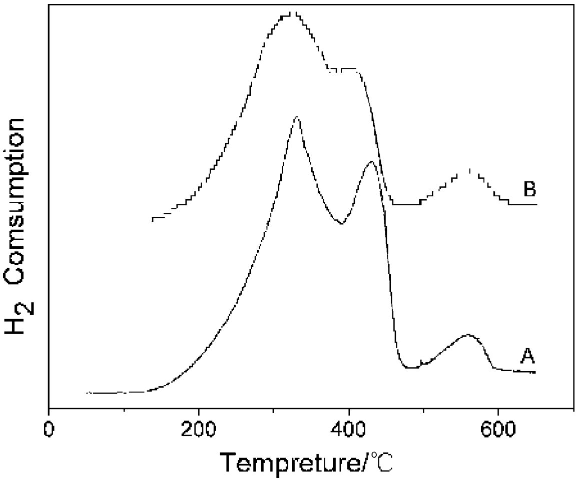

Fig. 3. TPR profiles of $Mn_{0.4}Zr_{0.6}$ (A) and $Mn_{0.4}Zr_{0.6}$–CP (B).

3.2. Effect of the Mn/Zr molar ratios

Fig. 4 shows toluene conversion versus reaction temperature over the Mn–Zr mixed oxides calcined at 450 °C with various Mn/Zr molar ratios. It is clear that the catalytic activity gradually increases with an increase of Mn content mixed with ZrO_2 prepared by reverse microemulsion method. For the $Mn_{0.2}Zr_{0.8}$ sample with 20 mol% Mn, the conversion of toluene was 86% at 300 °C; In the case of $Mn_{0.5}Zr_{0.5}$, with the Mn content increasing to 50 mol%, the temperature for 95% of the conversion of toluene was lowered to 260 °C. As expected, the result indicates that manganese species are the active component on the catalysts for the oxidation of toluene.

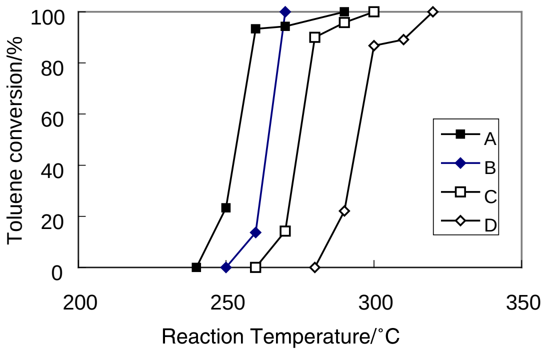

Fig. 4. Toluene conversion vs. reaction temperature over the Mn–Zr mixed oxides calcined at 450 °C with various Mn/Zr molar ratios: (A) Mn/Zr = 1:1; (B) Mn/Zr = 2:3; (C) Mn/Zr = 3:7; (D) Mn/Zr = 1:4.

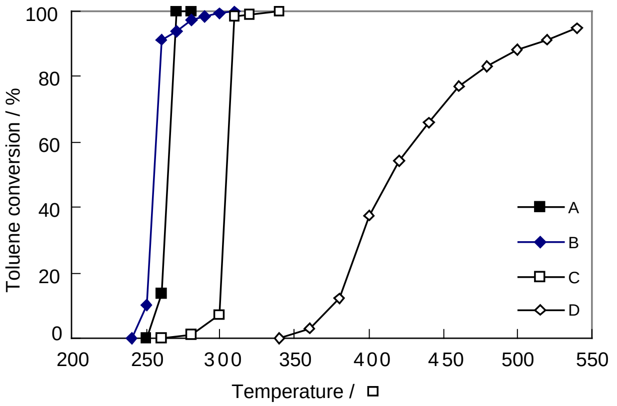

Fig. 5. Toluene conversion vs. reaction temperature over the $Mn_{0.4}Zr_{0.6}$ sample calcined at various temperatures: (A) 450 °C; (B) 600 °C; (C) 750 °C; (D) 900 °C.

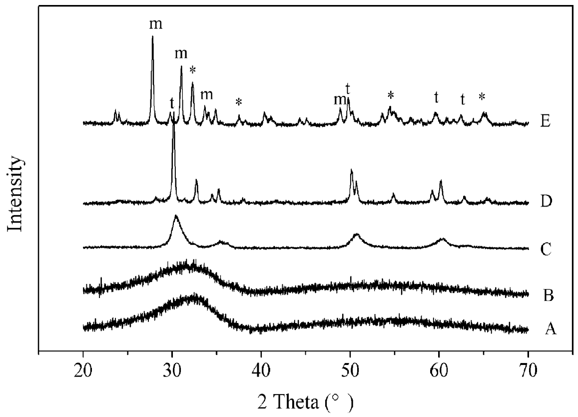

Fig. 6. XRD patterns of the $Mn_{0.4}Zr_{0.6}$ sample calcined at various temperatures: (A) 450 °C; (B) 600 °C; (C) 800 °C; (D) 900 °C; (E) 1000 °C. Note—t: tetragonal, m: monoclinic, ∗: Mn_2O_3.

3.3. Effect of calcination temperatures

As calcination of the catalysts leads to sintering of manganese oxide particles, we examined the effect of calcination temperatures of the samples on the catalytic activities in combustion of toluene. We compared the activity of the $Mn_{0.4}Zr_{0.6}$ catalyst calcined at 450–900 °C as shown in Fig. 5, and tried to estimate the stability of the catalyst activity. We found that heat treatment of the $Mn_{0.4}Zr_{0.6}$ catalysts led to the decrease in the activity of toluene conversion as expected. It is shown that the temperature for 99% of toluene conversion increased to 320 °C after calcination up to 750 °C as compared to the value of 260 °C for 92% of toluene conversion. When further heating the catalyst up to 900 °C, a much higher temperature, i.e., 540 °C, was needed for 95% of toluene conversion. From Fig. 1, it is clear that the activity of toluene conversion remained high, after calcination of the $Mn_{0.4}Zr_{0.6}$ sample up to 750 °C, which implies the catalyst is relatively thermally stable.

The crystallite structures of the $Mn_{0.4}Zr_{0.6}$ catalyst after calcinations at elevated temperatures were revealed by XRD analysis as shown in Fig. 6. It is observed that below 600 °C, the catalyst was amorphous or nano-crystallite due to their crystal sizes below the value of detection limit of the X-ray technique. When heating the catalyst to 800 °C, the XRD patterns of the samples showed only the characteristic peaks of tetragonal zirconia; Further heating to 900 °C, the single tetragonal phase of zirconium oxide remained unchanged although the peak intensity of the XRD pattern became more sharp, indicating the growth of the crystal sizes of the sample; Heating the catalyst up to 1000 °C led to more complex crystallite structures, i.e., a dominant amount of monoclinic zirconia was appeared together with a trace amount of Mn_2O_3 and tetragonal phase of zirconia. From Fig. 6, It is inferred that the interaction between MnO_x and ZrO_2 would restrained the phase transformation of tetragonal zirconia into monoclinic zirconia phase as well as retarding the sintering of the sample because of the better dispersion of MnO_x species on ZrO_2 during the synthesis process. It is proposed that the sintering of the catalyst may play a major role in the deactivation of the $Mn_{0.4}Zr_{0.6}$ catalyst with the temperature increase during calcinations of the catalyst.

Fig. 7 shows the catalytic activities on the $Mn_{0.5}Zr_{0.5}$ catalyst versus time on stream. It is clearly seen that the conversion of toluene remained around 95% within 26 h. The result indicates that the $Mn_{0.5}Zr_{0.5}$ catalyst prepared by microemulsion method is relatively stable catalyst. The further longevity test of the catalysts is in progress in our laboratory.

3.4. Effect of adding MO_x (M = Fe, Co or Cu) into manganese oxides

As shown in Fig. 4, the catalytic activity increases with an increase of Mn content mixed with ZrO_2 prepared by reverse microemulsion method. Based on the results above, the pure manganese oxide was assumed to have a higher activity and therefore prepared by microemulsion method and then tested for the catalytic oxidation of toluene. The results are shown in Table 1 where ignition temperature and combustion temperature are referred to the tempera-

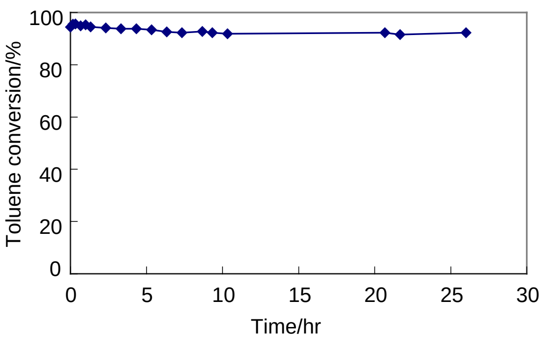

Fig. 7. Toluene conversion vs. reaction time on stream over the $Mn_{0.5}Zr_{0.5}$ sample calcined at 450 °C. Experimental conditions: 0.35% C_7H_8, 8.8% O_2, and argon as balance gas, 0.1 g of catalyst.

Table 1
Activity of toluene oxidation over manganese oxides doped with Co, Ce, and Fe in comparison with that on the $Mn_{0.4}Zr_{0.6}$ sample

Sample	Molar ratio	Activity of toluene oxidation	
		Ignition temperature[a] (°C)	Combustion temperature[b] (°C)
$Mn_{0.4}Zr_{0.6}$	Mn/Zr = 2:3	255	280
Mn_2O_3	–	260	280
$Mn_{0.4}Fe_{0.6}$	Mn/Fe = 2:3	280	300
$Mn_{0.4}Co_{0.6}$	Mn/Co = 2:3	250	270
$Mn_{0.4}Cu_{0.6}$	Mn/Cu = 2:3	230	240
$Mn_{0.67}Cu_{0.33}$	Mn/Cu = 2:1	210	220

[a] Ignition temperature is referred to the temperature where the toluene conversion reaches around 3%.

[b] Combustion temperature is referred to the temperature where the toluene conversion reaches above 98%.

ture where the toluene conversion reaches around 3% and 98%, respectively. It seems that both ignition temperature and the combustion temperature are very similar with that for the $Mn_{0.4}Zr_{0.6}$ sample. Furthermore, Fe, Co, Cu oxide species were mixed with manganese oxide by microemulsion method. These samples were then tested for the catalytic oxidation of toluene after heat treatment of these samples at 450 °C in air, and the results were also shown in Table 1. It is found that addition of iron oxide into manganese oxides led an increase in both the ignition temperature and the combustion temperature for the catalytic oxidation of toluene. On the other hand, addition of cobalt oxide or copper oxide into manganese oxide resulted in a decrease in the two values for the catalytic oxidation of toluene. Specially, it is noteworthy that among all these mixed oxide catalysts the $Mn_{0.67}Cu_{0.33}$ sample showed a lowest temperature (i.e., 220 °C), which is very close to that on a commercial 0.5 wt.% Pd/Al_2O_3 [2]. The further works on this type of catalysts are under way in our laboratory.

4. Conclusion

In conclusion, catalytic conversion of toluene on the Mn–Zr mixed oxides prepared by reverse microemulsion method is much higher than that on the Mn–Zr mixed oxides prepared by conventional coprecipitation with the same chemical compositions. The catalytic activity is closely related with Mn content in the Mn–Zr mixed oxides prepared by microemulsion method, which indicates manganese species are the active sites for the reaction as expected. Heat treatment of the catalysts led to the decrease in the activity of toluene conversion, however the toluene conversion remained still high, i.e., 99% at 320 °C after calcination up to 750 °C, which implied the catalyst was highly thermally stable. In addition, Fe–Mn, Co–Mn and Cu–Mn mixed oxides were also synthesized by reverse microemulsions method, and tested for catalytic oxidation of toluene. Among these metal oxides, the Cu–Mn catalyst gives the highest activity for complete oxidation of toluene. $Mn_{0.67}$–$Cu_{0.33}$ (Cu loading 33 mol%) shows the total oxidation of toluene at about 220 °C, which is very close to the activity of the widely investigated Pd catalyst for the reaction. It was proposed that the best dispersion of the active phase resulting from preparation of the catalysts by microemulsion method may contribute significantly to the highly activity of toluene oxidation over the mixed oxide catalysts presented in this report.

Acknowledgements

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