AuRu/meso-Mn$_2$O$_3$: A Highly Active and Stable Catalyst for Methane Combustion

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Abstract. Three-dimensionally ordered mesoporous Mn$_2$O$_3$ (meso-Mn$_2$O$_3$) and its supported Au, Ru, and AuRu alloy (0.49 wt% Au/meso-Mn$_2$O$_3$, 0.48 wt% Ru/meso-Mn$_2$O$_3$, and 0.97 wt% AuRu/meso-Mn$_2$O$_3$ (Au/Ru molar ratio = 0.98)) nanocatalysts were prepared using the KIT-6-templating and polyvinyl alcohol-protected reduction methods, respectively. Physicochemical properties of the samples were characterized by means of numerous techniques, and their catalytic activities were evaluated for the combustion of methane. It is found that among all of the samples, 0.48 wt% Ru/meso-Mn$_2$O$_3$ and 0.97 wt% AuRu/meso-Mn$_2$O$_3$ performed the best (the reaction temperature ($T_{90\%}$) at 90% methane conversion was 530–540°C), but the latter showed a better thermal stability than the former. The partial deactivation of 0.97 wt% AuRu/meso-Mn$_2$O$_3$ due to H$_2$O or CO$_2$ introduction was reversible. It is concluded that the good catalytic activity and thermal stability of 0.97 wt% AuRu/meso-Mn$_2$O$_3$ was associated with the high dispersion of AuRu alloy NPs (2–5 nm) on the surface of meso-Mn$_2$O$_3$ and good low-temperature reducibility.

1. Introduction

As the main component of natural gas, methane shows much higher greenhouse effect than CO$_2$[1], and more serious pollutants, such as CO, NO$_x$, and unburned hydrocarbons, are usually detected in the outlets of methane flame combustion [2]. Catalytic combustion is considered to be one of the most promising approaches for the suppression of the pollutants, in which the key issue is the availability of high-performance and stable catalysts. Hence, the development of novel high-efficiency and stable catalysts is of practical significance. Supported noble metals (e.g., Au, Pd, Pt, and Ru) perform well at low temperatures, but they are poor in high-temperature stability. Although the Pd-based catalysts show good catalytic performance for methane combustion at low temperatures, these materials have some major drawbacks: (i) Pd-based catalysts often have a poor stability in the steady-state methane combustion processes [3,4]; and (ii) exposure of Pd-based catalysts to water or sulfur-containing compounds may cause a significant loss in activity via formation of inactive Pd(OH)$_2$ and stable Pdsulfate phases [5–7]. To overcome these problems, a second metal is expected to be added to palladium to generate a bimetallic alloy catalyst. For instance, the doping of Pt to Pd could increase low-temperature methane combustion activity,
hinder the growth of Pd or PdO particles [8], improve the catalyst thermal stability [9,10], and enhance the resistant ability of sulfur or water vapor poisoning [7]. Transition-metal oxides (e.g., MnO₂ [11,12] and CoO [13]) have also been used as catalyst for methane combustion, among which MnO₂ has widely been studied and considered as alternative catalysts due to their multiple oxidation states and oxygen vacancies [14]. For example, Han et al. [12] observed that the complete conversion of methane could be achieved over α-MnO₂ at ca. 600 °C, and this catalyst exhibited ultrahigh stability. Three-dimensionally ordered mesoporous MnO₂ (meso-MnO₂) possesses a higher surface area and good redox ability, thus suitable for the use of catalyst and support. A high surface area is beneficial for the dispersion of active sites on the support surface, and a uniform pore size is favourable for the inhibition of agglomeration of noble metal nanoparticles (NPs), hence improving the high-temperature stability of the supported noble metal catalyst.

Herein, we report the preparation of meso-MnO₂-supported AuRu alloy nanocatalysts and their catalytic performance for methane combustion. It is found that the AuRu/meso-MnO₂ catalyst was highly active and stable under the adopted reaction conditions.

2. Experimental

2.1. Catalyst preparation

Mesoporous silica (KIT-6) was synthesized by adopting the procedures described in the literature [15]. Ordered mesoporous MnO₂ was synthesized according to the method reported previously [16]. In a typical synthesis, 1.0 g of KIT-6 was suspended in 50 mL of n-hexane. After stirring at 65 °C for 0.5 h, 20.00 mmol of Mn(NO₃)₂; aqueous solution (50 wt%) was added under vigorous stirring. The mixture was further stirred at 65 °C for 3 h. Then, the powders were obtained after filtration and drying at room temperature (RT). The precursor@silica composite was put in a crucible, and then calcined in a muffle furnace at a ramp of 1 °C/min from RT to 600 °C and kept at this temperature for 6 h. The silica template was removed by etching twice with a hot NaOH aqueous solution (2.00 mol/L). The template-free mesoporous MnO₂ (meso-MnO₂) was obtained after centrifugation, washing with deionized water and ethanol, and drying at 80 °C.

The meso-MnO₂-supported gold–ruthenium alloy nanocatalyst was prepared via a polyvinyl alcohol (PVA, MW_{av} = 10,000 g/mol)-protected reduction route with NaBH₄ as reducing agent [17]. The typical preparation procedures were as follows: A desired amount of PVA was added to the HAuCl₄ and RuCl₃ mixed aqueous solution (100 mg/L, theoretical Au/Ru molar ratio = 1.0 : 1.0, noble metal/PVA mass ratio = 2.0 : 3.0) in an ice bath under vigorous stirring for 30 min. A certain amount of NaBH₄ aqueous solution (0.1 mol/L, noble metal/NaBH₄ molar ratio = 1.0 : 5.0) was quickly added to the above mixed solution, generating a dark brown noble metal sol. Then, a desired amount of meso-MnO₂ powders was added to the noble metal sol (theoretical Au–Ru loading = 1.0 wt%) under stirring for 4 h. After that, the mixture was filtered, washed with deionized water, and dried at 80 °C for 12 h. The dried powders were then calcined in a muffle furnace at a ramp of 1 °C/min from RT to 600 °C and kept at this temperature for 6 h, thus obtaining the xAuRu/meso-MnO₂ samples.

For comparison purposes, the xAu/meso-MnO₂ (theoretical Au loading = 0.5 wt%) and xRu/meso-
MnO₂ (theoretical Ru loading = 0.5 wt%) samples were also prepared using the above-mentioned method. The results of inductively coupled plasma atomic emission spectroscopic (ICP–AES) investigations reveal that the real loading (x) of noble metals was 0.97, 0.49, and 0.48 wt% in the xAuRu/meso-MnO₂, xAu/meso-MnO₂, and xRu/meso-MnO₂ samples, respectively; and the real Au/Ru molar ratio in the xAuRu/meso-MnO₂ sample was 0.98.

2.2. Catalyst characterization

X-ray diffraction (XRD) patterns of the samples were recorded on a Bruker D8 Advance diffractometer with Cu Ka radiation and nickel filter (λ = 0.15406 nm). Elemental analyses of the noble metal loadings were performed using the ICP–AES technique on a Thermo Electron IRIS Intrepid ER/S spectrometer. Transmission electron microscopic (TEM) images of the samples were
obtained using the JEOL-2010 equipment (operating at 200 kV). BET (Brunauer-Emmett-Teller) surface areas of the samples were measured via N₂ adsorption at −196 °C on a Micromeritics ASAP 2020 analyzer with the samples outgassed at 250 °C for 2.5 h under vacuum before measurement, and their pore size distributions were calculated based on the desorption branches of the isotherms.

Hydrogen temperature-programmed reduction (H₂-TPR) experiments were carried out on a chemical adsorption analyzer (Autochem II 2920, Micromeritics). Before TPR measurement, ca. 0.050 g of catalyst (40–60 mesh) was loaded to a quartz fixed-bed U-shaped microreactor (i.d. = 4 mm) and pretreated in an O₂ flow of 20 mL/min at 250 °C for 1 h. After being cooled at the same atmosphere to RT, then with helium flow of 30 mL/min purge for other 15 min. Finally, the pretreated sample was exposed to a flow (50 mL/min) of 5% H₂−95% Ar (v/v) mixture and heated from RT to 600 °C at a ramp of 10 °C/min. The alteration in H₂ concentration of the effluent was monitored online by the chemical adsorption analyzer. The reduction peak was calibrated against that of the complete reduction of a known standard powdered CuO (Aldrich, 99.995%).

2.3. Catalytic evaluation
Catalytic activities of the samples were evaluated in a continuous flow fixed-bed quartz tubular microreactor (i.d. = 6.0 mm). To minimize the effect of hot spots, 50 mg of the sample (40–60 mesh) was diluted with 0.25 g of quartz sands (40–60 mesh). Before the test, each sample was treated in an oxygen flow of 20 mL/min at 250 °C for 1 h. The reactant mixture was composed of 2.5 vol% CH₄ + 20 vol% O₂ + 77.5 vol% N₂ (balance), and the total flow was 16.6 mL/min, thus giving a CH₄/O₂ molar ratio of 1/8 and a space velocity (SV) of ca. 20,000 mL/(g h)). In the case of CO₂ introduction, 5.0 vol% CO₂ from a CO₂ cylinder (balanced with N₂) was introduced to the reaction system through a mass flow controller. Furthermore, in the case of water vapor introduction, 3.0 vol% H₂O was introduced by passing the feed stream through a water saturator at a certain temperature. Reactants and products were analyzed online by gas chromatography (GC-14C, Shimadzu) equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD), using a stabilwaxB column (30 m in length) for methane separation and a Carboxen 1000 column (3 m in length) for permanent gas detection. The balance of carbon throughout the catalytic system was estimated to be 99.5%. Catalytic activities of the samples were evaluated using the temperatures (T₃₀%, and T₉₀%) required for achieving methane conversions of 50 and 90%, respectively. CH₄ conversion was defined as \((c_{\text{inlet}} - c_{\text{outlet}})/c_{\text{inlet}}\) × 100%, where the \(c_{\text{inlet}}\) and \(c_{\text{outlet}}\) are CH₄ concentrations of the inlet and outlet feed stream, respectively.

3. Results and discussion

3.1. Crystal phase composition, morphology, pore structure, and surface area
Figure 1 shows the wide- and small-angle XRD patterns of the samples. By comparing to the XRD pattern (JCPDS PDF# 41-1442) of the standard Mn₂O₃ sample, one can realize that all of the Bragg diffraction peaks (figure 1A) of each sample could be well indexed to a cubic meso-Mn₂O₃ crystal structure. Furthermore, only cubic Mn₂O₃ phase was detected in the meso-Mn₂O₃, Au/meso-Mn₂O₃, Ru/meso-Mn₂O₃, and AuRu/meso-Mn₂O₃ samples. This result might be due to low noble metal loadings and good dispersion of Au, Ru or AuRu NPs on the surface of meso-Mn₂O₃. As seen from figure 1B, there were two peaks at 2θ = 1.10° and 1.80° in the small-angle XRD pattern of the meso-Mn₂O₃ and AuRu/meso-Mn₂O₃ samples, indicating formation of ordered mesopores in the two samples. According to the Scherrer equation, the calculated crystallite sizes of meso-Mn₂O₃ in the samples were in the range of 19.6–20.2 nm (table 1).
Figure 1. (A) Wide-angle and (B) small-angle XRD patterns of (a) meso-Mn$_2$O$_3$, (b) 0.49Au/meso-Mn$_2$O$_3$, (c) 0.48Ru/meso-Mn$_2$O$_3$, and (d) 0.97AuRu/meso-Mn$_2$O$_3$.

Table 1. BET surface areas, pore volumes, average pore sizes, Mn$_2$O$_3$ crystallite sizes ($D_{Mn2O3}$), noble metal particle sizes, real Au or Ru contents, and real Au/Ru molar ratios of the samples.

| Sample                  | Surface area (m$^2$/g) | Pore volume (cm$^3$/g) | Average pore size (nm) | $D_{Mn2O3}$ (nm) | Real Au/Ru content$^b$ (wt%) | Real Au/Ru molar ratio$^b$ (mol/mol) |
|-------------------------|------------------------|------------------------|------------------------|------------------|-------------------------------|--------------------------------------|
| meso-Mn$_2$O$_3$        | 104.8                  | 0.36                   | 11.0                   | 19.6             | --/--                         | --/--                                 |
| 0.49Au/meso-Mn$_2$O$_3$ | 100.6                  | 0.34                   | 10.1                   | 20.2             | 0.49/--                       | --/--                                 |
| 0.48Ru/meso-Mn$_2$O$_3$ | 99.7                   | 0.34                   | 10.0                   | 20.1             | --/0.48                       | --/0.48                               |
| 0.97AuRu/meso-Mn$_2$O$_3$ | 98.8                  | 0.35                   | 9.9                    | 19.9             | 0.63/0.33                     | 0.98                                  |

$^a$ Data were calculated according to the Scherrer equation using the FWHM of the (222) line of Mn$_2$O$_3$.

$^b$ Data were determined by the ICP–AES technique.

Figure 2 shows the TEM images of meso-Mn$_2$O$_3$, 0.49Au/meso-Mn$_2$O$_3$, 0.48Ru/meso-Mn$_2$O$_3$, and 0.97AuRu/meso-Mn$_2$O$_3$. It can be clearly seen that all of the samples displayed an ordered mesoporous structure with an average pore size of 10–11 nm. Since the method for the synthesis of AuRu NPs was the same as that for the synthesis of AuPd NPs with an alloy structure [17], the obtained AuRu NPs would also possess an alloy structure. From the TEM images of the supported noble metal samples, one can observe that the noble metal particles were 2–5 nm in diameter. Figure 3 shows the N$_2$ adsorption–desorption isotherms and pore-size distributions of the samples. The meso-Mn$_2$O$_3$ and its supported noble metal samples displayed a type IV isotherm with a hysteresis loop in the relative pressure range of 0.5–1.0 (figure 3A), indicating generation of a mesoporous structure in these samples. From the pore-size distribution curves (figure 3B), one can observe two peaks in the ranges of 2–6 and 10–16 nm, respectively. As summarized in table 1, surface area of meso-Mn$_2$O$_3$ was 104.8 m$^2$/g. After loading of noble metal NPs, surface areas (98.8–100.6 m$^2$/g) of the 0.49Au/meso-Mn$_2$O$_3$,
0.48Ru/meso-Mn$_2$O$_3$, and 0.97AuRu/meso-Mn$_2$O$_3$ samples decreased only slightly. Pore volumes (0.34–0.36 cm$^3$/g) of all of the samples were also similar.

![TEM images of (a, b) meso-Mn$_2$O$_3$, (c, d) Au/meso-Mn$_2$O$_3$, (e, f) Ru/meso-Mn$_2$O$_3$, and (g, h) AuRu/meso-Mn$_2$O$_3$.](image)

**Figure 2.** TEM images of (a, b) meso-Mn$_2$O$_3$, (c, d) Au/meso-Mn$_2$O$_3$, (e, f) Ru/meso-Mn$_2$O$_3$, and (g, h) AuRu/meso-Mn$_2$O$_3$.

![Nitrogen adsorption–desorption isotherms and pore-size distributions of (a) meso-Mn$_2$O$_3$, (b) 0.49Au/meso-Mn$_2$O$_3$, (c) 0.48Ru/meso-Mn$_2$O$_3$, and (d) 0.97AuRu/meso-Mn$_2$O$_3$.](image)

**Figure 3.** (A) Nitrogen adsorption–desorption isotherms and (B) pore-size distributions of (a) meso-Mn$_2$O$_3$, (b) 0.49Au/meso-Mn$_2$O$_3$, (c) 0.48Ru/meso-Mn$_2$O$_3$, and (d) 0.97AuRu/meso-Mn$_2$O$_3$.

3.2. Reducibility

It is well known that, the reduction of Mn$_2$O$_3$ can be divided by the successive processes [18,19]: Mn$_2$O$_3$ → Mn$_3$O$_4$ → MnO. The reduction signals in the H$_2$-TPR profile may be detected due to the reduction of species at different local environments [19]. Figure 4 illustrates the H$_2$-TPR profiles of the samples and their H$_2$ consumptions are summarized in table 2. There were two main reduction peaks centered at 372 and 524 °C for the meso-Mn$_2$O$_3$ sample, attributable to the reduction of Mn$_2$O$_3$ to Mn$_3$O$_4$ and Mn$_3$O$_4$ to MnO [18–20], respectively. After loading of the noble metals, the reduction
peaks of the samples shifted to low temperatures, especially for the 0.48Ru/meso-Mn$_2$O$_3$ and 0.97AuRu/meso-Mn$_2$O$_3$ samples (111–112°C and 182–183°C, respectively), which was a result due to the strong interaction between the noble metal NPs and the meso-Mn$_2$O$_3$ support [21]. The H$_2$-TPR study demonstrates the improvement in low-temperature reducibility, which was due to the reduction of Mn$_2$O$_3$ promoted by the activated H atoms on the noble metals. The 0.48Ru/meso-Mn$_2$O$_3$ and 0.97AuRu/meso-Mn$_2$O$_3$ samples exhibited the best low-temperature reducibility. The total H$_2$ consumption (14.80 mmol/g$_{cat}$) of the meso-Mn$_2$O$_3$ sample was slightly higher than those (13.71–14.25 mmol/g$_{cat}$) of the meso-Mn$_2$O$_3$-supported noble metal samples.

### Table 2. H$_2$ consumptions and catalytic activities of the samples at SV = 20,000 mL/(g h).

| Sample         | H$_2$ consumption (mmol/g$_{cat}$) | Methane combustion activity |
|----------------|-----------------------------------|-----------------------------|
| meso-Mn$_2$O$_3$ | 14.80                             | 486                         | > 600                      |
| 0.49Au/meso-Mn$_2$O$_3$ | 13.71                             | 480                         | 580                        |
| 0.48Ru/meso-Mn$_2$O$_3$ | 13.84                             | 465                         | 530                        |
| 0.97AuRu/meso-Mn$_2$O$_3$ | 14.25                             | 470                         | 540                        |

#### 3.3. Catalytic performance

In the blank experiment (only quartz sands were loaded in the microreactor), no conversion of methane was detected at SV = 20,000 mL/(g h) and below 600 °C. In other words, there were no gas-phase reactions in the catalytic system under the adopted conditions. Fig. 5A and B shows the catalytic activities of the samples and the effect of SV on methane conversion over the 0.97AuRu/meso-Mn$_2$O$_3$ sample for methane combustion, respectively. It is observed that methane conversion monotonously
increased with the rise in temperature over meso-Mn$_2$O$_3$; however, methane conversion first increased, then decreased, and finally increased over the supported noble metal samples, which might be due to the active oxidized noble metal (AuO and/or RuO$_x$) on the surface of the sample decomposed to less active metallic noble metal (Au$^0$ and/or Ru$^0$) at 380–390°C and the metallic noble metal was re-oxidized to the oxidized noble metal above 400°C. Obviously, the loading of noble metal improved the catalytic performance of meso-Mn$_2$O$_3$. As shown in figure 5A and table 2, the meso-Mn$_2$O$_3$-supported Ru or AuRu sample performed the best: $T_{50\%}$ = 465°C and $T_{90\%}$ = 530°C over 0.48Ru/meso-Mn$_2$O$_3$; $T_{50\%}$ = 470°C and $T_{90\%}$ = 540°C over 0.97AuRu/meso-Mn$_2$O$_3$ at SV = 20,000 mL/(g h). From figure 5B, one can see that methane conversion decreased with the rise in SV, a result due to the shorting in contact time of the reactants with the catalyst.

![Graph](image-url)

**Figure 5.** (A) Methane conversion as a function of temperature over the samples at SV = 20,000 mL/(g h) and (B) effect of SV on methane conversion over the 0.97AuRu/meso-Mn$_2$O$_3$ sample.

| Catalyst               | Reaction condition | $T_{50\%}$ (°C) | $T_{90\%}$ (°C) | Ref.   |
|------------------------|--------------------|-----------------|-----------------|--------|
| meso-Mn$_2$O$_3$       | 2.5 vol% CH$_4$, SV = 20,000 mL/(g h) | 465             | 530             | Present work |
| 0.49Au/meso-Mn$_2$O$_3$| 2.5 vol% CH$_4$, SV = 20,000 mL/(g h) | 470             | 540             | Present work |
| La$_2$:Ag$_{0.3}$Mn$_3$O$_5$ | 1 vol% CH$_4$, SV = 10,000 mL/(g h) | 690             | 750             | [22]    |
| La$_2$:Sr$_2$:Mn$_3$O$_5$ | 1 vol% CH$_4$, SV = 10,000 mL/(g h) | 720             | 780             | [22]    |
| La$_2$:Ce$_{0.3}$Mn$_3$O$_5$ | 1 vol% CH$_4$, SV = 10,000 mL/(g h) | 740             | 810             | [22]    |
| 1.0 wt% Pd/Al$_2$O$_3$  | 5 vol% CH$_4$, SV = 30,000 mL/(g h) | 640             | 710             | [23]    |
| 1.0 wt% Pd/ZrO$_2$      | 5 vol% CH$_4$, SV = 30,000 mL/(g h) | 600             | 650             | [23]    |
| 1.1 wt% Pt/3DOM Ce$_0.5$Zr$_{0.5}$Y$_3$O$_2$ | 2 vol% CH$_4$, SV = 30,000 mL/(g h) | 479             | 598             | [24]    |

**Table 3.** Comparison on methane oxidation activity of the samples reported in the literature.
In the past years, a number of works on methane combustion over the Mn-based and supported noble metal catalysts have been reported in the literature, and their results are summarized in Table 3. Apparently, the $T_{50\%}$ and $T_{90\%}$ over 0.48Ru/meso-Mn$_2$O _3 or 0.97AuRu/meso-Mn$_2$O _3 were much lower than those over La$_{0.7}$Ag$_{0.3}$MnO$_3$ [22], La$_{0.7}$Sr$_{0.3}$MnO$_3$ [22], La$_{0.7}$Ce$_{0.3}$MnO$_3$ [22], 1.0 wt% Pd/Al$_2$O$_3$ [50], 1.0 wt% Pd/ZrO$_2$ [23], and 1.1 wt% Pt/3DOM Ce$_{0.6}$Zr$_{0.3}$Y$_{0.1}$O$_2$ [24].

3.4. Catalytic stability and effects of water and carbon dioxide on catalytic activity

Figure 6 shows the conversion of methane as a function of on-stream reaction time over the 0.48Ru/meso-Mn$_2$O$_3$ and 0.97AuRu/meso-Mn$_2$O$_3$ samples at SV = 20,000 mL/(g h). It is observed that methane conversion over the 0.48Ru/meso-Mn$_2$O$_3$ sample decreased from 90 to 67% after 30 h of on-stream reaction, however, there was no significant loss in catalytic activity over the 0.97AuRu/meso-Mn$_2$O$_3$ sample within 30 h of on-stream methane combustion. This result demonstrates that the 0.97AuRu/meso-Mn$_2$O$_3$ sample was catalytically more stable than the 0.48Ru/meso-Mn$_2$O$_3$ sample.

Alloying of Ru with Au could significantly promote the adsorption and activation of oxygen, possibly enhancing the migration of activated oxygen to the noble metal alloy–Mn$_2$O$_3$ interface, hence stabilizing the catalytic activity. The excellent catalytic stability of 0.97AuRu/meso-Mn$_2$O$_3$ might be associated with its enhanced oxygen activation ability and better low-temperature reducibility.

**Figure 6.** Methane conversion versus on-stream methane oxidation time over (A) 0.48Ru/meso-Mn$_2$O$_3$ and (B) 0.97AuRu/meso-Mn$_2$O$_3$ at SV = 20,000 mL/(g h).
Figure 7. Effect of 3.0 vol% H₂O or 5.0 vol% CO₂ on methane conversion over the 0.97AuRu/meso-Mn₂O₃ sample at SV = 20,000 mL/(g h).

To examine the effects of water vapor and carbon dioxide on catalytic activity, we conducted the combustion of methane over 0.97AuRu/meso-Mn₂O₃ sample in the presence of 3.0 vol% H₂O or 5.0 vol% CO₂, and the results are shown in Fig. 7. It is clearly observed that with the introduction of 3.0 vol% H₂O or 5.0 vol% CO₂ to the reaction system, methane conversion over 0.97AuRu/meso-Mn₂O₃ decreased by 6 or 4%, respectively; after 3.0 vol% H₂O or 5.0 vol% CO₂ was cut off, however, methane conversion was restored to their original value in the absence of H₂O or CO₂. The partial deactivation of this sample was due to formation of hydroxyls or carbonates on the surface of the meso-Mn₂O₃ support that could hinder the oxygen exchange between the support and active sites [28]. The above results indicate that the partial deactivation of the 0.97AuRu/meso-Mn₂O₃ sample due to H₂O or CO₂ addition was reversible.

4. Conclusions
3D ordered meso-Mn₂O₃ and its supported Au, Ru, and AuRu alloy (0.49Au/meso-Mn₂O₃, 0.48Ru/meso-Mn₂O₃, and 0.97AuRu/meso-Mn₂O₃) nanocatalysts could be prepared via the KIT-6-templating and PVA-protected reduction routes, respectively. The meso-Mn₂O₃ support possessed a cubic crystal structure and an ordered mesoporous architecture. The noble metal nanoparticles were highly dispersed on the surface of meso-Mn₂O₃, and the AuRu in 0.97AuRu/meso-Mn₂O₃ was possibly present in an alloy. Among all of the samples, 0.48Ru/meso-Mn₂O₃ and 0.97AuRu/meso-Mn₂O₃ showed the highest catalytic activity (T₉₀% = 530–540°C), but the latter exhibited a better thermal stability than the former. Furthermore, the partial deactivation of 0.97 wt% AuRu/meso-Mn₂O₃ due to H₂O or CO₂ addition was reversible. It is concluded that high dispersion of AuRu alloy NPs (2–5 nm) on the surface of meso-Mn₂O₃ and good low-temperature reducibility were responsible for the good catalytic activity and thermal stability of 0.97 wt% AuRu/meso-Mn₂O₃.

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