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COMMUNICATION

Novel Rh-substituted hexaaluminate catalysts for N₂O decomposition

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Novel Rh-substituted hexaaluminate catalysts were prepared for the first time for N₂O decomposition as green propellant. The catalytic tests revealed that $x = 0.3$ of Rh content into BaRh_xMn_{1-x}Al₁₁O₁₉ structure is able to decompose N₂O from 250 °C and maintain the stability at 1200 °C as adiabatic temperature.

Nitrous oxide (N₂O) has been recognized as a potential contributor for destruction of the ozone in the stratosphere and acknowledged as a relatively strong greenhouse gas.^{1,2} The continuous increase of its concentration, both due to natural and anthropogenic sources (adipic acid production, nitric acid production, fossil fuels and biomass burning) and longer atmospheric residence time (150 years), entails the need to develop efficient catalysts for its decomposition to nitrogen and oxygen. The N₂O catalytic decomposition has been intensively studied over several catalysts.^{3–8} However, the catalytic activity towards N₂O decomposition would be significantly affected by various gases that coexist in real exhaust or flue gases. For instance, the presence of excess oxygen is one of the causes for catalyst inhibition.⁵ It is essential to synthesize active catalysts for N₂O decomposition at low temperature. For example, spinels,^{9–11} ex-hydrotalcites,^{12,13} zeolite-based catalysts¹⁴ or alumina supported noble metal (Ir and Rh) catalysts^{15,16} are active at around 400 °C. The most catalysts were instable at high temperatures. In fact, the total degradation of these samples were engendered at above 1200 °C due to structural collapse, phase transformation, sintering phenomena or active phase volatility.¹⁷ Metal-substituted hexaaluminates are considered as promising materials for the catalytic decomposition at high temperatures.^{18–20} It was believed that the high surface area of hexaaluminate supports was necessary to maintain a superior catalytic performance in high temperature catalytic applications above 1200 °C, typically for decomposition of green propellants. Recently, an adequate Ir-hexaaluminate catalyst was developed by Zhu et al. which can initiate N₂O decomposition

at 350 °C.¹⁷

Introduced metal content into hexaaluminate catalysts were tested on N₂O abatement.^{21–24} In fact, Mn, Fe and Ni were proposed as transition metals for substituted-hexaaluminates which were active only at temperatures higher than 600 °C.

The activity of spinel and hexaaluminate catalysts can be improved by the incorporation of noble metals into frameworks without influence on the novel catalytic properties. However, a little study has been performed on the reactions other than methane combustion and biomass gasification catalyzed by metal-substituted hexaaluminates.^{25–27}

Since Rh/Al₂O₃ has been reported as a highly active catalyst for N₂O catalytic decomposition,¹² novel Rh-substituted hexaaluminate catalysts were prepared to achieve main goals: high catalytic activity at low temperatures and thermal stability at high temperatures. The catalysts have been characterized by sensitive physico-chemical techniques such as; X-ray diffraction (XRD), N₂-physisorption, Inductively coupled plasma (ICP) and H₂ temperature-programmed reduction (TPR).

Several samples of BaRh_xMn_{1-x}Al₁₁O₁₉ ($x = 0-1$) were synthesized by co-precipitation at 60 °C. RhCl₃ was used as precursor, mixed with urea. The thermal treatment was conducted through drying overnight at 120 °C and calcination in air at 1200 °C for 8 h after precipitation was occurred. Then, 3 % Rh loading has been deposited by wet impregnation into BaMnAl₁₁O₁₉ hexaaluminate (denoted: Rh/H) and on alumina (denoted: Rh/A). Rh/H was calcined (air/Ar) and reduced (H₂/Ar) for 4 h. However, Rh/A was calcined (air/Ar) at 1200 °C for 4 h and reduced (H₂/Ar) at 450 °C.

Catalytic tests were performed in isothermal mode in a quartz fixed bed flow-reactor. The catalysts were tableted, pulverized and sieved into 30-50 mesh and placed into the reactor. A mass of 200 mg of catalyst samples were pretreated for 30 min at 450 °C in N₂ and cooled down. Catalysts were then preheated at 450 °C for 1 h in O₂ flow to eliminate the adsorbed impurities. Finally, the system; reactor and catalyst; was cooled down to room temperature. N₂O/He mixture (1000 ppm) was used with a total gas flow of 100 ml min⁻¹ (GHSV = 20000 h⁻¹). Moreover, re-startability test of the most active hexaaluminate catalyst has been performed. The catalyst was preheated at different initial temperatures in the range

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† Electronic Supplementary Information (ESI) available: ICP measurements, textural properties of BaRh_xMn_{1-x}Al₁₁O₁₉, and H₂-TPR profiles of Rh/A and BaRh_{0.3}Mn_{0.7}Al₁₁O₁₉ catalysts. See DOI: 10.1039/x0xx00000x

of 300–450 °C. The N₂O conversion was measured for four cycles at same temperature. The gas composition was analyzed by GC-MS-2010 Plus (Shimadzu) chromatograph equipped with 5 Å molecular sieves and Porapak Q columns, and a TCD detector (SRI 310 CG). The reaction progress was monitored by mass fragmentation (*m/z*) to identify different species. For allowing accurate measurement of catalytic conversion of the intrinsic reaction kinetics, the effect of all transport limiting phenomena was avoided. In fact, the absence of mass transport limitations was confirmed by experiments and by satisfying the four dimensionless criteria published by Kapteijn et al.²⁸ Furthermore, a flat velocity profile and a negligible axial dispersion can be assumed because the velocity profile $d_i/d_p \approx 40$ and axial dispersion $L/d_p \approx 100$,²⁸ and this justifies using an ideal plug flow reactor to analyze the conversion data.

Fig. 1 showed the XRD patterns of BaRh_xMn_{1-x}Al₁₁O₁₉ with *x* = 0.3; 0.5 and 0.8 of Rh contents. For BaMnAl₁₁O₁₉ sample, well crystallized Ba-β-Al₁₂O₁₉ phase was observed. After introduction of Rh-content, Rh₂O₃ phase was detected by the appearance of two peaks located at 2θ = 24° and 47° which they are more intense in accordance with the increasing of the introduced Rh content. Indeed, it caused by the presence of Rh₂O₃ particles that cannot be incorporated into hexaaluminates. Moreover, α-Al₂O₃ and the BaAl₁₂O₁₉ spinel can be identified along-side the Rh₂O₃ and hexaaluminate phases. Therefore, XRD patterns confirmed that Rh was not totally incorporated into hexaaluminates. The lattice parameters *a*₀ (Table 1S) of BaRh_xMn_{1-x}Al₁₁O₁₉ samples were increased after Rh incorporation; confirming that Rh-content was successively introduced in hexaaluminate structure. When *x*_{Rh} ≥ 0.5, *a*₀ cell parameters were almost constant indicating that Rh attains its maximum content to be incorporated into the structure. However, the excess of Rh occurred as Rh₂O₃ on the surface.

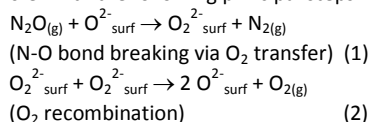
The measurements of textural properties; surface area and pore volume; have been performed and illustrated in Table 1S. The BET surface areas of hexaaluminate samples were varied between 20–23 m² g⁻¹, larger than that of Rh/A catalyst (13 m² g⁻¹) and Rh/H catalyst (15 m² g⁻¹). In fact, surface areas and pore volumes of BaRh_xMn_{1-x}Al₁₁O₁₉ samples were increased after incorporation of Rh into the structure, indicating that the texture of supports partially modified and Rh particles were involved in the contribution of the surface areas of final catalysts by interaction with Al.

The final composition of prepared catalysts was quantified by ICP and the structures were presented in Table 1S. Rh contents are significantly similar to the desired contents for all samples. Thus, Rh₂O₃ phase appeared in Rh/A catalyst with more intense patterns comparing to hexaaluminate catalysts. According to this attribution, hexaaluminates lead to homogeneous and highly distribution of Rh content into the frameworks.

The H₂-TPR measurements (Fig. 1S) have been performed for Rh/A and BaRh_xMn_{1-x}Al₁₁O₁₉ (*x* = 0.3, 0.5 and 0.8) catalysts to demonstrate the catalytic performance of Rh species in different catalysts. Rh species in BaRh_xMn_{1-x}Al₁₁O₁₉ structures could be slightly reduced by H₂ in two steps from 120 and 260 °C.

Thus, Rh/A catalyst can be reduced by H₂ with onset temperature at 150 °C and reached the maximum at 220 °C. H₂-TPR measurements showed that the influence of the introduced Rh into hexaaluminates is negligible.

BaRh_xMn_{1-x}Al₁₁O₁₉, Rh/H and Rh/A catalysts were tested for N₂O decomposition. Fig. 2 presented the results of the catalytic tests to N₂ and O₂. BaMnAl₁₁O₁₉ and Rh/H catalysts are poorly active for N₂O decomposition. The N₂O conversion is below 5 % in the whole studied temperature range (200–600 °C). As it was reported,¹⁶ N₂O conversion reached 100 % at 600 °C over Rh/A catalyst. Introduction of Rh into hexaaluminate caused a significant increasing of its activity in the process of N₂O decomposition. BaRh_{0.3}Mn_{0.7}Al₁₁O₁₉ catalyst is more active than BaMnAl₁₁O₁₉. The reaction started at about 250 °C and N₂O conversion increases with the increasing of reaction temperature and reaches 100 % at 450 °C. Therefore, Rh seemed to play an important role as an active site for N₂O decomposition. The growth of Rh content up to *x* = 0.8 has a significant influence on the activity of BaRh_xMn_{1-x}Al₁₁O₁₉. In fact, N₂O conversion slightly decreased from 100 % at 450 °C (*x* = 0.3) to 88 % (*x* = 0.5) at same temperature. Whereas, BaRh_{0.7}Mn_{0.3}Al₁₁O₁₉ and BaRh_{0.8}Mn_{0.2}Al₁₁O₁₉ catalysts are sharply less active and the N₂O conversion suddenly decreased from 75 % to 40 % at 450 °C, respectively. This influence could be explained by the presence of other Rh-species such as Rh₂O₃. Therefore, the amount of introduced Rh into BaMnAl₁₁O₁₉ framework seemed to be a principal factor for the catalytic performance, and it should be noted that the introduction of *x* = 0.3 of Rh is optimal and sufficient to obtain catalyst with high activity. While, BaRh_{0.1}Mn_{0.9}Al₁₁O₁₉ is slightly less active and its conversion was 95 % at 450 °C. The active site is probably different than Rh in this case and it can be explained by an anionic red-ox process which can be initiated by the oxygen-atom transfer with the following principal steps:²⁹

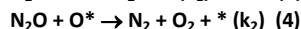
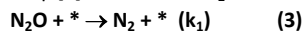


In this case, the recombination of O₂²⁻_{surf} to produce final O₂(g) occurred (2). Obviously, some possible variants of the oxygen migration and recombination steps are also possibly invoking the same species, acting as the active sites for N₂O catalytic decomposition.

The catalytic decomposition of propellants seeks catalysts that can be highly active and thermally stables. According to these characteristics, it was obvious to compare the catalytic activities of BaRh_{0.3}Mn_{0.7}Al₁₁O₁₉ and Rh/A catalysts (Fig. 3) at high temperature (i.e. 1200 °C). The N₂O conversion to N₂ and O₂ have been decreased for both catalysts. However, the deactivation of Rh/A catalyst is faster from *t* = 6 h of its calcination. The N₂O conversion is sharply decreased from 95 % to 26 % at 450 °C for Rh/A catalyst. Whereas, the catalytic activity of BaRh_{0.3}Mn_{0.7}Al₁₁O₁₉ catalyst was slightly decreased. Therefore, BaRh_{0.3}Mn_{0.7}Al₁₁O₁₉ catalyst has been considered as adequate catalyst for N₂O decomposition and thermal stability during reaction.

Fig. 4 showed the GHSV effect on N₂O conversion at different temperatures over BaRh_{0.3}Mn_{0.7}Al₁₁O₁₉ catalyst. N₂O conversion shifted to higher temperature versus high space velocity. The N₂O conversion reached 20 % (kinetic regime) over BaRh_{0.3}Mn_{0.7}Al₁₁O₁₉ catalyst at 290, 320 and 370 °C at 20000; 30000 and 40000 h⁻¹ GHSV, respectively. The approach published by Hall et al.^{30,31} was used for the N₂O decomposition which followed a kinetic regime. In fact, they found an absence of oxygen inhibition and a pure first order

behavior for nitrous oxide. This can be accounted for only if N_2O adsorption is rate limiting, but then the catalytic sites must be in a reduced state, while it could be observed that the catalyst was rich on oxygen. Therefore they proposed (4) as the irreversible oxygen removal reaction, in combination with the oxidation step of (3), resulting in Eq. [8] for the total N_2O conversion rate:



The re-startability as key parameter for space application was carried out for $\text{BaRh}_{0.3}\text{Mn}_{0.7}\text{Al}_{11}\text{O}_{19}$ catalyst. Fig. 5 showed that the activity was slightly decreased after four reaction cycles due to the loss of catalyst activities. This phenomena can be explained by the partial oxidation of Rh deposited outside the framework to Rh_2O_3 . Therefore, $\text{BaRh}_{0.3}\text{Mn}_{0.7}\text{Al}_{11}\text{O}_{19}$ catalyst demonstrated good re-startability.

Conclusion

$\text{BaRh}_{0.3}\text{Mn}_{0.7}\text{Al}_{11}\text{O}_{19}$ can be considered as promising catalyst for N_2O decomposition due to its wide advantages such as high activity, thermal stability and restartability.

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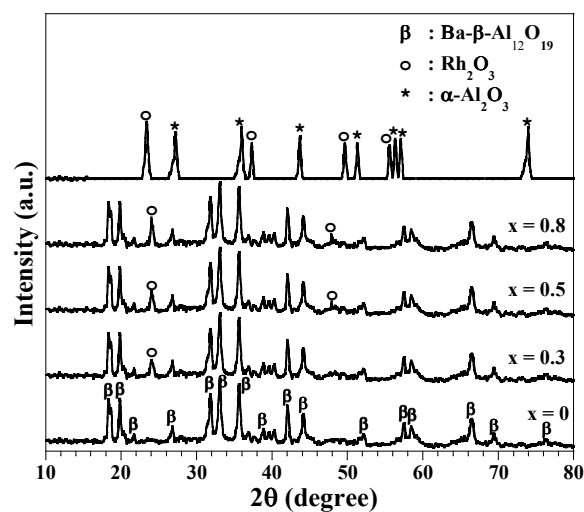


Fig. 1. XRD patterns of hexaaluminate and Rh-substituted hexaaluminate catalysts.

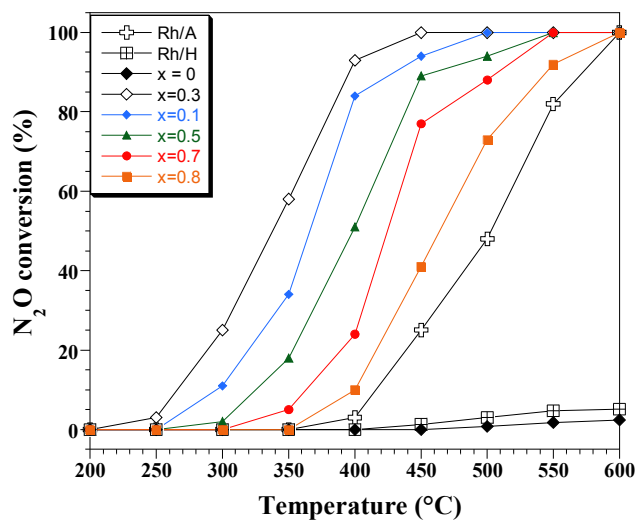


Fig. 2 N₂O conversion (%) over BaRh_xMn_{1-x}Al₁₁O₁₉ (x = 0-0.8) catalysts, and Rh/H and Rh/A catalysts at different temperatures.

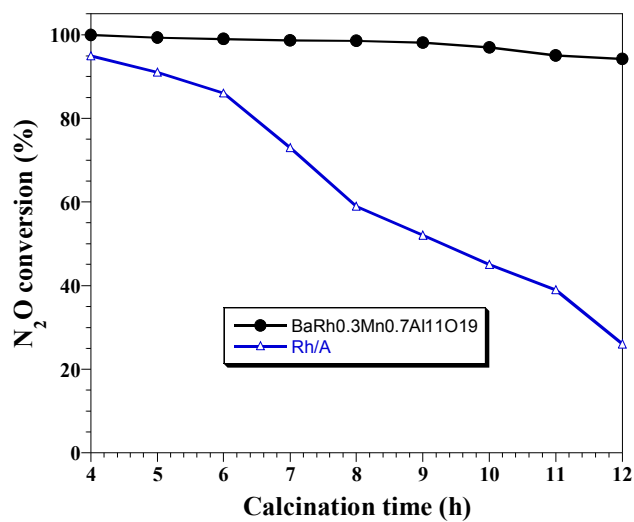


Fig. 3 Effect of calcination time at 1200 °C on catalytic activities of BaRh_{0.3}Mn_{0.7}Al₁₁O₁₉ and Rh/A catalysts.

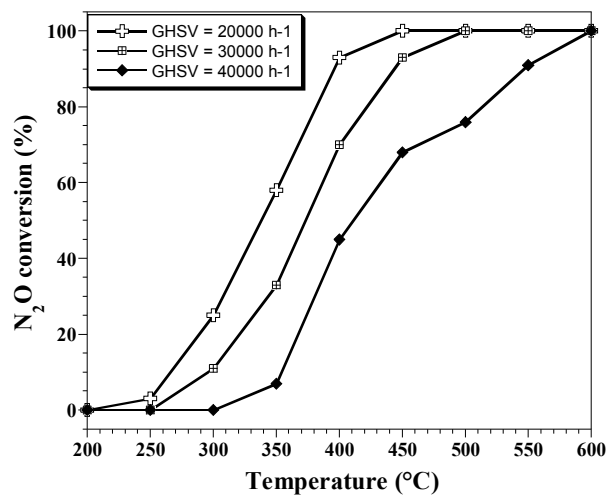


Fig. 4 N₂O conversion (%) over BaRh_{0.3}Mn_{0.7}Al₁₁O₁₉ catalyst at different GHSV.

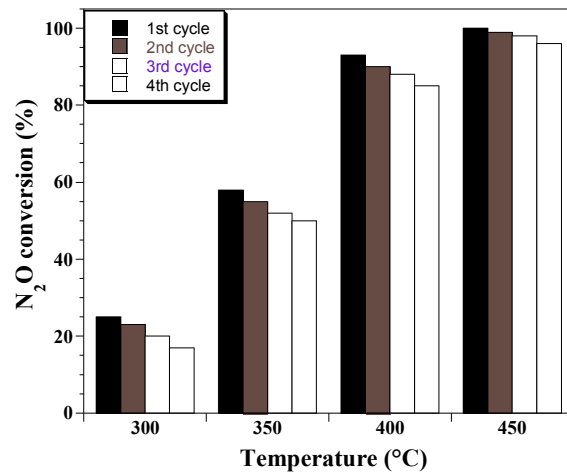


Fig. 5 N₂O conversion (%) over BaRh_{0.3}Mn_{0.7}Al₁₁O₁₉ catalyst between 300-450 °C for four cycles.

