

Original Research

# Study on N<sub>2</sub>O Catalytic Decomposition over NiO-Mn<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub> Catalyst

Yuanyang Zhang<sup>1</sup>\*, Kun Bao<sup>1</sup>, Wenqian Zhang<sup>1</sup>, Yongle Zhao<sup>1</sup>, Linqi Wang<sup>2</sup><sup>1</sup>School of New Materials and Chemical Engineering, Tangshan University, Tangshan 063000, China<sup>2</sup>School of Artificial Intelligence, Tangshan University, Tangshan 063000, China

Received: 12 September 2024

Accepted: 2 December 2024

## Abstract

A series of NiO/SiO<sub>2</sub> catalysts with different NiO loadings were first prepared using the impregnation method. The basic characterization of NiO/SiO<sub>2</sub> samples was characterized by BET and XRD. The performance of NiO/SiO<sub>2</sub> on catalytic decomposition of N<sub>2</sub>O was evaluated in a fixed bed reactor, which indicated that the best performance on catalytic decomposition of N<sub>2</sub>O was the sample when the loading of NiO was 16.0 (wt%), NiO(16.0%)/SiO<sub>2</sub>. On this basis, a series of NiO(16.0%)-Mn<sub>2</sub>O<sub>3</sub>(x%)/SiO<sub>2</sub> catalysts were prepared, respectively. The experimental results showed that when the loadings of Mn<sub>2</sub>O<sub>3</sub> was 6.0 (wt%), i.e., NiO(16.0%)-Mn<sub>2</sub>O<sub>3</sub>(6.0%)/SiO<sub>2</sub>, its performance on catalytic N<sub>2</sub>O decomposition was the best. The NiO (16.0%)-Mn<sub>2</sub>O<sub>3</sub>(x%)/SiO<sub>2</sub> samples were characterized by using XRD and H<sub>2</sub>-TPR. The stability test in the laboratory fixed bed reactor lasted for 100 hours and showed that the NiO(16.0%)-Mn<sub>2</sub>O<sub>3</sub> (6.0%)/SiO<sub>2</sub> catalyst had good stability for the N<sub>2</sub>O catalytic decomposition, which provided the basis for further relative research.

**Keywords:** nitrous oxide, impregnant method, catalysts, catalytic decomposition

## Introduction

As early as 1997, the Kyoto Protocol specified six major greenhouse gases: carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>), nitrous oxide (N<sub>2</sub>O), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), and sulfur hexafluoride (SF<sub>6</sub>), which have been included in the United Nations Framework Convention on Climate Change. Among them, N<sub>2</sub>O has extremely stable properties and can exist in the atmosphere for about 150 years [1, 2]. The main hazard of N<sub>2</sub>O is its destruction of the ozone layer, the formation of ozone holes, and ultimately, the greenhouse

effect, which has been regarded as a major contributor to global warming and ozone layer depletion [3]. Research has shown that N<sub>2</sub>O is growing at a rate of approximately 0.2-0.3% per year. Although the concentration of N<sub>2</sub>O in the atmosphere is much lower than that of the greenhouse gas CO<sub>2</sub>, its global warming potential (GWP) is about 310 times that of carbon dioxide, and its contribution to the greenhouse effect is about 6-10%. The emission of greenhouse gases seriously pollutes the environment, resulting in melting glaciers, rising sea levels, changes in climate zones, etc., which has led to species extinction because of the greenhouse effect. The greenhouse effect can also cause rapid changes in local weather conditions, resulting in environmental problems such as high temperatures, heat waves, tropical storms, tornadoes, etc. [4]. Consequently, addressing

\*e-mail: yyzhang90@126.com

Tel.: +86-315-2010649

Fax: +86-315-2792159

°ORCID iD: 0000-0001-6322-7972

N<sub>2</sub>O emissions has emerged as a critical research focus in efforts to mitigate its global warming potential [5].

The main sources of N<sub>2</sub>O in the atmosphere are the emissions of nature and human activities; the former mainly comes from the ocean [6, 7] and natural soil [8], and the latter mainly comes from human agricultural production activities [9], fossil fuel combustion [10], industrial production emissions [11, 12], and wastewater discharge [13, 14]. The emission of N<sub>2</sub>O from industrial production is about 0.9Tg/year, accounting for 15-20% of the total direct anthropogenic emissions [4, 9, 11], which mainly come from chemical production processes such as nitric acid, nylon-66, and adipic acid. Among them, the emission of N<sub>2</sub>O from adipic acid plants accounts for about 70-80% of the total industrial exhaust emissions [15]. Although the proportion of N<sub>2</sub>O generated from industrial exhaust to total human emissions is relatively low, with the development of industry, the demand for chemical products has gradually increased, and the proportion of N<sub>2</sub>O generated from industrial exhaust to total human emissions has gradually increased. Countries around the world have been paying more and more attention to reducing N<sub>2</sub>O emissions from industrial exhaust. In China's 14<sup>th</sup> Five-Year Plan of Clean and Efficient Utilization of Coal Technology, it is further required to reduce the pollutant emissions from coal combustion significantly. The value of N<sub>2</sub>O emission is limited to 80 mg/Nm<sup>3</sup>, which has not yet been met by many coal-fired power plants. It is, therefore, imperative to develop N<sub>2</sub>O emission reduction technology that takes NO into account to explore a completely integrated pollutant management method [16, 17]. The chemical properties of N<sub>2</sub>O are extremely stable, and how to decompose or treat it to reduce its impact on air pollution has been a research hotspot in the field of chemical engineering in recent years.

Currently, the reported N<sub>2</sub>O emission reduction technologies mainly include separation and purification [15], thermal decomposition [18], selective catalytic reduction using reducing agents such as H<sub>2</sub>, CH<sub>4</sub>, CO, and NH<sub>3</sub> [19-22], and catalytic decomposition [23]. The cost of separation and purification technology is high, and direct thermal decomposition technology can only be achieved under high-temperature conditions, resulting in significant equipment investment. Although selective catalytic reduction could catalyze the decomposition of N<sub>2</sub>O at lower temperatures, the use of some reducing agents could lead to the production of the greenhouse gas CO<sub>2</sub>, which is not conducive to energy conservation and emission reduction. It is generally believed that catalytic decomposition is a promising technology for N<sub>2</sub>O emission reduction. The reported catalytic decomposition methods mainly focus on precious metal catalysts [24, 25], hydrotalcite-like catalysts [26], and supported transition metal oxide catalysts [27-31]. So far, the domestic N<sub>2</sub>O decomposition catalyst technology is still in the development stage, mostly in small-scale research. Therefore, developing high-performance N<sub>2</sub>O decomposition catalysts to reduce

greenhouse gas emissions is of great significance for the goal of achieving a carbon peak before 2030 and carbon neutrality before 2060 in China. This article basically reported the use of the composite metal oxides of nickel and manganese supported on SiO<sub>2</sub> to achieve N<sub>2</sub>O decomposition.

## Materials and Methods

### Materials

All of the SiO<sub>2</sub> powder, nickel (II) nitrate hexahydrate [Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O], and 50% manganese (II) nitrate aqueous solution [Mn(NO<sub>3</sub>)<sub>2</sub>] are analytical grade (AR) provided by Sinopharm Chemical Reagent Co., Ltd., China. Nitrogen (N<sub>2</sub>) and oxygen (O<sub>2</sub>) are both produced by Tangshan Zhongsheng Industrial Gas Co., Ltd., China, with a purity of 99.99 (v/v)%. Nitrous oxide (N<sub>2</sub>O), produced by Luoyang Feilier Special Gas Co., Ltd., China, has a purity of 99.999 (v/v)%. The deionized water used in the experiment was prepared by using the Milli-Q ultrapure water system in the laboratory (conductivity ≤ 0.055 μS/cm).

### Sample Preparation

The catalysts used in this study were prepared by the impregnation method. The SiO<sub>2</sub> used was ground and sieved to obtain a carrier with a mesh size of 40-20 (0.425-0.850 mm), which was firstly dried in a drying oven at 110-120°C lasted for 10-12 hr. A suitable precursor aqueous solution based on the preprepared catalyst components and content was prepared, and the solution was sonicated at room temperature for 0.5-2.0 hr to ensure the formation of a uniform precursor aqueous solution before use. During the impregnation process, the prepared precursor aqueous solution was first transferred into a beaker, which was located in a constant temperature water bath at 45.0 ± 5.0°C; then, the prepared SiO<sub>2</sub> carrier was slowly added to the precursor solution under stirring conditions. After the SiO<sub>2</sub> carrier was completely added to the precursor solution while stirring continuously for 0.5-1.0 hr, it was filtered and dried in a drying oven at 105-110°C for 16-24 hr. Then, the precursor catalyst was treated at 550°C for 4-6 hr in a muffle furnace through the programmed heating method. After calcination, the sample with 40-20 mesh was collected and used to evaluate its catalytic decomposition performance of N<sub>2</sub>O. The content of active components was determined by X-ray fluorescence spectroscopy (XRF) analysis.

### Characterization

The specific surface area and pore structure were analyzed by using N<sub>2</sub> adsorption/desorption on a Micromeritics ASAP 2460 analyzer. X-ray fluorescence spectroscopy (XRF) was performed using a Philips

Magix PW2424 X-ray fluorescence spectrometer, and X-ray diffraction (XRD) was performed on a Rigaku SmartLab X-ray diffractometer by using CuK alpha radiation, tube voltage of 40 kV, and tube current of 100 mA. The microstructure of the photocatalyst before and after the reaction was observed using a Hitachi S-4800 scanning electron microscope (SEM) with an acceleration voltage of 5.0 kV during the imaging process. The Temperature Programmed Reduction ( $H_2$ -TPR) analysis was performed on an AMI-300IR fully automatic chemical adsorption instrument. 0.1 g (40-60 mesh) of catalyst was placed in a microreactor and pretreated at the temperature of 150-300°C in an argon atmosphere for 30 min. After cooling to room temperature, it was switched to an  $H_2$ /Ar atmosphere as well, and the baseline stabilized. The temperature was raised to 800°C at a rate of 10-20°C/min. The hydrogen signal of the reaction tail gas was detected online by using a GAM 200 gas mass spectrometer (Inprocess Instruments, Germany).

### Activity Evaluation

The performance of catalytic decomposition of  $N_2O$  was evaluated in a fixed bed reactor system, and the experimental setup is shown in Fig. 1. The reactor material was made of 310S stainless steel with an inner diameter of 8.0 mm. The outlet of the reactor was connected to a cooler, and the reaction products were condensed and entered the gas-liquid separator. The gas mixture was discharged through a back pressure valve and accumulated through a metal float flowmeter. It could be directly analyzed by gas chromatography by switching through a four-way valve. It was analyzed by using gas chromatography GC-2010 PLUS (Shimadzu), with a 5A molecular sieve and Porapak Q packed column, and a TCD detector. The conversion ratio or activity of the catalyst was calculated based on the following method.

$$N_2O \text{ conversion } (\%) = \frac{(N_2O_{\text{conversion}(in)} - N_2O_{\text{conversion}(out)})}{N_2O_{\text{conversion}(in)}} \times 100\%$$

### Results and Discussion

$SiO_2$ -supported catalysts with different NiO contents were first prepared by using the impregnation method. The designed contents (wt) supported on  $SiO_2$  were 4.0%, 8.0%, 12.0%, 16.0%, and 20.0%, respectively. X-ray fluorescence spectroscopy (XRF) results indicated that the actual loadings of NiO were 4.01%, 7.96%, 12.05%, 15.68%, and 19.69%, respectively, which was basically the designed value. In the following discussion, the loadings of NiO in the series of catalysts were based on the designed value for the reason of simplicity.

The specific surface areas of the carrier  $SiO_2$  and samples of NiO(4.0%)/ $SiO_2$ , NiO(8.0%)/ $SiO_2$ , NiO(12.0%)/ $SiO_2$ , NiO(16.0%)/ $SiO_2$ , and NiO(20.0%)/ $SiO_2$  were 292  $m^2/g$ , 288  $m^2/g$ , 280  $m^2/g$ , 275  $m^2/g$ , 268  $m^2/g$ , and 259  $m^2/g$ , respectively. It indicated that the specific surface area of the prepared NiO/ $SiO_2$  catalysts gradually decreased with the increase in the content of active components on support. This could probably be because the agglomeration phenomenon of NiO on the surface of the support was gradually increasing as well, and some pores of the support were blocked with the increasing of NiO content, which resulted in a decreasing trend in specific surface area.

The XRD spectra of the prepared catalysts NiO(4.0%)/ $SiO_2$ , NiO(8.0%)/ $SiO_2$ , NiO(12.0%)/ $SiO_2$ , NiO(16.0%)/ $SiO_2$ , and NiO(20.0%)/ $SiO_2$  were shown in Fig. 2, respectively. The broad diffraction peak appearing in  $2\theta$  at approximately 22° was the characteristic peak of  $SiO_2$  [32], while the appearing diffraction peaks at approximately 37°, 43°, 63°, 75°, and 79° were the diffraction peaks of the face-centered cubic crystal faces (111), (200), (220), (311), and (222) of NiO (JCPDS No. 47-1049), respectively [33, 34]. Using the Scherrer

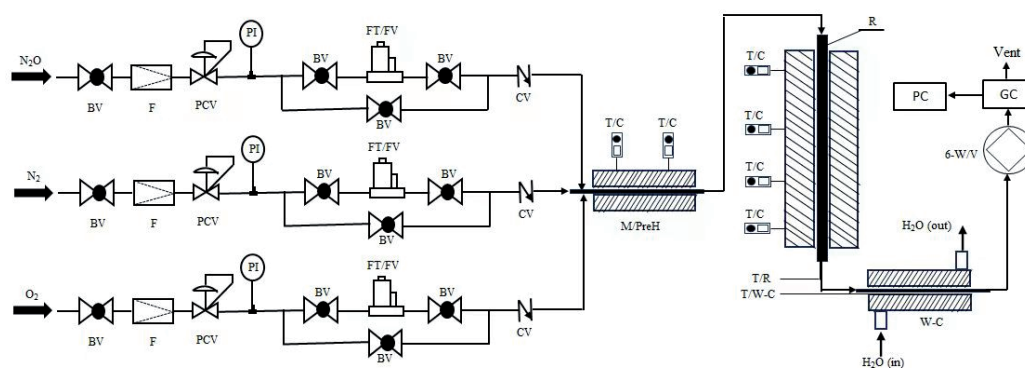


Fig. 1. The schematic diagram of the fixed bed reactor used for catalyst performance evaluation.

BV-ball valve, CV-check valve, F-filter, FT/FV-mass flow meter, GC-gas chromatography,  $H_2O$ (in)-condensate inlet,  $H_2O$ (out)-condensate outlet, M/PreH-gas mixing preheater, PC-chromatography workstation, PCV-automatic pressure reducing valve, PI-pressure sensor, R-fixed bed reactor, TC-controlled thermocouple, T/R-reactor bed temperature thermocouple, T/W-C-condenser temperature thermocouple, Vent-gas vent. W-C-water-cooled condenser, 6-W/V-gas six way valve.

formula, the average particle sizes of NiO on support for catalysts of NiO(4.0%)/SiO<sub>2</sub>, NiO(8.0%)/SiO<sub>2</sub>, NiO(12.0%)/SiO<sub>2</sub>, NiO(16.0%)/SiO<sub>2</sub>, and NiO(20.0%)/SiO<sub>2</sub> were 12.4 nm, 13.6 nm, 14.5 nm, 15.8 nm, and 16.4 nm, respectively. This indicated that the average particle size of NiO distributed on the SiO<sub>2</sub> support showed a slight increasing trend under the experimental conditions of preparation with the increasing of NiO loadings.

The conversion ratio of N<sub>2</sub>O decomposition over the above prepared NiO(x%)/SiO<sub>2</sub> catalysts was shown in Fig. 3 as a function of reaction temperature. The experimental conditions are listed below: gas composition (v/v) 14.6% N<sub>2</sub>O+55.2% N<sub>2</sub>+30.2% O<sub>2</sub>, volume space velocity of 5000 h<sup>-1</sup>, and system pressure of 0.1 MPa. The experimental results showed that the activity of decomposing N<sub>2</sub>O over the prepared

NiO(x%)/SiO<sub>2</sub> catalysts was basically increasing with the increasing loadings of NiO on support under the experimental conditions of preparation and performance evaluation used. It showed that when the NiO loading reached 16.0 (wt%), further increasing the loadings of NiO slightly decreased its activity of the catalyst for decomposing N<sub>2</sub>O, indicating that the NiO(16.0%)/SiO<sub>2</sub> catalyst had the best performance on N<sub>2</sub>O decomposition under experimental conditions used with 16.0 (wt%) loadings of NiO on SiO<sub>2</sub> support.

The results of the specific surface area showed that for NiO(x%)/SiO<sub>2</sub> catalysts, as the increasing content of active component of NiO on support, the specific surface area of NiO(x%)/SiO<sub>2</sub> catalysts gradually decreased, indicating that for supported catalysts the variation of specific surface area occurring within a certain range, it did not significantly affect the activity of the catalysts

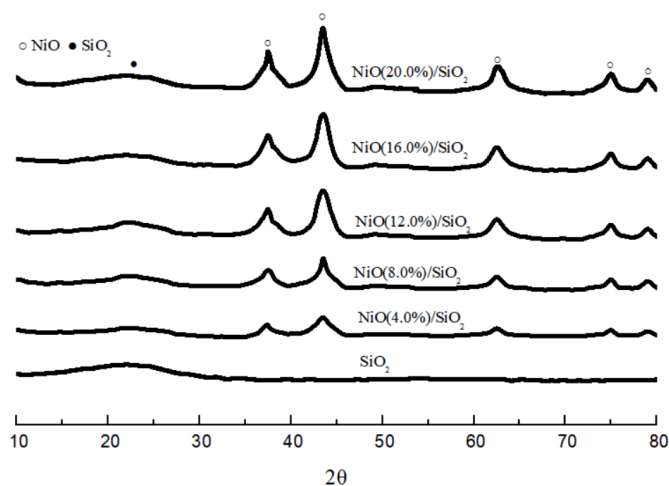


Fig. 2. XRD characterization results over NiO/SiO<sub>2</sub> samples with different NiO loadings.

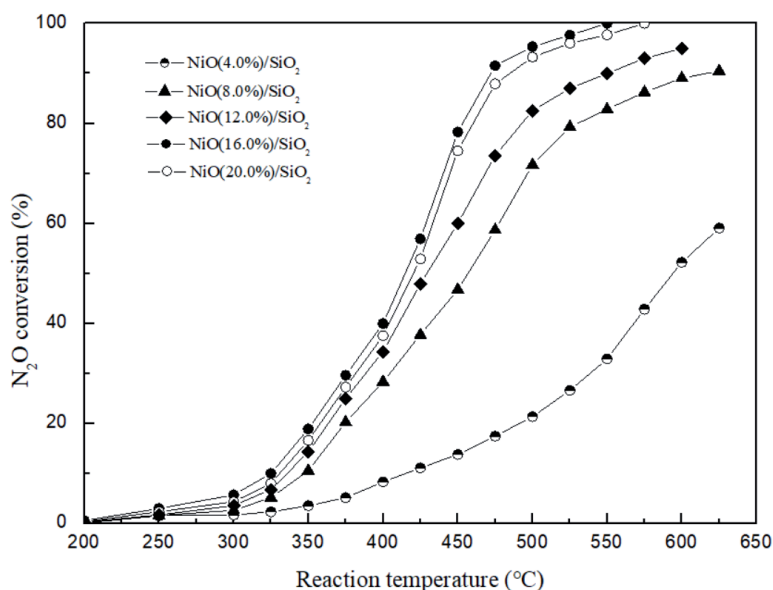


Fig. 3. The variation of N<sub>2</sub>O conversion with reaction temperature on the prepared NiO(x%)/SiO<sub>2</sub> catalysts.



on N<sub>2</sub>O decomposition. XRD characterization results indicated that for the NiO(x%)/SiO<sub>2</sub> catalysts when the amount of NiO loadings was relatively small, the active components were well dispersed on the support, which could fully use the catalytic function of the active components. At the same time, the amount of active component loadings would have a significant effect on the number of active centers. Taking into account the dispersion state of the active components on support and the number of active centers, the NiO(16.0%)/SiO<sub>2</sub> catalyst showed the best performance on N<sub>2</sub>O decomposition under experimental conditions. The experimental results showed that under the above experimental conditions, the conversion ratio of N<sub>2</sub>O on NiO(16.0%)/SiO<sub>2</sub> catalyst reached 100% when the reaction temperature was about 550°C.

A series of NiO(16.0%)-Mn<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> catalysts were prepared based on the above experimental results. The designed contents (wt) of Mn<sub>2</sub>O<sub>3</sub> supported on NiO(16.0%)/SiO<sub>2</sub> were 2.0%, 4.0%, 6.0%, and 8.0%, respectively, which was basically the same as the actual value through comparing with XRF results. In the following discussion, the loadings of active components in the series of catalysts were still based on the designed value for the reason of simplicity, including NiO(16.0%)-Mn<sub>2</sub>O<sub>3</sub>(2.0%)/SiO<sub>2</sub>, NiO(16.0%)-Mn<sub>2</sub>O<sub>3</sub>(4.0%)/SiO<sub>2</sub>, NiO(16.0%)-Mn<sub>2</sub>O<sub>3</sub>(6.0%)/SiO<sub>2</sub>, and NiO(16.0%)-Mn<sub>2</sub>O<sub>3</sub>(8.0%)/SiO<sub>2</sub>, in order to further investigate the possibility of improving the activity of supported NiO/SiO<sub>2</sub> catalyst on N<sub>2</sub>O decomposition. Sequentially, the specific surface areas of the prepared samples were 243 m<sup>2</sup>/g, 238 m<sup>2</sup>/g, 226 m<sup>2</sup>/g, and 219 m<sup>2</sup>/g, respectively, which indicated that the specific surface area of the prepared samples was slightly decreasing with the increase of Mn<sub>2</sub>O<sub>3</sub> on NiO(16.0%)/SiO<sub>2</sub> under experimental prepared conditions, while compared with traditionally supported catalysts, the prepared samples still had relatively large specific surface area.

XRD spectra of the prepared series of samples of NiO(16.0%)-Mn<sub>2</sub>O<sub>3</sub>(y%)/SiO<sub>2</sub> were shown in Fig. 4,

which showed that it did not obviously appear in the characteristic peaks belonging to Mn<sub>2</sub>O<sub>3</sub> on the XRD spectrum when the loading of Mn<sub>2</sub>O<sub>3</sub> was 2.0% and 4.0%, respectively, which was probably because the Mn<sub>2</sub>O<sub>3</sub> crystalline structure did not clearly form when the loading of Mn<sub>2</sub>O<sub>3</sub> was lower under the prepared experimental conditions used. It showed two characteristic diffraction peaks at approximately 33° and 35° at 2θ when the loadings of Mn<sub>2</sub>O<sub>3</sub> were 6.0% and 8.0%, respectively, which could be the diffraction peaks of Mn<sub>2</sub>O<sub>3</sub> (222) and (123) crystal planes (JCPDF No. 78-0390), respectively [35,36].

In order to investigate the ability of reduction for the prepared NiO-Mn<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub> samples, H<sub>2</sub>-TPR performance performed on the prepared series of catalysts of NiO(16.0%)-Mn<sub>2</sub>O<sub>3</sub>(y%)/SiO<sub>2</sub> was tested, and results were shown in Fig. 5, respectively. The results showed that there were mainly two H<sub>2</sub>-TPR hydrogen consumption peaks at approximately 300-470°C and 510-620°C for the catalysts of NiO(16.0%)-Mn<sub>2</sub>O<sub>3</sub>(y%)/SiO<sub>2</sub> with different loadings, respectively. The hydrogen consumption peak at a low temperature of 300-470°C could be attributed to the weak interaction between NiO and the support of SiO<sub>2</sub> in the free state of NiO, while the hydrogen consumption peak at a high temperature of 510-620°C could be attributed to the strong interaction between NiO and the support of SiO<sub>2</sub>, respectively [37].

The peak area related to the hydrogen consumption at low-temperature (300-470°C) (A1) and high-temperature (510-620°C) (A2) were calculated, respectively, by using Origin peak integration (Table 1). It showed that the peak area of hydrogen consumption (A1) and (A2) both increased with the increasing content of Mn<sub>2</sub>O<sub>3</sub> with the loading of Mn<sub>2</sub>O<sub>3</sub> (wt%) ≤ 6.0%, indicating that the ability to reduce for the catalysts increased with the increasing content of Mn<sub>2</sub>O<sub>3</sub>. However, it showed that the peak area of hydrogen consumption (A1) and hydrogen consumption (A2) was actually decreased when the content of Mn<sub>2</sub>O<sub>3</sub> (wt%) was higher than that of 6.0%,

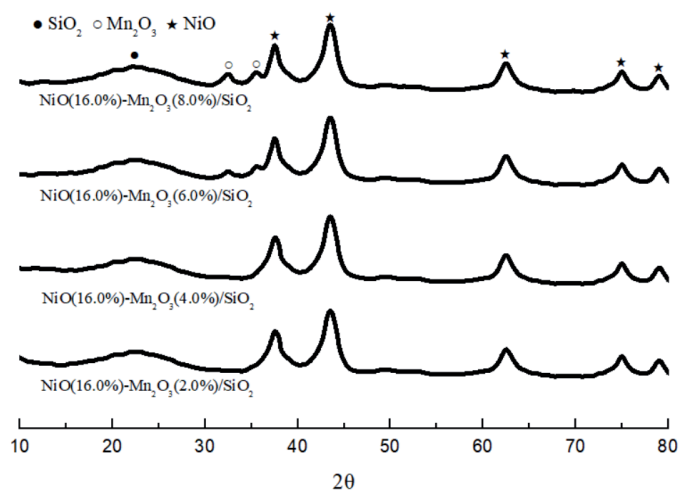


Fig. 4. XRD characterization results over NiO(16.0%)-Mn<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> samples with different Mn<sub>2</sub>O<sub>3</sub> loadings.

Table 1. The peak area of hydrogen consumption for H<sub>2</sub>-TPR over NiO and NiO-Mn<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub> catalysts.

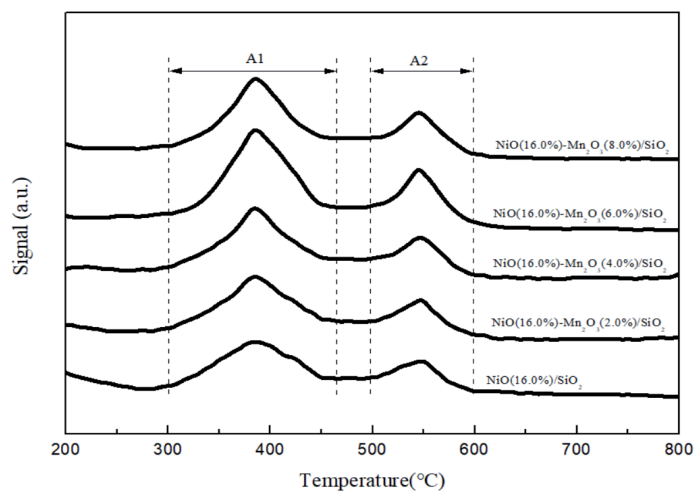
Samples	Relative peak area (a.u.)	
	A1(300~470°C)	A2(510~620°C)
NiO(16.0%)/SiO <sub>2</sub>	507.54	95.27
NiO(16.0%)-Mn <sub>2</sub> O <sub>3</sub> (2.0%)/SiO <sub>2</sub>	600.90	185.11
NiO(16.0%)-Mn <sub>2</sub> O <sub>3</sub> (4.0%)/SiO <sub>2</sub>	657.20	247.14
NiO(16.0%)-Mn <sub>2</sub> O <sub>3</sub> (6.0%)/SiO <sub>2</sub>	980.14	485.16
NiO(16.0%)-Mn <sub>2</sub> O <sub>3</sub> (8.0%)/SiO <sub>2</sub>	820.36	440.86

indicating that the ability to reduce for the catalyst was decreased with the further increasing the content of Mn<sub>2</sub>O<sub>3</sub> when the content of Mn<sub>2</sub>O<sub>3</sub> was higher than that of 6.0%. This implied that the sample of NiO(16.0%)-Mn<sub>2</sub>O<sub>3</sub>(6.0%)/SiO<sub>2</sub> had the best ability of reduction for the prepared catalysts of NiO(16.0%)-Mn<sub>2</sub>O<sub>3</sub>(y%)/SiO<sub>2</sub> under the experimental preparation conditions used. For N<sub>2</sub>O decomposition catalysts, research results have shown that the stronger the ability to reduce, the higher the catalytic decomposition activity of N<sub>2</sub>O under certain experimental conditions [19, 23].

Fig. 6 shows the experimental results of the N<sub>2</sub>O conversion over the prepared catalysts of NiO(16.0%)-Mn<sub>2</sub>O<sub>3</sub>(y%)/SiO<sub>2</sub> as the function of reaction temperature. The experimental conditions are listed below: gas composition (v/v) 14.6% N<sub>2</sub>O+55.2% N<sub>2</sub>+30.2% O<sub>2</sub>, volume space velocity of 5000 h<sup>-1</sup>, and system pressure of 0.1 MPa, respectively. It indicated that the catalytic activity performing on N<sub>2</sub>O decomposition was improved to some degrees under experimental conditions for the supported catalysts of composite NiO-Mn<sub>2</sub>O<sub>3</sub> metal oxides, NiO(16.0%)-Mn<sub>2</sub>O<sub>3</sub>(y%)/SiO<sub>2</sub> under experimental condition. Rational design of bimetallic catalysts has progressed in recent studies owing to the understanding of synergy and strong mutual interaction between metal oxide species [38].

The theoretical analysis results of the relationship between the ionization potential (ev) and the ratio of effective nuclear charge/ion radius for the representative oxides of transition and alkali metals indicated that NiO and Mn<sub>2</sub>O<sub>3</sub> belong to alkaline oxides and amphoteric metal oxides, respectively [39]. Further research showed that the catalytic performance of composite metal oxides prepared by doping modification of alkaline metal oxides with amphoteric metal oxides was better than that of single alkaline metal oxides or amphoteric metal oxides [40, 41]. Meanwhile, according to the mechanism of N<sub>2</sub>O catalytic decomposition [42, 43], the desorption of O\* on the active sites (•) from the catalyst surface would play an important role in the catalytic decomposition of N<sub>2</sub>O, while the surface of Mn<sub>2</sub>O<sub>3</sub> metal oxide could provide abundant of O active sites. Therefore, the catalysts of NiO-Mn<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> prepared under experimental conditions would have better performance on N<sub>2</sub>O decomposition than that of NiO/SiO<sub>2</sub> catalysts, which was basically consistent with the experimental results (Fig. 6).

The experimental results in Fig. 6 also indicated that the activity of the prepared NiO(16.0%)-Mn<sub>2</sub>O<sub>3</sub>(y%)/SiO<sub>2</sub> catalyst performing on N<sub>2</sub>O decomposition was increased with the increasing of Mn<sub>2</sub>O<sub>3</sub> content when the content of Mn<sub>2</sub>O<sub>3</sub> was lower than that of 6.0 (wt%), while

Fig. 5. H<sub>2</sub>-TPR characterization results over NiO(16.0%)-Mn<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> samples with different Mn<sub>2</sub>O<sub>3</sub> loadings.

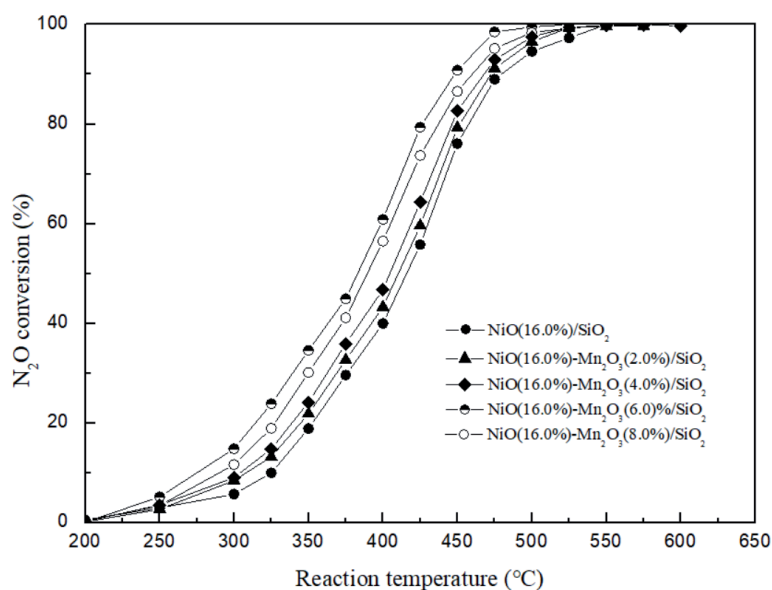


Fig. 6. The variation of  $N_2O$  conversion with reaction temperature on the prepared  $NiO(16.0\%)-Mn_2O_3(y\%)/SiO_2$  catalysts.

the activity of the prepared  $NiO(16.0\%)-Mn_2O_3(y\%)/SiO_2$  catalyst performing on  $N_2O$  decomposition was decreased with the increasing of  $Mn_2O_3$  content when the content of  $Mn_2O_3$  was higher than that of 6.0 (wt%), indicating that it existed an appropriate composition ratio for the synergistic catalytic function between the composite metal oxides of  $NiO-Mn_2O_3$ . Under the experimental preparation conditions, the catalyst prepared for  $NiO(16.0\%)-Mn_2O_3(6.0\%)/SiO_2$  showed the best activity in  $N_2O$  decomposition. At the reaction temperature of  $525^\circ C$  and other experimental conditions used, the conversion of  $N_2O$  over the catalyst of  $NiO(16.0\%)-Mn_2O_3(6.0\%)/SiO_2$  was 100%, which was consistent with the  $H_2$ -TPR characterization results. Under the same experimental conditions used, the conversion of  $N_2O$  over the catalyst of  $NiO(16.0\%)/SiO_2$

reached 100% at the reaction temperature of  $550^\circ C$ . The stability test in the laboratory fixed bed reactor lasted for 100 hr under the following experimental conditions: gas composition (v/v) 14.6%  $N_2O+55.2\% N_2+30.2\% O_2$ , volume space velocity of  $5000 h^{-1}$ , system pressure of 0.1 MPa, and reaction temperature of  $525^\circ C$ . It showed that the  $NiO(16.0\%)-Mn_2O_3(6.0\%)/SiO_2$  catalyst had good stability for the  $N_2O$  catalytic decomposition, and the conversion ratio of  $N_2O$  was 100% under the experimental conditions used. Fig. 7 showed SEM characterization results of  $NiO(16.0\%)-Mn_2O_3(6.0\%)/SiO_2$  catalyst before and after the reaction lasted for 100 hours, which indicated that there was no significant variation regarding the surface morphology and particle size of the catalyst before and after the reaction, respectively, which also indicated that

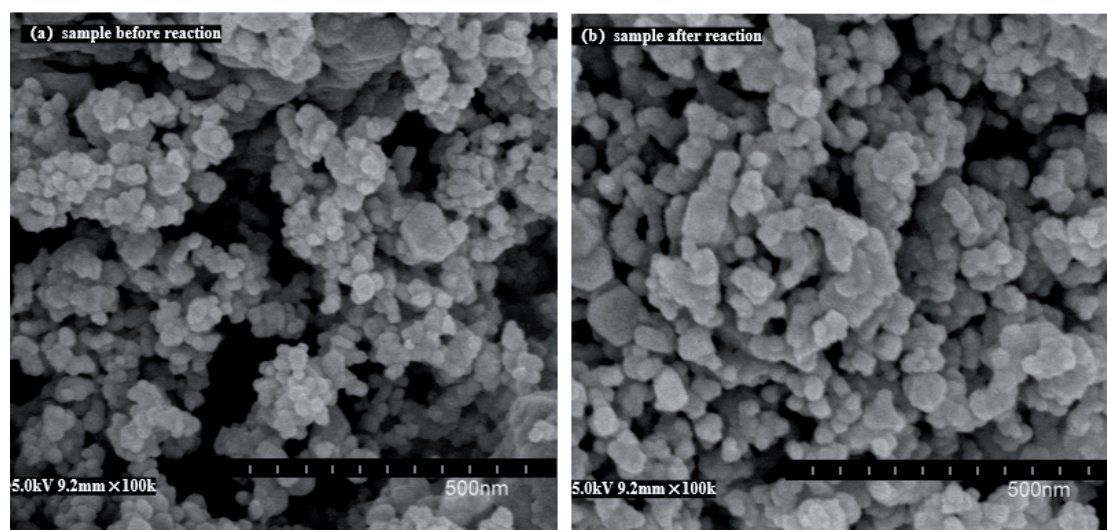


Fig. 7. SEM characterization over samples before and after the reaction lasted for 100 hours.

the prepared sample had good stability for the N<sub>2</sub>O catalytic decomposition and provided the basis for further relative research.

## Conclusions

The activity results performed on NiO(x%)/SiO<sub>2</sub> catalysts showed that under experimental conditions, when the content of NiO was 16.0 (wt%), NiO(16.0%)/SiO<sub>2</sub> had good performance over N<sub>2</sub>O decomposition. Based on this basis, NiO(16.0%)-Mn<sub>2</sub>O<sub>3</sub>(x%)/SiO<sub>2</sub> catalysts were prepared, respectively. H<sub>2</sub>-TPR characterization results showed that when the content of Mn<sub>2</sub>O<sub>3</sub> content was 6.0 (wt%), NiO(16.0%)-Mn<sub>2</sub>O<sub>3</sub>(6.0%)/SiO<sub>2</sub>, it exhibited the best reduction performance through H<sub>2</sub>-TPR. It showed that the prepared catalyst of NiO(16.0%)-Mn<sub>2</sub>O<sub>3</sub>(6.0%)/SiO<sub>2</sub> had the best activity in N<sub>2</sub>O decomposition among catalysts of NiO(16.0%)-Mn<sub>2</sub>O<sub>3</sub>(x%)/SiO<sub>2</sub>. At the reaction temperature of 525°C and other experimental conditions used, the conversion of N<sub>2</sub>O reached 100% for the catalyst of NiO(16.0%)-Mn<sub>2</sub>O<sub>3</sub>(6.0%)/SiO<sub>2</sub>, which was consistent with the H<sub>2</sub>-TPR characterization results, while under same experimental conditions used, the conversion of N<sub>2</sub>O over the catalyst of NiO(16.0%)/SiO<sub>2</sub> reached 100% at the reaction temperature of 550°C. The experimental results showed that the activity of the composite metal oxides of the NiO-Mn<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> catalyst was superior to that of the single component of the NiO/SiO<sub>2</sub> catalyst.

## Acknowledgments

The authors thank the Science and Technology Research Projects of the Department of Education in Hebei Province for its generous financial support through the grant of CXY2023018.

## Conflict of Interest

The authors declare no conflict of interest.

## References

- ZHANG Y.Y., GUO Y.Q., LI N., FENG Y.Y. Research status and progress on N<sub>2</sub>O abatement and recycling technique N<sub>2</sub>O. *Environmental Protection of Chemical Industry*. **38** (1), 499, **2018**.
- YUAN C.J. Nitrous Oxide: Laughing gas should not be laughed off. *Huaxue Tongbao*. **86** (2), 244, **2023**.
- LI A Q., WANG P., ZHANG L.D., ZHAO H.Y., JIN M.M., LEI L.L. Effect of different skeleton structures on N<sub>2</sub>O decomposition from ammonia-fueled engines using Fe-based zeolite catalysts. *Fuel*. **378**, 132888, **2024**.
- CHIPPERFIELD M.P., BEKKI S., DHOMSE S., HARRIS NEIL R.P., HASSLER B., HOSSAINI R., STEINBRECHT W., THIÉBLEMONT R., WEBER M. Detecting recovery of the stratospheric ozone layer. *Nature*. **549** (7671), 211, **2017**.
- ZHAO H.Y., WANG P., LI Z.L., AO C.C., ZHAO X.T., LIN H. Improved activity and significant O<sub>2</sub> resistance of Cs doped Co<sub>3</sub>O<sub>4</sub> catalyst for N<sub>2</sub>O decomposition. *Journal of Environmental Chemical Engineering*. **12** (5),113907, **2024**.
- GONÇALVES C., NOGUEIRA M., OLIVEIRA A. Greenhouse gas (N<sub>2</sub>O) emission from Portuguese estuaries. Conference: IMMR, International Meeting on Marine Research 2014 , Peniche, Portugal. *Frontiers in Marine Science*. **2014**.
- YANG F., MIAO Y.Q., YE A.Z., CUI Q., SUN Y.L., LUO H., HONG W.L., SUN F.H. Characterization of N<sub>2</sub>O emission at the water-gas interface and influence of Lake Chaohu. *Journal of Lake Science*. **35** (6), 2000, **2023**.
- HUANG Y.H., SHE D.L., SHI Z.Q., HU L., PAN Y.C. Effect of different soil salinities on N<sub>2</sub>O emission: A meta-analysis. *Environmental Science*. **45** (4), 1, **2023**.
- TANG H.B., LÜ X.H., LI F.S., ZHAO S.T. Characteristics of greenhouse gas emissions in global food system. *Research of Environmental Sciences*. **36** (11), 1, **2023**.
- LIU J.X., WANG X.C., LI C.Q., WANG H., SONG Y.J. Research progresses of metal oxide catalysts for direct catalytic decomposition of nitrous oxide. *Environmental Protection of Chemical Industry*. **41** (3), 263, **2021**.
- JIA G.W., YANG N., WU X.H. The situation and suggestions for the control of non-carbon dioxide greenhouse gas emissions in China. *Environmental Impact Assessment*. **45** (3), 1, **2023**.
- ZHANG C.H., YAO X. Path analysis and development trend of greenhouse gas treatment in tail gas of adipic acid industrial production. *Henan Chemical Industry*. **39** (9), 12, **2022**.
- WANG C.X., LI Y.K., LIU Y.C. Effect of modified biochar on the removal of nitrate with low concentration and N<sub>2</sub>O emission from water by a screened denitrifying bacterium. *China Environmental Science*. <https://doi.org/10.19674/j.cnki.issn1000-6923.20230802.006>. **2023** [In Chinese].
- WENG J.Y., XU R.Z., YANG J., CHEN L.L., FANG F. Current status and prospects of nitrogen oxides reduction and resource utilization in wastewater treatment systems. *Applied Chemical Industry*. **52** (9), 2637, **2023**.
- JIN D.X., LI S.F., PU R.J., HE Z.Y., JIANG G.Z., ZHANG F.J., LI G.Y., LU X.H., LI X.J., PU B.L. Method for recovering and purifying nitrous oxide from a gas mixture containing nitrous oxide. Chinese Patent 109476483A [P]. **2019** [In Chinese].
- MIAO M., ZHOU T., WANG T., LI C.R., ZHANG M., YANG H.R. Feasibility of using red mud as bed material for treating N<sub>2</sub>O in fluidized bed combustion. *Fuel*. **379**, 133068, **2025**.
- LIU H., YANG S., MI J.X., SUN C.Z., CHEN J.J., LI J.H. 4d-2p-4f gradient orbital coupling enables tandem catalysis for simultaneous abatement of N<sub>2</sub>O and CO on atomically dispersed Rh/CeO<sub>2</sub> catalyst. *Environmental Science & Technology*. **58** (38): 17125, **2024**.
- ZHANG D.Z., ZHAO Z., ZHANG C.H., LIU Z.J., TIAN Y.F., ZHONG R.X., LI Z.G., LI X.Y., YAO X., SONG M.M., FENG X., ZHAO X.W., LIU W., ZHANG S.W., SU Y.H. A high-temperature decomposition device and method for industrial exhaust gas containing N<sub>2</sub>O. Chinese Patent 114754363A [P]. **2022**.
- ZHAO F.L., ZENG J., XIAO R., QIU L., GUO W., CHEN H.H., CHANG H.Z. Selective catalytic reduction



- of  $N_2O$  by CO over lanthanum doped Fe-beta zeolite. *China Environmental Science*. **43** (3), 1044, **2023**.
20. MAUVEZIN M. Catalytic reduction of  $N_2O$  by  $NH_3$  in presence of oxygen using Fe-exchanged zeolites. *Catalysis Letters*. **62** (1), 41, **1999**.
  21. KAMEOKA S., SUZUKI T., YUZAKI K., TAKEDA T., TANAKA S. Selective catalytic reduction of  $N_2O$  with methane in the presence of excess oxygen over Fe-BEA zeolite. *Chemical communications*. **9**, 745, **2000**.
  22. ZENG J., CHEN S.Y., FAN Z.H., WANG C., LI J. Simultaneous selective catalytic reduction of NO and  $N_2O$  by  $NH_3$  over Fe-zeolite catalysts. *Industrial & Engineering Chemistry Research*. **59** (44), 19500, **2020**.
  23. SÁDOVSKÁ G., TABOR E., SAZAMA P., LHOTKA M., SOBALÍK Z. High temperature performance and stability of Fe-FER catalyst for  $N_2O$  decomposition. *Catalysis Communications*. **89**, 133, **2017**.
  24. ZHANG Y.Y., GUO Y.Q., LI N., FENG Y.Y. Catalytic decomposition of  $N_2O$  over supported  $RuO_2/MexOy$  (Me=La, Mg, Al) catalysts. *Industrial Catalysis*. **26** (7), 43, **2018**.
  25. CHATZIIONA V.K., CONSTANTINOU B.K., SAVVA P.G., OLYMPIOU G.G., KAPNISIS K., ANAYIOTOS A., COSTA C.N. Regulating the catalytic properties of  $Pt/Al_2O_3$  through nanoscale inkjet printing. *Catalysis Communications*. **103**, 69, **2018**.
  26. ZHANG Y.Y., GUO Y.Q., LI N., FENG Y.Y. The preparation of hydrotalcite-like composite metal oxides and investigation on  $N_2O$  catalytic decomposition. *Environmental Pollution & Control*. **41** (5), 510, **2019**.
  27. CAMPA M.C., PIETROGIACOMI D., TUTI S.C., LEA R., OCCHIUZZI M.  $N_2O$  decomposition on  $CoO_x$ ,  $CuO_x$ ,  $FeO_x$  or  $MnO_x$  supported on  $ZrO_2$ : The effect of zirconia doping with sulfates or  $K^+$  on catalytic activity. *Applied Catalysis B: Environmental*. **187** (15), 218, **2016**.
  28. YU H.B. WANG X.P. Apparent activation energies and reaction rates of  $N_2O$  decomposition via different routes over  $Co_3O_4$ . *Catalysis Communications*. **106**, 40, **2018**.
  29. SUN J.R., XIA L., LI J.Y., LI S.X., LIU X.G., WANG H., LI C.Q., SONG Y.J. Effect of crystallization temperature on catalytic performance of  $Co_3O_4$  catalysts in decomposition of  $N_2O$ . *Modern Chemical Industry*. **39** (4), 89, **2019**.
  30. JIA R., DONG W.Y., ZHANG L., YU H.B., JIANG X., ZHANG H.Z., LI S.J., QU M.H. Catalytic decomposition of  $N_2O$  over  $Co_3O_4/KIT-6$  catalyst. *Journal of Molecular Science*. **39** (2), 154, **2023**.
  31. WANG Y.F., WANG Y.T., WANG X.C., MA X.F., LI C.Q., WANG H., SONG Y.J. Study on catalytic decomposition of  $N_2O$  by  $SiO_2$  aerogel supported transition metal oxides. *Modern Chemical Industry*. **42** (9), 134, **2022**.
  32. CUI Y., LIN Y.B. Preparation and properties study on magnetic nanosilicon dioxide. *Journal of Changchun University of Science and Technology (Natural Science Edition)*. **39** (6), 53, **2016**.
  33. ZHOU H., LV B.L., XU Y., WU D. Synthesis and electrochemical properties of NiO nanospindles. *Materials Research Bulletin*. **50**, 399, **2014**.
  34. YANG P., WEI X.W., WANG J., YANG F., ZHENG X.Y. Research on oxidation mechanism and fabrication of nickel oxide nanowires via high temperature oxidation. *Journal of Xihua University (Natural Science)*. **34** (3), 70, **2015**.
  35. XIA H.Y., HU L., YAO Q.Z. Preparation and photocatalytic activity of  $Mn_2O_3$  microspheres. *Journal of Inorganic Materials*. **26** (3), 317, **2011**.
  36. LIN Y.L., WU F., XIE Z.J., GAO B., TANG M., LU Y.N., WANG Y.C., ZHANG S., LIU Y.H., LIU Y.H. High Temperature crystallization synthesis  $Mn_2O_3@MoS_2$  composite materials and their adsorption properties for Uranium. *Journal of Nuclear and Radiochemistry*. **44** (4), 457, **2022**.
  37. ZHAO D., TAN J.S., JI Q.Q., ZHANG J.T., ZHAO X.S., GUO P.Z.  $Mn_2O_3$  nanomaterials: Facile synthesis and electrochemical properties. *Chinese Journal of Inorganic Chemistry*. **26** (5), 832, **2010**.
  38. LIU L.J., LIU B., NAKAGAWA Y., LIU S.B., WANG L., YABUSHITA M., TOMISHIGE K. Recent progress on bimetallic catalysts for the production of fuels and chemicals from biomass and plastics by hydrodeoxygenation. *Chinese Journal of Catalysis*. **62** (7), 1, **2024**.
  39. ZHANG Y.Y. Catalytic decomposition of greenhouse gas  $N_2O$  – Investigation on preparation and performance of composite metal oxide catalysts [D]. East China University of Science and Technology. **2000**.
  40. HUANG Q.X., WANG F., LIU Y., ZHANG B.Y., GUO F.Y., JIA Z.Q., WANG H., YANG T.X., WU H.T., REN F.Z., YI F.F. Recent progress of two-dimensional metal-base catalysts in urea oxidation reaction. *Rare Metals*. **43** (8):3607, **2024**.
  41. VASAVAN H.N., BADOLE M., SAXENA S., SRIHARI V., DAS A.K., GAMI P., DAGAR N., DESWAL S., KUMAR P., POSWAL H.K., KUMAR S. Identification of optimal composition with superior electrochemical properties along the zero  $Mn^{3+}$  line in  $Na_{0.75}(Mn-Al-Ni)O_2$  pseudo ternary system. *Journal of Energy Chemistry*. **96** (9), 206, **2024**.
  42. LIU Z., ZHOU Z., HE F., CHEN B., ZHAO Y., XU Q. Catalytic decomposition of  $N_2O$  over NiO-CeO<sub>2</sub> mixed oxide catalyst. *Catalyst Today*. **293-294**, 56, **2017**.
  43. FRANKEN T., PALKOVITS R. Investigation of potassium doped mixed spinels  $Cu_xCo_{3-x}O_4$  as catalysts for an efficient  $N_2O$  decomposition in real reaction conditions. *Applied Catalysis B: Environmental*. **176-177**, 298, **2015**.