様　式　Ｃ－１９、Ｆ－１９－１、Ｚ－１９　（共通）

科学研究費助成事業　　研究成果報告書

令和　４ 年　 ６ 月　 ５ 日現在

機関番号：２２６０４
研究種目：若手研究
研究期間：2019～2021
課題番号：１９Ｋ１５３６３

研究課題名（和文）Developing efficient catalysts for elimination of ammonia at room temperature for air quality improvement

研究課題名（英文）Developing efficient catalysts for elimination of ammonia at room temperature for air quality improvement

研究代表者
林　明月（LIN, MINGYUE）

東京都立大学・都市環境科学研究科・特任助教

研究者番号：３０８１３３５７

交付決定額（研究期間全体）：（直接経費）　　3,200,000円

研究成果の概要（和文）：CO酸化反応とNH3選択的触媒酸化反応のための高活性Auナノ粒子担持固体触媒の開発に成功した。CO酸化反応では、Au/Nb205およびAu/Ta205触媒にて、室温で100%のCO転化率の触媒活性が達成された。NH3の選択的酸化反応では、温度は、反応温度を室温まで下げると同時に、N2の選択性を90%以上に上げることに成功した。さらに、この詳細な反応メカニズムを調査することで、より優れた触媒の設計と調製を可能にした。研究成果は、基礎研究と環境関連触媒への応用研究の両側面で、有益な知見を提供した。

研究成果の学術的意義や社会的意義
アンモニアは特有の強い刺激臭を有することで知られ、人間の健康と環境に悪影響を及ぼす。 国連の持続可能な開発目標（SDGs）の目標6（きれいな水と衛生）と目標11（持続可能な都市とコミュニティ）の達成に適した都市生活の質を向上させるために、室内の空気浄化の需要がより一層高まっている。
我々の研究成果は、NH3-SCOの反応温度を室温まで下げ、その一方でN2選択性を90%以上に上げることができた。これは科学的に重要であるだけでなく、低エネルギー消費で安全性の高い空気浄化システム開発に技術革新をもたらすことができる。これは、将来的に健全な社会システムを構築する上で大いに貢献できる。

研究成果の概要（英文）：Highly active Au/solid catalysts were successfully developed. 100% catalytic activity for CO oxidation at room temperature was achieved over Au/Nb205 and Au/Ta205 catalysts. Reaction temperature for selective catalytic oxidation of NH3 was successfully decreased to room temperature and meanwhile the N2 selectivity was increased to more than 90% over Au/Nb205. More importantly, the detailed reaction mechanisms were investigated and guided the design and synthesis of more excellent catalysts.The research results offer great scopes for both basic science and applications related to air quality improvement.

研究分野：Environmental Catalysis

キーワード：air purification　gold catalyst　solid acid　high catalytic activity　NH3 oxidation　high catalytic activity　high N2 selectivity

１．研究開始当初の背景

Ammonia is a well-known odor that has a characteristic pungent smell. It has adverse effects on human health and environment. Demand of indoor air purification is increasing in order to improve quality of life in cities which will also be suited for achieving Goal 6 (Clean Water and Sanitation) and Goal 11 (Sustainable Cities and Communities) in Sustainable Development Goals (SDGs) of United Nations.

Selective catalytic oxidation (SCO) of NH_3 to N_2 and H_2O is an ideal technology for its removal. However, the reported catalysts either need high reaction temperatures (>250 ℃) or present low selectivities to N_2. Decreasing the reaction temperature of NH_3-SCO to room temperature and meanwhile increasing the N_2 selectivity to more than 90% are scientifically attractive and challenging, which will bring technological innovation in air purification systems.

２．研究の目的

Developing highly efficient catalysts that exhibit high catalytic activity for NH_3-SCO at room temperature and high N_2 selectivity at the full conversion of NH_3 (> 90%) is the research target which will offer great scopes for both basic science and applications related to air quality improvement.

３．研究の方法

According to the preliminary results of the PI, acidic metal oxide supported Au catalysts present high N_2 selectivity towards NH_3-SCO. Besides, catalytic activity of Au catalysts is highly dependent on the size of Au nanoparticles. Designing and thus synthesizing Au/solid acid catalysts with high Brønsted acid sites and small Au size is the key to achieving the research target.

４．研究成果

4.1 Development of preparation method for highly active solid acid supported Au catalysts.

Highly active Au/solid acid catalyst contains two parts: the solid acid support with high acidity and redox properties, and the Au nanoparticles with small size. It is known that solid acid properties and redox properties differ depending on the crystal structure. As the typical solid acid, Nb_2O_5 and Ta_2O_5 have various crystal structures and their crystalline phase transformed depend on the heat treatment. Thus, we have successfully synthesized various crystal phase Nb_2O_5 and Ta_2O_5 (as shown in **Figure 1**). The influence of crystal phases of Nb_2O_5 and Ta_2O_5 on the preparation of Au catalysts and their catalytic activities for CO oxidation have also been investigated (*J. Jpn. Pet. Inst.*, 2022, 65(2): 58-66).

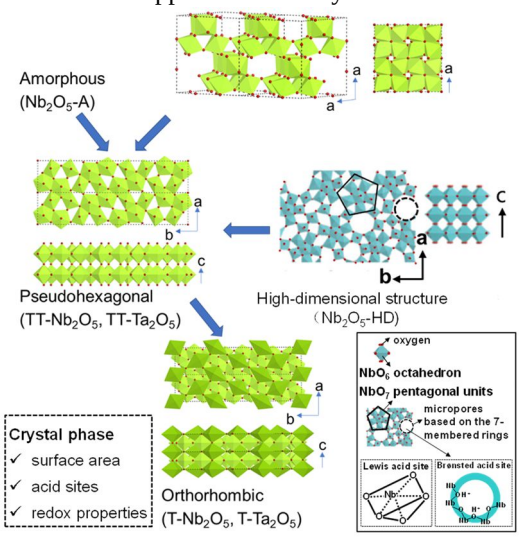


Figure 1. Crystal models of Nb_2O_5 and Ta_2O_5 (Arrows indicate the heat treatment process).

The perimeter interface between Au and metal oxide has been reported to be the active site for the activation of the oxygen. Thus, the size of Au nanoparticles is an important factor for the high catalytic activity. It is technical difficult to prepare Au/solid acid catalyst by the conventional deposition-precipitation method due to the charge repels between the negatively charged gold precursor $[Au(OH)_4]^-$/$[AuCl(OH)_3]^-$ and the negatively charged surface of solid acid. Therefore, in order to develop highly active Au catalysts that supported on Nb_2O_5 and Ta_2O_5 with different crystal phases, sol immobilization method was used and further developed. As shown in **Figure 2**, 1-dodecanethiol protected gold colloid (d = 1.8 nm) and 2-phenylethanethiol protected gold colloid (d = 1.2 nm) were synthesized as the gold precursor and were successfully deposited on the high-dimensional Nb_2O_5 with the average size of 2.8 nm and 2.1 nm. The effect of the thiolate ligand on the preparation of Au/Nb_2O_5 was investigated and a small amount of sulfur species still remained on the catalyst after the calcination at 300 ℃, which played an important role for preventing the aggregation of the gold nanoparticles to give ca. 2.8 nm in a mean diameter (*J. Catal.*, 2020, 389: 9-18). Furthermore, in order to avoid the use of toxic organic solvents and simplify the preparation method, the water/ethanol soluble poly

(N-vinylpyrrolidone) (PVP) protected Au-PVP colloid was synthesized and the prepared Au(-PVP)/Nb_2O_5 showed the average Au size of 6.4 nm. Thus, the solid acid—Nb_2O_5 and Ta_2O_5 with various kinds of crystal phases as well as the improved preparation method of gold catalyst were developed and highly active Au/Nb_2O_5 and Au/Ta_2O_5 were successfully obtained.

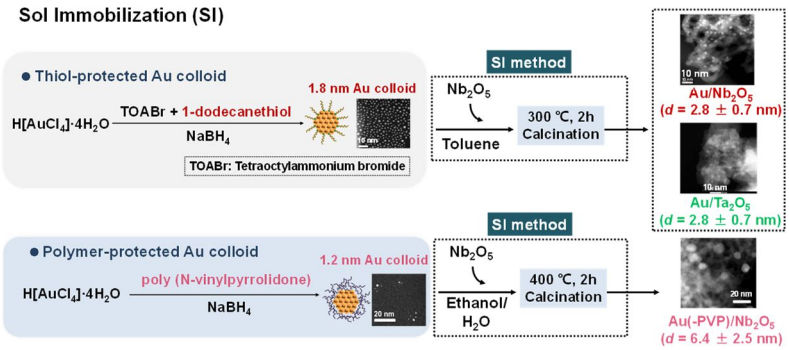


Figure 2. Sol immobilization method by using different ligand-protected Au colloids as the Au precursor.

CO oxidation was selected as the model reaction to evaluate the catalytic activity of the prepared Au/Nb_2O_5 and Au/Ta_2O_5 catalysts. As shown in **Figure 3**(a), Au/Nb_2O_5 and Au/Ta_2O_5 that prepared by using thiolate protected gold colloid as the gold precursor showed extremely high catalytic activity for CO oxidation. The reasons might be the small sizes of Au nanoparticles which were 2.8 nm, and the high-dimensional Nb_2O_5 (Nb_2O_5-HD) and pseudohexagonal Ta_2O_5 (TT-Ta_2O_5) would provide more oxygen defect sites. The detailed reaction mechanism (**Figure 3**(b)) was studied over Au/Ta_2O_5 with different crystal phases via *in situ* DRIFT measurements (*ACS Catal.*, 2020, 10(16): 9328-9335). Besides, although the Au size of Au(-PVP)/Nb_2O_5 was a little bit large (average size of 6.4 nm) compared to Au/Nb_2O_5 that prepared from thiolate ligand (average size of 2.8 nm), the catalytic activities for both gas-phase CO oxidation and liquid-phase furfural oxidation were also reasonably good (*Catal. Today*, 2022, doi: https://doi.org/10.1016/j.cattod.2022.03.034).

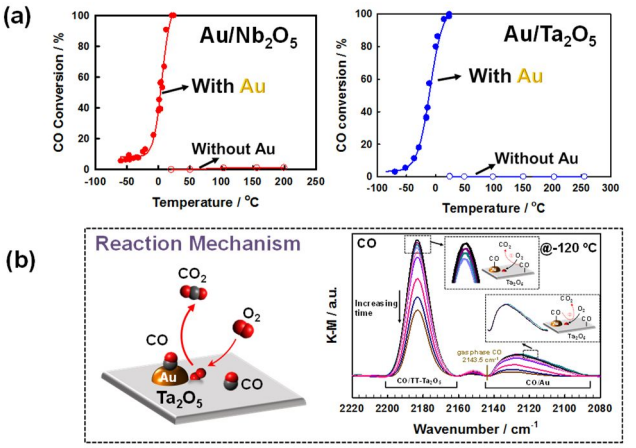
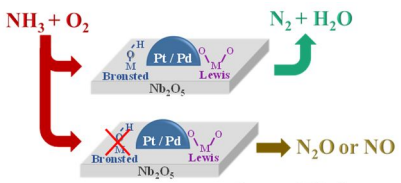


Figure 3. High catalytic activity of Au/Nb_2O_5 and Au/Ta_2O_5 for CO oxidation.

4.2 Highly active catalysts developed for selective catalytic oxidation of NH_3 (NH_3-SCO).

Developing efficient catalysts that can work at room temperature with high N_2 selectivity in ambient air is a dauting challenge, which would offer great scopes for applications related to air quality improvement and control of odors. However, the reported catalysts either needed high reaction temperature (T>250 ℃) or showed low selectivity to N_2 with the formation of NO_x as the byproduct. We have found that the Au/Nb_2O_5 catalyst that using high-dimensional structure Nb_2O_5 (Nb_2O_5-HD) as the support with the Au size of 2.8 nm showed room-temperature catalytic activity for NH_3-SCO and high N_2 selectivity at the 100% conversion of NH_3 at 250 ℃ (>95%). The high-dimensional structure Nb_2O_5 (Nb_2O_5-HD) consists of NbO_6 octahedra, NbO_7, and micropores based on the 7-membered ring in its structure with corner-sharing in the *c*-direction, which notably has the feature of large surface area that exceeds 200 m^2/g and high acid amount of Brønsted acid sites, making it to be a good solid acid support (*ACS Catal.*, 2019, 9(3): 1753-1756). In addition, the detailed reaction mechanism revealed that the Brønsted acid sites played an essential role for N_2 selectivity and small Au size was responsible for the room-temperature activity. According to the finding that Brønsted acid sites were important for N_2 selectivity of NH_3-SCO, Nb_2O_5-HD was selected as the support for the preparation of Pt and Pd catalysts. In the previous report, the Pt and Pd catalysts suffered the problem of low selectivity to N_2 in NH_3-SCO, but Pt/Nb_2O_5 and Pd/Nb_2O_5 showed 98% and 100% selectivity to N_2 at the 100% NH_3 conversion, respectively (*J. Catal.*, 2020, 389, 366-374). The N_2 selectivities greatly decreased after utilizing NaOH to block Brønsted acid sites of Pt/Nb_2O_5 and Pd/Nb_2O_5



Catalyst	NH_3 conv.	N_2 select.
Pt/Nb_2O_5	100%	98%
Pd/Nb_2O_5	100%	100%

Using Brønsted acid sites of Nb_2O_5 greatly improved the N_2 selectivity of Pt and Pd catalysts (> 98%)

Figure 4. NH_3-SCO over Pt/Nb_2O_5 and Pd/Nb_2O_5.

catalysts, suggesting the important roles of Brønsted acid sites. Furthermore, ZHM20 supported Au-Pt alloy nanoparticles catalysts further proved this conclusion (*J. Catal.*, 2021, 402: 101-113).

In addition to the research results of that the Brønsted acid sites are extremely important for the N_2 selectivity in NH_3-SCO. We investigated the size/structure effect of Ag particles on the NH_3-SCO. The results showed that Ag/MnO_2 with Ag particles of 2.4 nm diameter provided the highest density of Ag particles over rod-shaped MnO_2 during the reaction, which would be favorable for the formation of adsorbed NO and NH_2NO intermediates to form N_2 and H_2O. Therefore, the Ag size/structure plays an essential role in controlling the N_2 selectivity and the type of byproduct. This work provides a new angle in designing highly active catalysts for NH_3-SCO with high selectivity to N_2 (*ACS Catal.*, 2021, 11(14): 8576-8584). Based on this finding, Ag/Al_2O_3 with high catalytic activity and high N_2 selectivity for NH_3-SCO was developed and highly dispersed Ag species supported on Al_2O_3 was found to present > 99% N_2 selectivity at the temperature less than 200 °C. More importantly, this work not only provides a convenient and effective approach to obtain excellent N_2 selectivity in NH_3–SCO but also affords a systematic insight into the reaction pathways over Ag/Al_2O_3 catalysts (*ACS Catal.*, 2022, 12: 6108-6118).

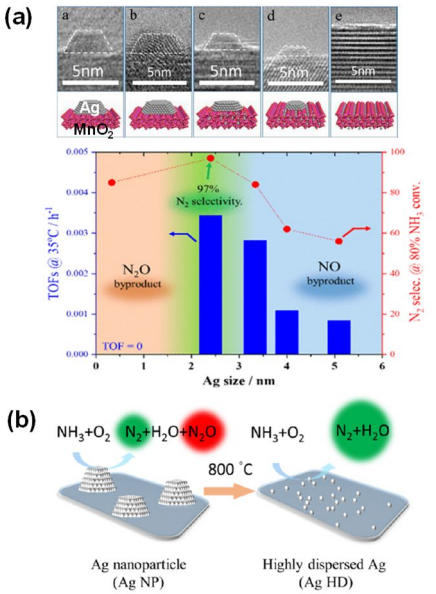


Figure 5. NH_3-SCO over Ag catalysts.

５．主な発表論文等

〔雑誌論文〕　計11件（うち査読付論文　11件／うち国際共著　7件／うちオープンアクセス　0件）

１．著者名 Haifeng Wang, Toru Murayama*, Mingyue Lin, Norihito Sakaguchi, Masatake Haruta, Hiroki Miura, and Tetsuya Shishido*	４．巻 12
２．論文標題 Understanding the distinct effects of Ag nanoparticles and highly dispersed Ag species on N2 selectivity in NH3-SCO reaction	５．発行年 2022年
３．雑誌名 ACS Catalysis	６．最初と最後の頁 6108-6118
掲載論文のDOI（デジタルオブジェクト識別子） なし	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 －

１．著者名 Haifeng Wang, Mingyue Lin, Toru Murayama*, Shixiang Feng, Masatake Haruta, Hiroki Miura, and Tetsuya Shishido*	４．巻 11(14)
２．論文標題 Ag Size/Structure-dependent effect on low-temperature selective catalytic oxidation of NH3 over Ag/MnO2	５．発行年 2021年
３．雑誌名 ACS Catalysis	６．最初と最後の頁 8576-8584
掲載論文のDOI（デジタルオブジェクト識別子） なし	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 －

１．著者名 Toru Murayama*, Mingyue Lin	４．巻 65(2)
２．論文標題 Development of solid acid-supported gold nanoparticle catalysts for air purification at room temperature	５．発行年 2022年
３．雑誌名 Journal of the Japan Petroleum Institute	６．最初と最後の頁 58-66
掲載論文のDOI（デジタルオブジェクト識別子） なし	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

１．著者名 Mingyue Lin*,Chihiro Mochizuki, Tamao Ishida, Ying Zhang, Masatake Haruta, Toru Murayama*	４．巻
２．論文標題 Effect of poly (N-vinylpyrrolidone) ligand on catalytic activities of Au nanoparticles supported on Nb205 for CO oxidation and furfural oxidation	５．発行年 2022年
３．雑誌名 Catalysis Today	６．最初と最後の頁 －
掲載論文のDOI（デジタルオブジェクト識別子） 10.1016/j.cattod.2022.03.034	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

1．著者名 Chihiro Mochizuki, Yusuke Inomata, Shunsaku Yasumura, Mingyue Lin, Ayako Taketoshi, Tetsuo Honma, Norihito Sakaguchi, Masatake Haruta, Ken-ichi Shimizu, Tamao Ishida, and Toru Murayama*	4．巻 12, 6149-6158
2．論文標題 Defective NiO as a Stabilizer for Au Single-Atom Catalysts	5．発行年 2022年
3．雑誌名 ACS Catalysis	6．最初と最後の頁 6149-6158
掲載論文のDOI（デジタルオブジェクト識別子） なし	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

1．著者名 Weixuan Zhao‡, Junjie Shi‡*, Mingyue Lin, Libo Sun, Huijuan Su, Xun Sun, Toru Murayama, Caixia Qi*	4．巻 12 (9)
2．論文標題 Praseodymia-titania mixed oxide supported gold as efficient water gas shift catalyst: modulated by the mixing ratio of oxides	5．発行年 2022年
3．雑誌名 RSC advances	6．最初と最後の頁 5374-5385
掲載論文のDOI（デジタルオブジェクト識別子） なし	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

1．著者名 Haifeng Wang, Mingyue Lin, Toru Murayama*, Shixiang Feng, Masatake Haruta, Hiroki Miura, Tetsuya Shishido*	4．巻 402
2．論文標題 Selective catalytic oxidation of ammonia to nitrogen over zeolite-supported Pt-Au catalysts: Effects of alloy formation and acid sites	5．発行年 2021年
3．雑誌名 Journal of Catalysis	6．最初と最後の頁 101-113
掲載論文のDOI（デジタルオブジェクト識別子） なし	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

1．著者名 Mingyue Lin, Baoxiang An, Takashi Takei, Tetsuya Shishido, Tamao Ishida, Masatake Haruta, Toru Murayama*	4．巻 389
2．論文標題 Features of Nb205 as a metal oxide support of Pt and Pd catalysts for selective catalytic oxidation of NH3 with high N2 selectivity	5．発行年 2020年
3．雑誌名 Journal of Catalysis	6．最初と最後の頁 366-374
掲載論文のDOI（デジタルオブジェクト識別子） 10.1016/j.jcat.2020.05.040	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 —

1．著者名 Mingyue Lin, Chihiro Mochizuki, Baoxiang An, Yusuke Inomata, Tamao Ishida, Masatake Haruta, and Toru Murayama*	4．巻 10(16)
2．論文標題 Elucidation of Active Sites of Gold Nanoparticles on Acidic Ta205 Supports for CO Oxidation	5．発行年 2020年
3．雑誌名 ACS Catalysis	6．最初と最後の頁 9328-9335
掲載論文のDOI（デジタルオブジェクト識別子） 10.1021/acscatal.0c01966	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 －

1．著者名 Mingyue Lin, Chihiro Mochizuki, Baoxiang An, Tetsuo Honma, Masatake Haruta, Tamao Ishida, Toru Murayama*	4．巻 389
2．論文標題 Ligand Effect of Gold Colloid in the Preparation of Au/Nb205 for CO Oxidation	5．発行年 2020年
3．雑誌名 Journal of Catalysis	6．最初と最後の頁 9-18
掲載論文のDOI（デジタルオブジェクト識別子） 10.1016/j.jcat.2020.05.014	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

1．著者名 Tinku Baidya*, Toru Murayama*, Subramanian Nellaiappan, Nirmal Kumar Katiyar, Parthasarathi Bera, Olga Safonova, Mingyue Lin, Kaustubh R. Priolkar, Samapti Kundu, Bolla Srinivasa Rao, Patrick Steiger, Sudhanshu Sharma, Krishanu Biswas, Swapan Kumar Pradhan, Nakka Lingaiah, Kirtiman Deo Malviya, and Masatake Haruta	4．巻 123
2．論文標題 Ultra-Low-Temperature CO Oxidation Activity of Octahedral Site Cobalt Species in Co304 Based Catalysts: Unravelling the Origin of the Unique Catalytic Property	5．発行年 2019年
3．雑誌名 The Journal of Physical Chemistry C	6．最初と最後の頁 19557-19571
掲載論文のDOI（デジタルオブジェクト識別子） 10.1021/acs.jpcc.9b04136	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

〔学会発表〕　計10件（うち招待講演　0件／うち国際学会　4件）

1．発表者名 Mingyue Lin, Haifeng Wang, Hiroki Miura, Tetsuya Shishido, Masatake Haruta, Toru Murayama
2．発表標題 Au-Pt alloy nanoparticles supported on zeolite for the highly efficient removal of ethylene at 0 ℃
3．学会等名 第128回触媒討論会
4．発表年 2021年

１．発表者名
Mingyue Lin, Haifeng Wang, Tetsuya Shishido, Hiroki Miura, Masatake Haruta, Toru Murayama

２．発表標題
Highly efficient removal of ethylene at 0 ℃ over Au-Pt/zeolite

３．学会等名
函館大会（第51回石油・石油化学討論会）

４．発表年
2021年

１．発表者名
Mingyue Lin, Baoxiang An, Yohei Jikihara, Fukui Yoko, Tsuruo Nakayama,Toru Murayama, Masatake Haruta, Tamao Ishida, Sadao Yasui, Takashi Takei,Tetsuya Shishido, Toru Murayama

２．発表標題
Effects of solid acidity of the support on the selective catalytic oxidation of NH3 by the niobium oxide supported precious metals catalysts

３．学会等名
第126回触媒討論会

４．発表年
2020年

１．発表者名
Mingyue Lin, Baoxiang An, Takashi Takei, Tetsuya Shishido, Tamao Ishida, Masatake Haruta, Toru Murayama

２．発表標題
Role of acid sites for selective catalytic oxidation of NH3: the case of niobium oxide supported precious metals catalysts

３．学会等名
熊本大会(第50回石油・石油化学討論会)

４．発表年
2020年

１．発表者名
Mingyue Lin, Baoxiang An, Nao Niimi, Yohei Jikihara, Tsuruo Nakayama, Takashi Takei, Tetsuya Shishido, Tamao Ishida, Masatake Haruta, Toru Murayama*

２．発表標題
Efficient removal of ammonia by using niobium oxide supported gold catalyst with high nitrogen selectivity

３．学会等名
The 8th Asia Pacific Congress on Catalysis（国際学会）

４．発表年
2019年

１．発表者名
Mingyue Lin, Baoxiang An, Yoko Fukui, Yohei Jikihara, Tsuruo Nakayama, Takashi Takei, Tetsuya Shishido, Tamao Ishida, Masatake Haruta, Toru Murayama*

２．発表標題
Selective Catalytic Oxidation of NH3 by using Au/Nb205

３．学会等名
The 10th National Conference on Environmental Chemistry

４．発表年
2019年

１．発表者名
Mingyue Lin,Baoxiang An, Nao Niimi, Yohei Jikihara, Tsuruo Nakayama, Takashi Takei, Tetsuya Shishido, Tamao Ishida, Masatake Haruta, and Toru Murayama *

２．発表標題
Selective Catalytic Oxidation of NH3 with High N2 Selectivity over Au/Nb205

３．学会等名
水素社会のための第4回国際シンポジウムプログラム（国際学会）

４．発表年
2019年

１．発表者名
Mingyue Lin, Chihiro Mochizuki, Baoxiang An, Yusuke Inomata, Tamao Ishida, Masatake Haruta, Toru Murayama*

２．発表標題
High catalytic activity for CO oxidation below room temperature over Au/Ta205

３．学会等名
第124回触媒討論会

４．発表年
2019年

１．発表者名
Mingyue Lin, Chihiro Mochizuki, Baoxiang An, Yusuke Inomata , Tamao Ishida, Masatake Haruta, Toru Murayama*

２．発表標題
High catalytic activity for CO oxidation below room temperature over Au/Ta205

３．学会等名
Au-Sdarc Symposium on Gold Catalysis 2019（国際学会）

４．発表年
2019年

１．発表者名 Mingyue Lin, Baoxiang An, Yoko Fukui, Yohei Jikihara, Tsuruo Nakayama, Takashi. Takei, Tetsuya Shishido, Tamao Ishida, Masatake Haruta, Toru Murayama*
２．発表標題 Role of acid sites in selective catalytic oxidation of NH3 with high N2 selectivity
３．学会等名 9th East Asia Joint Symposium on Environmental Catalysis and Eco-materials（国際学会）
４．発表年 2019年

〔図書〕　計0件

〔出願〕　計1件

産業財産権の名称	発明者	権利者
脱臭触媒	2020	同左
産業財産権の種類、番号	**出願年**	**国内・外国の別**
特許、特願2020-148138	2020年	国内

〔取得〕　計0件

〔その他〕

６．研究組織

	氏名 （ローマ字氏名） （研究者番号）	所属研究機関・部局・職 （機関番号）	備考

７．科研費を使用して開催した国際研究集会

〔国際研究集会〕　計0件

８．本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関