

## Supporting information

### **Catalytic conversion to ammonia through solid-state nitrate as a proposal for emerging usage of nitrogen oxides**

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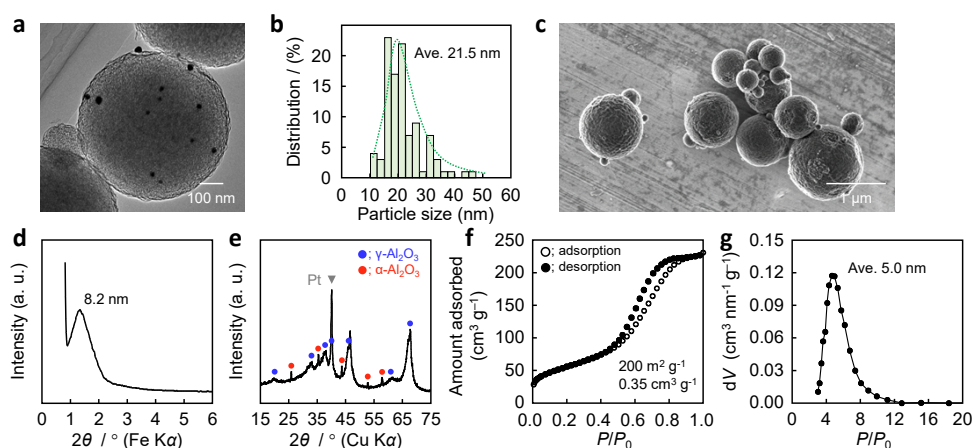
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**Table S1** Structural features of AEM/PGM@mAl<sub>2</sub>O<sub>3</sub> type nanocomposite catalysts.

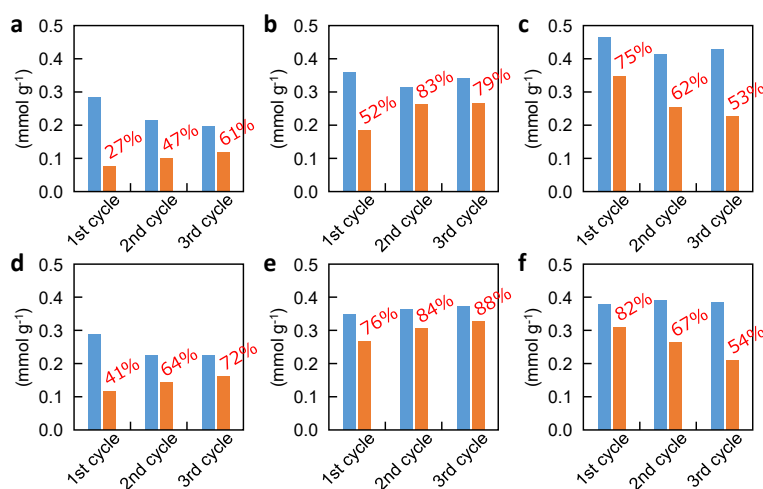
Nanocomposite catalyst / mass ratio	Amount of Pt NPs / mass %	Specific surface area / m <sup>2</sup> g <sup>-1</sup>	Total pore volume / cm <sup>3</sup> g <sup>-1</sup>	Pore diameter / nm	Size, ave. PGM NPs / nm	
					TEM	XRD
$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	-	-	-	-	-	-
10Ba/1.00Pt/100 $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	0.90	-	-	-	13	17
1.00Pt@100mAl <sub>2</sub> O <sub>3</sub> ( $\gamma$ )	-	200	0.35	5.0	22	23
10Ba/1.00Pt@100mAl <sub>2</sub> O <sub>3</sub> ( $\gamma$ )	-	180	0.32	5.0	21	25
10Ba/1.00Pd@100mAl <sub>2</sub> O <sub>3</sub> ( $\gamma$ )	-	190	0.44	7.5	51	15 (PdO)
10Ba/1.00Ir@100mAl <sub>2</sub> O <sub>3</sub> ( $\gamma$ )	-	190	0.33	5.1	>100	32 (IrO <sub>2</sub> )
10Ba/1.00Rh@100mAl <sub>2</sub> O <sub>3</sub> ( $\gamma$ )	-	230	0.49	5.8	19	15 (Rh <sub>2</sub> O <sub>3</sub> )
2.7Ca/0.93Pt@100mAl <sub>2</sub> O <sub>3</sub> ( $\gamma$ )	0.90	180	0.33	4.2	21	22
4.0Ca/1.00Pt@100mAl <sub>2</sub> O <sub>3</sub> ( $\gamma$ )	0.95	180	0.32	5.1	22	23
5.6Ca/0.96Pt@100mAl <sub>2</sub> O <sub>3</sub> ( $\gamma$ )	0.90	150	0.27	4.2	24	20
7.2Ca/0.97Pt@100mAl <sub>2</sub> O <sub>3</sub> ( $\gamma$ )	0.90	170	0.26	4.0	21	16
8.8Ca/0.99Pt@100mAl <sub>2</sub> O <sub>3</sub> ( $\gamma$ )	0.90	140	0.19	3.5	20	15

**Table S2** Direct NH<sub>3</sub> synthesis in a flow of 1000 ppm NO with 1% H<sub>2</sub> by using typical nanocomposite catalysts.

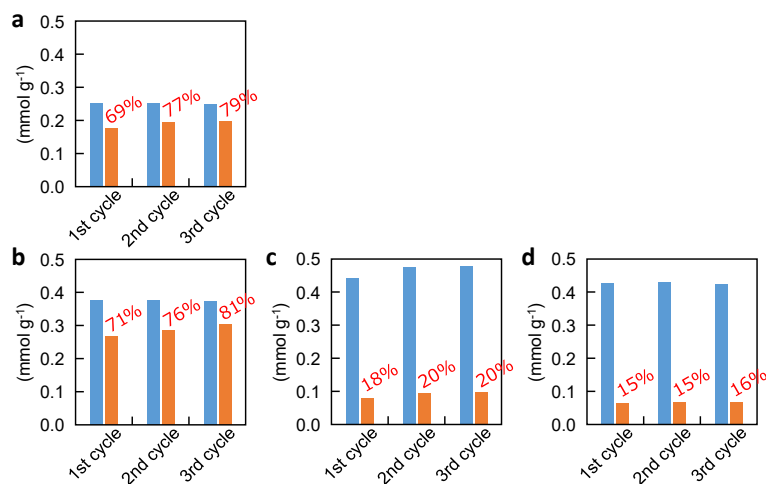
	Temperature / °C	NO / ppm	H <sub>2</sub>	NH <sub>3</sub>	N <sub>2</sub>	N <sub>2</sub> O	NO <sub>2</sub>
1.00Pt/100 $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	150 °C	0	7890	841	34	53	0
	200 °C	0	7840	899	27	23	0
	250 °C	0	7780	925	23	11	0
	300 °C	0	7790	941	20	0	0
	350 °C	0	7780	959	12	0	0
	400 °C	0	7790	967	8	0	0
	450 °C	0	7810	977	6	0	0
10Ba/1.00Pt@100mAl <sub>2</sub> O <sub>3</sub> ( $\gamma$ )	150 °C	0	8330	597	195	0	0
	200 °C	0	8200	722	144	0	0
	250 °C	0	7990	849	69	0	0
	300 °C	0	7880	912	51	0	0
	350 °C	0	7890	947	27	0	0
	400 °C	0	7970	933	28	0	0
	450 °C	0	7940	915	47	0	0
5.6Ca/0.96Pt@100mAl <sub>2</sub> O <sub>3</sub> ( $\gamma$ )	150 °C	0	8190	715	95	55	0
	200 °C	0	8010	866	63	0	0
	250 °C	0	7860	924	47	0	0
	300 °C	0	7860	959	34	0	0
	350 °C	0	7820	967	28	0	0
	400 °C	0	7830	973	28	0	0
	450 °C	0	7840	962	34	0	0



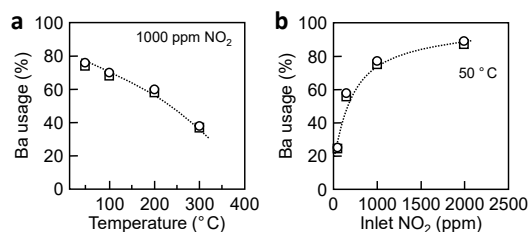
**Fig. S1** Characterization of 1Pt@mAl<sub>2</sub>O<sub>3</sub>( $\gamma$ ) prepared in one-pot by spray-drying a precursor solution for obtaining mAl<sub>2</sub>O<sub>3</sub> in the presence of Pluronic P123 with H<sub>2</sub>PtCl<sub>6</sub>; a) representative TEM image with b) resultant size distribution of Pt NPs, c) typical SEM image, d) low- and e) wide-angle XRD patterns and f) N<sub>2</sub> adsorption-desorption isotherm with g) corresponding pore size distribution curve.



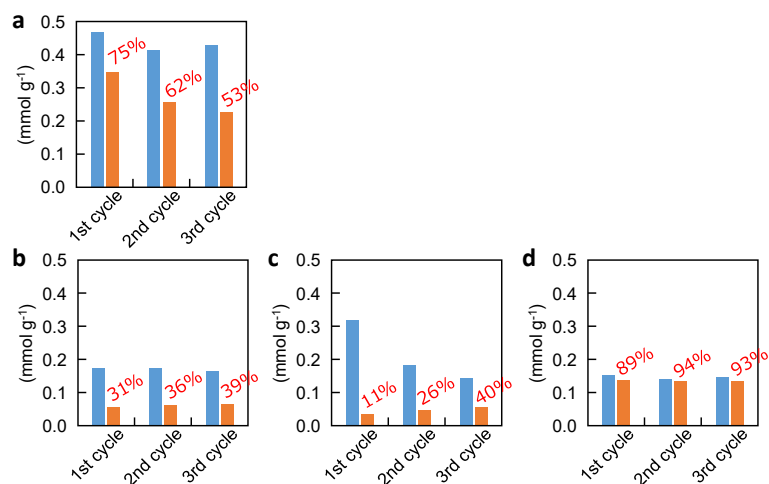
**Fig. S2** Amounts of ■ NO<sub>x</sub> storage and ■ NH<sub>3</sub> recovery of 10Ba/1Pt@mAl<sub>2</sub>O<sub>3</sub>( $\gamma$ ) with the selectivity to NH<sub>3</sub> during the operation cycles by alternate gas-switching between 1000 ppm NO with 10% O<sub>2</sub> and 1% H<sub>2</sub> at a) 200 °C, b) 250 °C, and c) 300 °C or 5% H<sub>2</sub> for NH<sub>3</sub> recovery at d) 200 °C, e) 250 °C, and f) 300 °C.



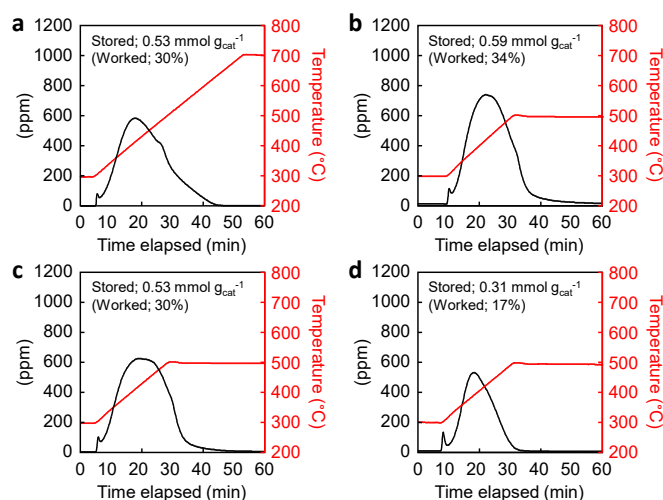
**Fig. S3** A preliminary study for  $\blacksquare$ NO<sub>x</sub> storage and  $\blacksquare$ NH<sub>3</sub> recovery by using a common 10Ba/1Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> type catalyst, prepared through step-by-step impregnation of H<sub>2</sub>PtCl<sub>6</sub> and Ba(OOCCH<sub>3</sub>)<sub>2</sub> over a commercially available  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, with the selectivity to NH<sub>3</sub> during the operation cycles by alternate gas-switching between 1000 ppm NO with 10% O<sub>2</sub> and 1% H<sub>2</sub> at a) 175 °C, b) 200 °C, c) 250 °C and d) 300 °C.



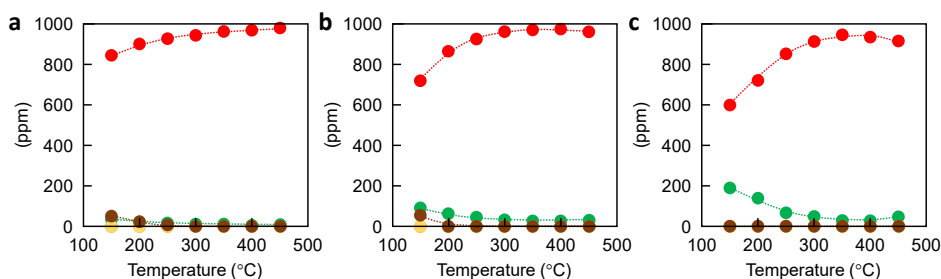
**Fig. S4** Direct NO<sub>2</sub> storage property of 10Ba/1Pt@mAl<sub>2</sub>O<sub>3</sub>( $\gamma$ ), being calculated as  $\circ$ BaCO<sub>3</sub> and  $\square$ BaO monolayers at the surface of mAl<sub>2</sub>O<sub>3</sub>( $\gamma$ ), during a) storage of NO<sub>2</sub> at different temperatures ranging from 300 °C down to 50 °C for 60 min in a flow of 1000 ppm NO<sub>2</sub> and b) that at 50 °C for 60 min in a flow of different NO<sub>2</sub> concentration from 300 ppm up to 2000 ppm.



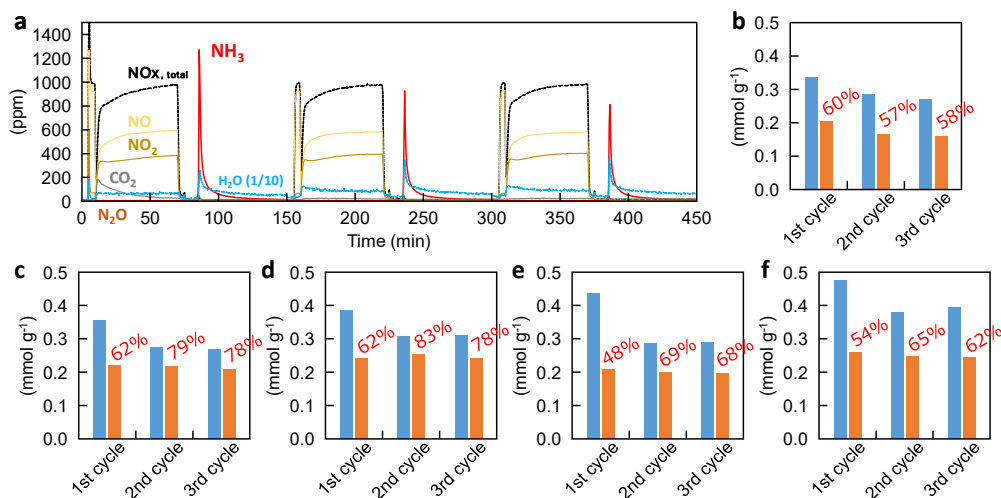
**Fig. S5** Amounts of  $\blacksquare$ NO<sub>x</sub> storage and  $\blacksquare$ NH<sub>3</sub> recovery with the selectivity to NH<sub>3</sub> by using a) 10Ba/1Pt@mAl<sub>2</sub>O<sub>3</sub>( $\gamma$ ), b) 10Ba/1Pd@mAl<sub>2</sub>O<sub>3</sub>( $\gamma$ ), c) 10Ba/1Ir@mAl<sub>2</sub>O<sub>3</sub>( $\gamma$ ) and d) 10Ba/1Rh@mAl<sub>2</sub>O<sub>3</sub>( $\gamma$ ) during the operation cycles at 300 °C by alternate gas-switching between 1000 ppm NO with 10% O<sub>2</sub> and 1% H<sub>2</sub>.



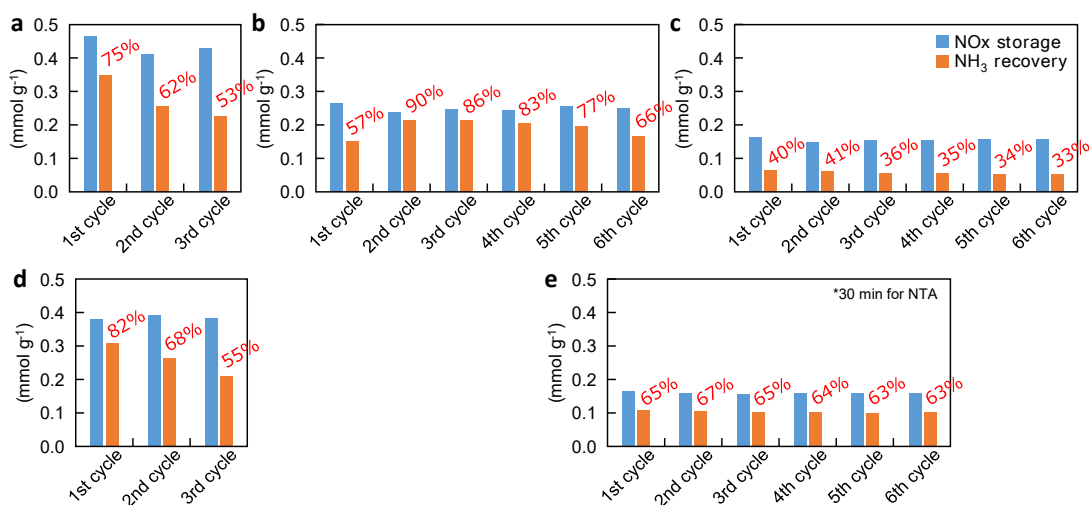
**Fig. S6** NO<sub>x</sub>-TPD profiles in a flow of 1000 ppm NO with 10% O<sub>2</sub> at 300 °C by using a) 10Ba/1Pt@mAl<sub>2</sub>O<sub>3</sub>( $\gamma$ ) and other catalysts such as b) Sr/1Pt@mAl<sub>2</sub>O<sub>3</sub>( $\gamma$ ), c) Ca/1Pt@mAl<sub>2</sub>O<sub>3</sub>( $\gamma$ ) and d) Mg/1Pt@mAl<sub>2</sub>O<sub>3</sub>( $\gamma$ ) during the heating from 300 °C up to 700 °C and/or 500 °C.



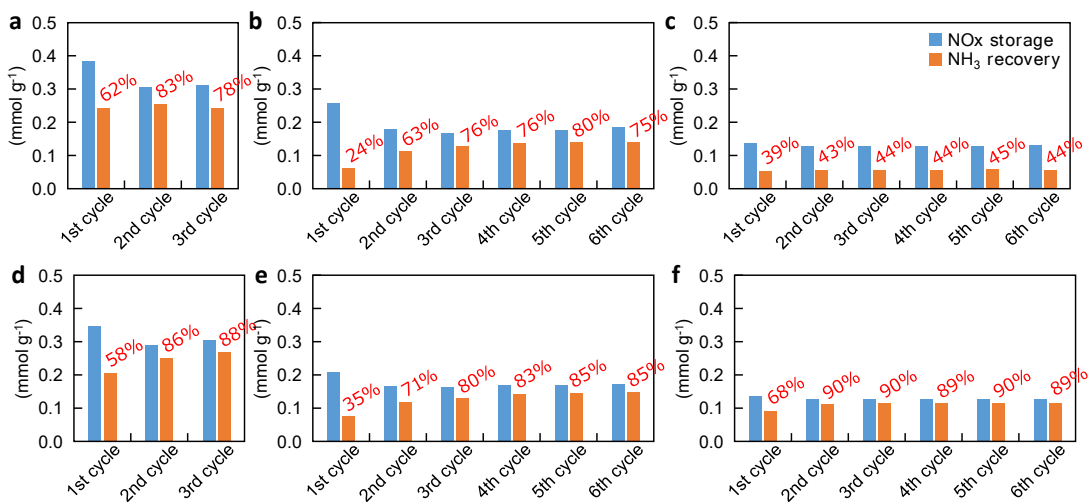
**Fig. S7** Direct catalytic conversion of NO with H<sub>2</sub> to nitrogen sources such as ●NH<sub>3</sub>, ●NO, ●NO<sub>2</sub>, ●N<sub>2</sub>O, and ●N<sub>2</sub> during the reaction in a flow of 1000 ppm NO with 1% H<sub>2</sub> by using a) 1Pt@mAl<sub>2</sub>O<sub>3</sub>( $\gamma$ ), b) 5.6Ca/0.96Pt@mAl<sub>2</sub>O<sub>3</sub>( $\gamma$ ) and c) 10Ba/1Pt@mAl<sub>2</sub>O<sub>3</sub>( $\gamma$ ) at temperatures ranging from 150 °C up to 450 °C.



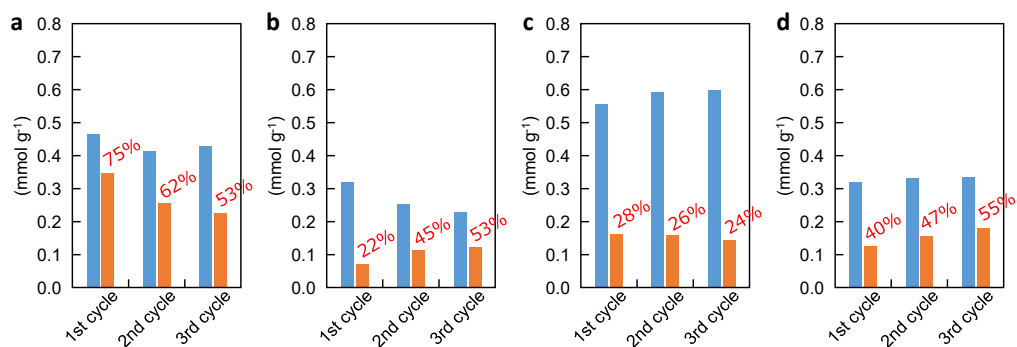
**Fig. S8** Amounts of ■NO<sub>x</sub> storage and ■NH<sub>3</sub> recovery with the selectivity to NH<sub>3</sub> by using a), b) 2.7Ca/0.9Pt@mAl<sub>2</sub>O<sub>3</sub>( $\gamma$ ) during the operation cycles at 300 °C by alternate gas-switching between 1000 ppm NO with 10% O<sub>2</sub> and 1% H<sub>2</sub> and those observed for c) 4.0Ca/1.0Pt@mAl<sub>2</sub>O<sub>3</sub>( $\gamma$ ), d) 5.6Ca/0.96Pt@mAl<sub>2</sub>O<sub>3</sub>( $\gamma$ ), e) 7.2Ca/0.97Pt@mAl<sub>2</sub>O<sub>3</sub>( $\gamma$ ) and f) 8.8Ca/0.99Pt@mAl<sub>2</sub>O<sub>3</sub>( $\gamma$ ).



**Fig. S9** A case study for maximizing NH<sub>3</sub> recovery by using 10Ba/1Pt@mAl<sub>2</sub>O<sub>3</sub>( $\gamma$ ); amounts of ■NO<sub>x</sub> storage and ■NH<sub>3</sub> recovery with the selectivity to NH<sub>3</sub> during the operation cycles at 300 °C by alternate gas-switching between 1000 ppm NO with 10% O<sub>2</sub> and 1% H<sub>2</sub> when the reaction time was reduced from a) 60 min to b) 20 min and c) 15 min for each reaction or 5% H<sub>2</sub> when the reaction time was reduced from d) 60 min for each reaction to e) 15 min for NO<sub>x</sub> storage and 30 min for NH<sub>3</sub> synthesis.



**Fig. S10** A case study for maximizing NH<sub>3</sub> recovery by using 5.6Ca/0.96Pt@mAl<sub>2</sub>O<sub>3</sub>( $\gamma$ ); amounts of ■NO<sub>x</sub> storage and ■NH<sub>3</sub> recovery with the selectivity to NH<sub>3</sub> during the operation cycles at 300 °C by alternate gas-switching between 1000 ppm NO with 10% O<sub>2</sub> and 1% H<sub>2</sub> when the reaction time was reduced from a) 60 min to b) 20 min and c) 15 min for each reaction or 5% H<sub>2</sub> when the reaction time was reduced from d) 60 min to e) 20 min and f) 15 min for each reaction.



**Fig. S11** Amounts of ■NO<sub>x</sub> storage and ■NH<sub>3</sub> recovery with the selectivity to NH<sub>3</sub> by using 10Ba/1Pt@mAl<sub>2</sub>O<sub>3</sub>( $\gamma$ ) during the operation cycles at 300 °C for totally 120 min by alternate gas-switching between 1000 ppm NO with 10% O<sub>2</sub> a) without CO<sub>2</sub> and H<sub>2</sub>O, b) with 10% CO<sub>2</sub>, c) with 10% H<sub>2</sub>O, and d) with 10% CO<sub>2</sub> and 10% H<sub>2</sub>O for 60 min and 1% H<sub>2</sub> for NH<sub>3</sub> recovery.