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PRODUCTION OF NITROUS OXIDE

This invention is directed to the production of nitrous oxide, N_2O , from ammonia and nitric oxide, NO , over a catalyst comprising a Group VIB metal oxide. Specifically, the catalyst of this invention comprises an oxide of a Group VIB metal
5 such as molybdenum oxide, that may optionally be supported on a Group IVB metal oxide support such as zirconia, or on a solid support material such as silica, and that may optionally comprise a Group VIIIB metal oxide component such as iron oxide.

One commercial process for making nitrous oxide involves the thermal decomposition of ammonium nitrate when heated from 200 to 260°C according to
10 the following equation:



However, extreme caution must be used in handling ammonium nitrate, which may be highly explosive under extreme shock or elevated temperatures. Therefore, improved methods for controlling the thermal decomposition of ammonium nitrate
15 have been disclosed. For example, the thermal decomposition of ammonium nitrate in the presence of a melt containing ammonium hydrogen sulfate and ammonium sulfate is described in U.S. Patent No. 4,154,806; the thermal decomposition of ammonium nitrate into an aqueous, strongly acid reaction liquor containing chloride ions as a catalyst is described in U.S. Patent No. 4,102,986; and the thermal
20 decomposition of ammonium nitrate in a chloride-containing aqueous solution of nitric acid and the presence of catalytically active ions of manganese, copper, cerium, lead, bismuth, cobalt or nickel, is described in U.S. Patent No. 3,656,899.

Another commercial process for producing nitrous oxide involves the reaction of ammonia and air using Mn and Bi oxides as catalysts. For example, Japanese
25 Patent No. 6122507 describes a process for preparing nitrous oxide by the oxidation of ammonia with oxygen in the presence of steam and a CuO/MnO_2 catalyst. Other methods for producing nitrous oxide include the reaction of a molten nitrate salt with ammonium chloride and the reaction of ammonia with at least one molten nitrate salt of an alkaline earth metal, as described in U.S. Patent No. 4,720,377.

30 The present invention is directed to the conversion of ammonia with nitric oxide and/or oxygen into nitrous oxide using a catalyst comprising a Group VIB



metal oxide. Accordingly, the present invention avoids the dangers associated with the use and handling of ammonium nitrate and is an alternative and novel nitrous oxide synthesis method that is inexpensive and safe.

The present invention is directed to a process for producing nitrous oxide comprising the step of reacting ammonia with nitric oxide and/or oxygen in the presence of a catalyst comprising a Group VIB metal oxide, to produce an effluent mixture comprising nitrous oxide.

The Catalyst

One embodiment of the present invention utilizes the Group VIB metal oxide alone as the catalyst for reaction.

A second embodiment utilizes a catalyst that comprises the Group VIB metal oxide in combination with the Group VIIIB metal oxide.

A third embodiment utilizes a catalyst that comprises the Group VIB metal oxide, in combination with the Group IVB metal oxide as a support.

A fourth embodiment utilizes a catalyst that comprises the Group VIB and Group VIIIB metal oxides, in combination with the Group IVB metal oxide as a support.

A fifth embodiment utilizes a catalyst that comprises the Group VIB metal oxide, in combination with a solid support material.

A sixth embodiment utilizes a catalyst that comprises the Group VIB and Group VIIIB metal oxides, in combination with the solid support material.

The Group VIB metal oxide of the present invention may be an oxide of chromium, molybdenum or tungsten. Preferably, the Group VIB metal oxide is molybdenum oxide, MoO_3 . Sources of the Group VIB metal oxide may include pure molybdenum oxide MoO_3 , ammonium heptamolybdate tetrahydrate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, and molybdenum halides and oxyhalides.

The Group IVB metal oxide of the present invention may be an oxide of titanium, zirconium or hafnium. Preferably, the Group IVB metal oxide is zirconia. Sources of the Group IVB metal oxide may include zirconyl chloride and zirconyl nitrate. When the Group IVB metal oxide is used in combination with the Group VIB metal oxide, the weight ratio of the Group VIB metal oxide to Group IVB metal oxide

is from 0.001:1 to 0.5:1, and preferably from 0.1:1 to 0.3:1.

Examples of the solid support materials include silica and the material designated M41S, which is described in U.S. Patent No. 5,102,643. A particular example of such an M41S material is a material designated MCM-41, which is described in U.S. Patent No. 5,098,684. When the Group VIB metal oxide is used in combination with the solid support material, the weight ratio of the Group VIB metal oxide to the solid support material is from 0.05:1 to 0.8:1, and preferably from 0.15:1 to 0.6:1.

The Group VIIIB metal oxide may be an oxide of iron. Preferably, the Group VIIIB metal oxide is iron oxide. Sources of the Group VIIIB metal oxide may include iron (II) sulfate heptahydrate $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, iron halides and iron nitrate. When the Group VIIIB metal oxide is used in combination with the Group VIB metal oxide alone, the Group VIB and Group IVB metal oxides, or the Group VIB metal oxide and the solid support material, the molar ratio of the Group VIIIB metal oxide to the Group VIB metal oxide is from 0.001:1 to 0.1:1, and preferably from 0.005:1 to 0.05:1.

Preparation of the Catalyst

The catalyst of the present invention may be prepared, for example, by combining a first liquid solution comprising a source of the Group VIB metal oxide, and a second liquid solution comprising a source of the Group IVB metal and/or a third liquid solution comprising a source of the Group VIIIB metal oxide, under conditions sufficient to cause precipitation of the catalyst. Examples of the precipitating reagent include ammonium hydroxide, alkylammonium hydroxide and alkaline hydroxides such as sodium hydroxide. Water is a preferred solvent for these solutions.

Optionally, the liquid solution from which the catalyst is precipitated may comprise a solid support material, in which case the components of the catalyst may be precipitated directly onto the solid support material. For example, the Group VIIIB metal oxide may optionally be co-precipitated from the liquid solution, along with the Group VIB metal oxide, directly onto the solid support material.

The temperature at which the liquid solution is maintained during precipitation may be less than 200°C, e.g., from 0 to 200°C. A particular range of such temperatures

is from 50 to 100°C. The pH range of the liquid solution during precipitation is from 4 to 11.

The catalyst may be recovered from the liquid solution by filtration, followed by drying. The catalyst may be subjected to a final calcination as described below to dehydrate the catalyst and to confer the required mechanical strength on the catalyst.

Calcination of the catalyst may be carried out, preferably in an oxidizing atmosphere, at atmospheric pressure to 6890 kPa (1000 psi); and at temperatures from 500 to 850°C. The calcination time may be up to 48 hours, e.g., for 0.5 to 24 hours, e.g., for 1.0 to 10 hours.

10 The Process

Nitric oxide and ammonia are converted to nitrous oxide in the present invention by a reaction which may be described by the following equation:



although other reactions may also occur.

15 An additional reaction that occurs when oxygen is present is the oxidation of ammonia with oxygen to form nitrous oxide which may be described by the following equation:



The molar feed ratio of nitric oxide to ammonia ranges from 0.01:1 to 10:1; the amount of oxygen fed to the reaction unit ranges from 0.01 to 35 molar %.

The method according to the present invention is carried out at a temperature ranging from 200 to 600°C, and preferably from 300 to 500°C; a pressure ranging from 0.1 to 100 atmospheres, and preferably from 0.5 to 5 atmospheres. The gas hourly space velocity for the reaction ranges from 1,000 to 10,000,000 hr⁻¹, and preferably from 20,000 to 1,000,000 hr⁻¹.

The effluent mixture comprises nitrogen, oxygen, nitric oxide, ammonia and the desired product, nitrous oxide. The nitrous oxide may be separated and recovered from the effluent mixture by conventional means known to skilled artisans or the entire effluent may be used as a feed to a separate reactor. Alternatively, the nitrous oxide can be utilized *in situ* as a selective oxidant for various substrates. For example, benzene could be co-fed with the reactants and phenol product recovered.

The invention will now be more particularly described with reference to the Examples, each of which discloses the conversion of a gaseous mixture containing ammonia together with nitric oxide and/or oxygen, with the balance in each case being helium.

5 Example I

Five hundred grams of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ were dissolved with stirring in 6.0 liters of distilled water. To this, a solution containing 33 grams of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ in 500 ml of H_2O was added. Finally, a solution containing 263 ml of conc. NH_4OH and 500 ml of distilled H_2O was added dropwise over a 30-45 minute period. The pH of the solution was approximately 9. This slurry was then placed in a steambox for 72 hours. The product formed was recovered by filtration, washed with excess water, and dried overnight at 85°C . The material was then calcined in air at 700°C for 3 hours. Chemical analysis of the dried materials showed a Mo/Zr ratio of 0.11 (weight basis); this corresponds to a water-free sample composition of approximately 7.3% Mo.

Table 1 shows the activity and selectivity of this sample for the conversion of 500 ppm each of ammonia and nitric oxide into N_2O at a space velocity of approximately $600,000 \text{ hr}^{-1}$. At 500°C , 60% of the inlet ammonia and nitric oxide is converted. The selectivity to N_2O is approximately 61%; the remaining 39% of the material is converted to N_2 .

inlet concentrations				outlet concentrations				selectivity to
T(°C)	O ₂ (%)	NH ₃ (ppm)	NO(ppm)	NH ₃ (ppm)	NO(ppm)	N ₂ (ppm)	N ₂ O(ppm)	N ₂ O
300	1	500	500	448	447	45	5	9.9%
350	1	500	500	399	397	84	14	14.4%
400	1	500	500	345	345	105	44	29.6%
450	1	500	500	273	288	109	107	49.7%
500	1	500	500	173	230	115	180	61.1%

Table 1. Conversion of NO and NH_3 to N_2O over catalyst described in Example I.

0.050 g catalyst used. Space velocity $\sim 600,000 \text{ hr}^{-1}$.

Example II

This catalyst was prepared in a manner identical to Example I except that it was calcined in air at 830°C for 3 hours. Table 2 shows that calcination of this material at a higher temperature gives higher selectivity to N₂O at temperatures of 400°C and below than the catalyst of Example I, but a lower selectivity at 500°C. The selectivity of this sample is much less affected by temperature than that of the catalyst used in Example I.

T(°C)	inlet concentrations			outlet concentrations				selectivity to
	O ₂ (%)	NH ₃ (ppm)	NO(ppm)	NH ₃ (ppm)	NO(ppm)	N ₂ (ppm)	N ₂ O(ppm)	N ₂ O
300	1	500	500	465	473	14	16	52.7%
350	1	500	500	397	432	37	47	55.7%
400	1	500	500	291	397	70	85	54.8%
450	1	500	500	193	378	101	110	52.2%
500	1	500	500	132	378	124	117	48.5%

Table 2. Conversion of NO and NH₃ to N₂O over catalyst described in Example II.

0.050 g catalyst used. Space velocity ~ 600,000 hr⁻¹.

Example III

Five hundred grams of ZrOCl₂·8H₂O were dissolved with stirring in 6.0 liters of distilled water. To this, a solution containing 66 grams of (NH₄)₆Mo₇O₂₄·4H₂O in 500 ml of H₂O was added. Finally, a solution containing 263 ml of conc. NH₄OH and 500 ml of distilled H₂O was added dropwise over a 30–45 minute period. The pH of the solution was adjusted to approximately 9 by the addition of 146 grams of concentrated NH₄OH. This slurry was then placed in a steambox for 72 hours. The product formed was recovered by filtration, washed with excess water, and dried overnight at 85°C. The material was then calcined in air at 600°C for 3 hours. Chemical analysis of the dried materials showed an Mo/Zr ratio of 0.19 (weight basis); this corresponds to a water-free sample composition of approximately 11.4% Mo. Table 3 shows the activity and selectivity of this sample for N₂O formation. The higher concentrations of molybdenum gives both higher activities and selectivities than observed in Example I.

T(°C)	inlet concentrations			outlet concentrations				selectivity to
	O ₂ (%)	NH ₃ (ppm)	NO(ppm)	NH ₃ (ppm)	NO(ppm)	N ₂ (ppm)	N ₂ O(ppm)	N ₂ O
300	1	500	500	385	385	91	15	14.5%
350	1	500	500	322	321	121	50	29.0%
400	1	500	500	252	269	109	125	53.5%
450	1	500	500	167	228	95	205	68.4%
500	1	500	500	92	211	99	250	71.7%

Table 3. Conversion of NO and NH₃ to N₂O over catalyst described in Example III.0.050 g catalyst used. Space velocity ~ 600,000 hr⁻¹.

5 Example IV

Five hundred grams of ZrOCl₂·8H₂O were dissolved with stirring in 6.0 liters of distilled water. To this, a solution containing 66 grams of (NH₄)₆Mo₇O₂₄·4H₂O in 500 ml of H₂O was added. Another solution containing 7.5 grams of FeSO₄·7H₂O in 500 ml of H₂O was added. Finally, a solution containing 263 ml of conc. NH₄OH and 500 ml of distilled H₂O was added dropwise over a 30-45 minute period. The pH of the solution was adjusted to approximately 9. This slurry was then placed in a steambox for 72 hours. The product formed was recovered by filtration, washed with excess water, and dried overnight at 85°C. The material was then calcined in air at 600°C for 3 hours. Chemical analysis of the dried materials showed an Mo/Zr ratio of 0.20 (weight basis) and an Fe/Zr ratio of 0.012; this corresponds to a water-free sample composition of approximately 12.1% Mo and 0.72% Fe. Table 4 shows the activity and selectivity of this iron-containing sample.

T(°C)	inlet concentrations			outlet concentrations				selectivity to
	O ₂ (%)	NH ₃ (ppm)	NO(ppm)	NH ₃ (ppm)	NO(ppm)	N ₂ (ppm)	N ₂ O(ppm)	N ₂ O
300	1	500	500	387	382	90	19	17.2%
350	1	500	500	310	314	117	62	34.4%
400	1	500	500	220	259	110	145	56.9%
450	1	500	500	132	226	101	216	68.1%
500	1	500	500	70	222	106	246	69.8%

Table 4. Conversion of NO and NH₃ to N₂O over catalyst described in Example IV.0.052 g catalyst used. Space velocity ~ 600,000 hr⁻¹.

Example V

250 grams of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ were dissolved with stirring in 1.5 liters of distilled water. This solution was heated to approximately 60°C . To this, a solution containing 33 grams of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ and 130 grams of conc. NH_4OH in 1250 ml of H_2O was added. This solution was also heated to approximately 60°C . The solution containing the zirconyl chloride was slowly added to the second solution with mixing. The pH of the solution was approximately 7. This slurry was then placed in a steambox for 72 hours. The product formed was recovered by filtration, washed with excess water, and dried overnight at 85°C . The material was then calcined in air at 600°C for 3 hours. Chemical analysis of the dried materials showed a Mo/Zr ratio of 0.24 (weight basis); this corresponds to a water-free sample composition of approximately 14.1% Mo. Table 5 shows that catalyst synthesis at a higher temperature results in a sample with slightly higher selectivity to N_2O , especially at temperatures of 400°C and below, as compared to Example III.

T ($^\circ\text{C}$)	inlet concentrations			outlet concentrations				selectivity to
	$\text{O}_2(\%)$	$\text{NH}_3(\text{ppm})$	$\text{NO}(\text{ppm})$	$\text{NH}_3(\text{ppm})$	$\text{NO}(\text{ppm})$	$\text{N}_2(\text{ppm})$	$\text{N}_2\text{O}(\text{ppm})$	N_2O
300	1	500	500	371	362	90	30	25.3%
350	1	500	500	272	279	117	93	44.2%
400	1	500	500	162	223	112	185	62.2%
450	1	500	500	78	202	106	246	69.9%
500	1	500	500	32	208	108	265	71.1%

Table 5. Conversion of NO and NH_3 to N_2O over catalyst described in Example V.

0.064 g catalyst used. Space velocity $\sim 450,000 \text{ hr}^{-1}$.

Example VI

This catalyst was prepared in a manner identical to Example V except that it was calcined in air at 700°C for 3 hours. Table 6 shows that calcining at 700°C lowers overall activity somewhat compared to Example V; selectivities to N_2O are higher at 400°C and below but are lower at 450 and 500°C .

	inlet concentrations			outlet concentrations				selectivity to
T (°C)	O ₂ (%)	NH ₃ (ppm)	NO(ppm)	NH ₃ (ppm)	NO(ppm)	N ₂ (ppm)	N ₂ O(ppm)	N ₂ O
300	1	500	500	402	403	62	30	32.8%
350	1	500	500	306	330	89	85	49.0%
400	1	500	500	197	280	98	157	61.7%
450	1	500	500	111	280	106	204	65.9%
500	1	500	500	57	281	115	220	65.8%

Table 6. Conversion of NO and NH₃ to N₂O over catalyst described in Example VI.

0.054 g catalyst used. Space velocity ~ 600,000 hr⁻¹.

5 Example VII

This catalyst was prepared in a manner identical to Example V except that it was calcined in air at 830°C for 3 hours. Table 7 shows that calcining at 830°C lowers both activity and selectivity to N₂O.

	inlet concentrations			outlet concentrations				selectivity to
T(°C)	O ₂ (%)	NH ₃ (ppm)	NO(ppm)	NH ₃ (ppm)	NO(ppm)	N ₂ (ppm)	N ₂ O(ppm)	N ₂ O
300	1	500	500	449	453	29	21	41.7%
350	1	500	500	376	401	54	57	51.1%
400	1	500	500	276	381	77	102	57.0%
450	1	500	500	183	336	97	140	59.2%
500	1	500	500	115	327	112	161	59.0%

Table 7. Conversion of NO and NH₃ to N₂O over catalyst described in Example VII.

0.052 g catalyst used. Space velocity ~ 600,000 hr⁻¹.

Example VIII

A solution containing 41.4 grams of (NH₄)₆Mo₇O₂₄·4H₂O and 200 grams of H₂O was prepared. The solution was slowly added to 150 grams of silica (HiSil 233) and placed in a polypropylene bottle. This mixture was mixed using a roller overnight. The product formed was recovered by filtration, washed with minimum water, and dried overnight at 85°C. The material was then calcined in air at 540°C

for 3 hours. From the preparation we expect this sample to contain approximately 15% Mo by weight. Table 8 shows that this Mo/SiO₂ catalyst can also convert nitric oxide and ammonia into N₂O, although in this case with a lower selectivity than most of the examples described above.

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T(°C)	inlet concentrations			outlet concentrations				selectivity to
	O ₂ (%)	NH ₃ (ppm)	NO(ppm)	NH ₃ (ppm)	NO(ppm)	N ₂ (ppm)	N ₂ O(ppm)	N ₂ O
300	1	500	500	471	472	21	10	31.1%
350	1	500	500	442	442	40	18	31.3%
400	1	500	500	392	401	66	32	32.8%
450	1	500	500	323	351	100	54	35.2%
500	1	500	500	205	280	150	92	38.1%

Table 8. Conversion of NO and NH₃ to N₂O over catalyst described in Example VIII.

0.147 g catalyst used. Space velocity ~ 200,000 hr⁻¹.

Example IX

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Table 9 shows that bulk MoO₃, obtained from the Aldrich Chemical Company, is also an effective catalyst for converting nitric oxide and ammonia into N₂O. Compared to the supported catalysts, selectivities at 350°C and below are higher, but fall steadily as temperature increases.

T(°C)	inlet concentrations			outlet concentrations				selectivity to
	O ₂ (%)	NH ₃ (ppm)	NO(ppm)	NH ₃ (ppm)	NO(ppm)	N ₂ (ppm)	N ₂ O(ppm)	N ₂ O
300	1	500	500	462	466	10	33	76.0%
350	1	500	500	386	415	29	73	71.4%
400	1	500	500	243	353	72	128	63.9%
450	1	500	500	32	340	151	148	49.5%
500	1	500	500	0	449	194	61	23.8%

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Table 9. Conversion of NO and NH₃ to N₂O over catalyst described in Example IX.

0.266 g catalyst used. Space velocity ~ 120,000 hr⁻¹.

Example X

The data shown in Table 10 were collected using the catalyst described in Example III. They show that selectivity to N₂O is not a strong function of inlet nitric

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oxide and ammonia concentration when nitric oxide and ammonia are fed in equimolar amounts. There is no reason to believe that feeding much higher concentrations of nitric oxide and ammonia would not also result in the formation of correspondingly high concentrations of N_2O .

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T(°C)	inlet concentrations			outlet concentrations				selectivity to
	O ₂ (%)	NH ₃ (ppm)	NO(ppm)	NH ₃ (ppm)	NO(ppm)	N ₂ (ppm)	N ₂ O(ppm)	N ₂ O
500	1	500	500	242	311	63	157	71.4%
500	1	200	200	84	132	25	68	73.4%
500	1	350	350	163	220	45	114	71.7%
500	1	750	750	387	463	95	230	70.9%
500	1	907	907	481	560	115	277	71.6%

Table 10. Conversion of NO and NH₃ to N₂O over catalyst described in Example III.
Effect of variations in inlet NO and NH₃ concentrations.
0.050 g catalyst used. Space velocity ~ 600,000 hr⁻¹.

10 Example XI

The data shown in Table 11 were collected using the catalyst described in Example V. They show that significant amounts of N_2O are formed even if nitric oxide and ammonia are not fed in equimolar amounts.

T(°C)	inlet concentrations			outlet concentrations				selectivity to
	O ₂ (%)	NH ₃ (ppm)	NO(ppm)	NH ₃ (ppm)	NO(ppm)	N ₂ (ppm)	N ₂ O(ppm)	N ₂ O
500	1	500	500	32	208	108	265	71.1%
500	1	625	375	54	108	148	260	63.7%

15 Table 11 Conversion of NO and NH₃ to N₂O over catalyst described in Example V.
Effect of variations in inlet NO and NH₃ concentrations.
0.064 catalyst used. Space velocity ~ 450,000 hr⁻¹.

Example XII

20 The data shown in Table 12 were collected using the catalyst described in Example IV. They show that some N_2O is formed even when no nitric oxide is fed, i.e., when only ammonia and oxygen are fed. Selectivities are lower, however, than when equimolar amounts of nitric oxide and ammonia are fed.

T(°C)	inlet concentrations			outlet concentrations				selectivity to
	O ₂ (%)	NH ₃ (ppm)	NO(ppm)	NH ₃ (ppm)	NO(ppm)	N ₂ (ppm)	N ₂ O(ppm)	N ₂ O
445	1	500	0	211	0	119	17	12.5%
445	2	500	0	212	0	124	20	13.9%
445	3	500	0	214	0	127	22	14.5%
550	1	500	0	48	16	149	61	29.0%
550	3	500	0	51	19	143	78	35.3%
550	0.6	500	0	54	14	146	58	28.5%
550	0.6	1000	0	145	12	316	90	22.2%
550	0.6	1840	0	337	9	606	125	17.1%

Table 12. Conversion of NO and NH₃ to N₂O over catalyst described in Example IV.
Effect of feeding only NH₃.
0.050 g catalyst used. Space velocity ~ 600,000 hr⁻¹.

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Example XIII

The data shown in Table 13 were collected using the catalyst described in Example 3 calcined at 600°C. They show that the conversion and N₂O selectivity are increased as increasing amounts of oxygen in the 1-4.5% range are fed

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T (°C)	inlet O ₂ (ppm)	Outlet concentrations				percent	selectivity to
		NH ₃ (ppm)	NO(ppm)	N ₂ (ppm)	N ₂ O(ppm)	conversion*	N ₂ O†
450	1	319	347	52	111	32.5	68.3
450	4.5	319	342	53	116	33.8	68.6
475	1	278	326	58	137	38.9	70.4
475	4.5	276	320	57	145	40.4	71.8
500	1	247	310	62	159	44.2	72.0
500	2	240	306	61	167	45.6	73.5

* defined as $(N_2 + N_2O)/(\text{inlet } NH_3 + \text{inlet } NO)$

† defined as $(N_2O)/(N_2 + N_2O)$

Table 13. Effect of oxygen concentration on conversion of NO and NH₃ over Mo/ZrO₂ calcined at 600°C.

GHSV: 1,375,000 hr⁻¹

Feed: NH₃ (500 ppm); NO (500 ppm); O₂ (1-4.5%)

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