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Selectivity for Nitrogen Formation in NH_3 Oxidation in Wet and Dry Systems over Mixed Molybdenum Oxides

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To overcome the problem of NH_3 formation and reoxidation to NO in automotive dual catalytic systems, it has been suggested to use mixed base metal oxides for the conversion of NH_3 to N_2. The present work reexamines this suggestion and the effect of the prevailing high H_2O/NH_3 ratio in the exhaust stream on its applicability. It has been found that, at high H_2O/NH_3 ratio in the treated gas, the range of conditions under which the formation of N≡N bonds prevails is drastically narrowed. The behavior of copper, cobalt and iron molybdates in this surface reaction was examined and that of the copper molybdate was compared with the activity and selectivity of the pure oxides—CuO and MoO_3.

INTRODUCTION

It is well established presently that the formation of ammonia in dual catalytic systems, where nitric oxide is reduced catalytically in streams containing hydrogen bearing species, is one of the major problems in treating the automotive exhaust (*1,2*). Among the various approaches to overcome this difficulty, it has been recently proposed (*3*) to incorporate a catalyst, which will cleanly reconvert ammonia to nitrogen in strongly oxidizing conditions. This catalyst is to be placed downstream of the reduction catalyst and ahead of the oxidation catalyst in a dual bed system. The conventional noble metal catalysts used for hydrocarbon and carbon monoxide oxidation do not accomplish this conversion cleanly, and in fact reconvert the ammonia largely back to nitric oxide, without defixation (*1,4*). The claim of Ref. (*3*) was that molybdenum oxide-based catalysts do possess the required selectivity during NH_3 oxidation and therefore their incorporation into the conventional oxidation catalysts will obviate the necessity of finding a stable catalyst that does not produce ammonia in the reduction stage, which has proven to be very difficult to accomplish (*5,6*). It is worth mentioning that the objective of the industrial oxidation of ammonia in the manufacture of nitric oxide is diametrically opposite, i.e., a clean conversion to NO is desired and to accomplish this the process is carried out at very high space velocities and high temperatures over noble metal gauzes. This subject has been summarized by Bond (*7*) and Longfield and Dixon (*8*). The catalytic oxidation of ammonia at lower temperatures over base metal oxides has also been studied extensively, especially in the first half of this century (*8,9*).

The aforementioned work of Wise (*3*), apparently prompted by analogies to oxidative dehydrogenation of hydrocarbons, employed a series of mixed oxides and has shown that, at temperatures of the order of 500°C and below, several of these mixed oxide catalysts (not only those of molybdenum) possess considerable selectivities towards conversion of NH_3 to N_2 or N_2O, at high space velocities and high oxygen contents. The ammonia levels in Wise's experiments were of the order of 1–10% at atmospheric pressure and above, and there was no water present in the gas stream. In exhaust streams, on the other hand, ammonia levels are expected to be smaller by more than an order of magnitude and the water levels are very high. The water levels exceed the NH_3 levels 100- to 1000-fold. Both facts can be expected to influence immensely, namely decrease, the surface coverage of the catalyst surface by ammonia and thereby decrease the pairing probability of N-atoms on the surface and the selectivity to N_2 (*2,4*). Therefore, it was deemed advisable to check the practicality of the approach under conditions corresponding closer to those prevailing in practice.

EXPERIMENTAL METHODS

Table 1 gives the description of the catalysts used in this work. These were chosen to include the best catalysts cited in Ref. (*3*). The samples designated (P) were supported on alumina pellets and those designated (M) were supported on American Lava monolithic cordierite using diluted colloidal alumina as the binding agent. Presynthesized powders of $CuMoO_4$, $CoMoO_4$ and $FeMoO_4$ for the monolithic catalysts were obtained from Climax Molybdenum Co. as were also the pelleted catalysts of Cu_2MoO_5 and $CuMoO_4$. The catalysts containing the pure oxides of CuO and MoO_3 were made from the corresponding nitrates by impregnation of American Cyanamid Aeroban Support, which is 95% Al_2O_3 + 5% SiO_2. The impregnated catalysts were dried at 120°C overnight and calcined at 600°C for 6 hr. The monolithic catalysts underwent the same pretreatment.

TABLE 1
DESCRIPTION OF CATALYSTS

Catalyst	BET area (m^2/g)	Composition (wt%)			
		Cu	Mo	Fe	Co
Cu_2MoO_5 (P)	160	9.6	7.3	—	—
$CuMoO_4$ (P)	171	5.6	8.7	—	—
$CuMoO_4$ (M)	~10	5.6	8.5	—	—
$CoMoO_4$ (M)	~10	—	8.4	—	5.7
$FeMoO_4$ (M)	~10	—	8.9	5.2	—
CuO (P)	200	10.0	—	—	—
MoO_3 (P)	200	—	10.0	—	—

Both monolithic and pelleted catalysts were tested in the integral flow apparatus used in our earlier studies (*4*) where the mode of gas analysis was also described. Since the carrier gas was nitrogen and no analysis for N_2O was performed (the only analysis for N-containing species was for NH_3 and NO), the sum of N_2 and N_2O was determined by difference and is lumped together as "defixed" N_2. For the purposes of this paper this is sufficient. A control experiment with helium as a carrier gas was performed to check the material balance and confirmed the correctness of the method.

RESULTS AND DISCUSSION

The results of the experiment are given for three selected catalysts in Fig. 1 and are presented for all catalysts at two selected temperatures in Table 2.

The three catalysts represented in Fig. 1 are the mixed oxide with the best selectivity $CuMoO_4$ and the catalysts made of the corresponding pure oxides. The top part of Fig. 1 gives the activity of NH_3 oxidation in dry systems, and the lower part in the presence of 10% of water. The plots give (a) the total conversion, (b) the selectivity – the (N_2 + N_2O) fraction of the converted part of NH_3, and (c) the fraction of total inlet NH_3 converted to N_2 + N_2O.

Examination of Fig. 1 shows the CuO is more active for NH_3 oxidation than MoO_3; $CuMoO_4$ behaves very much like copper oxide both in the dry and wet systems. The addition of 10% water vapor lowers the activity in all cases.

The selectivity of MoO_3 with respect to the formation of $N{\equiv}N$ bond in the dry system, is better than that of the copper oxide. The $CuMoO_4$ catalyst's selectivity

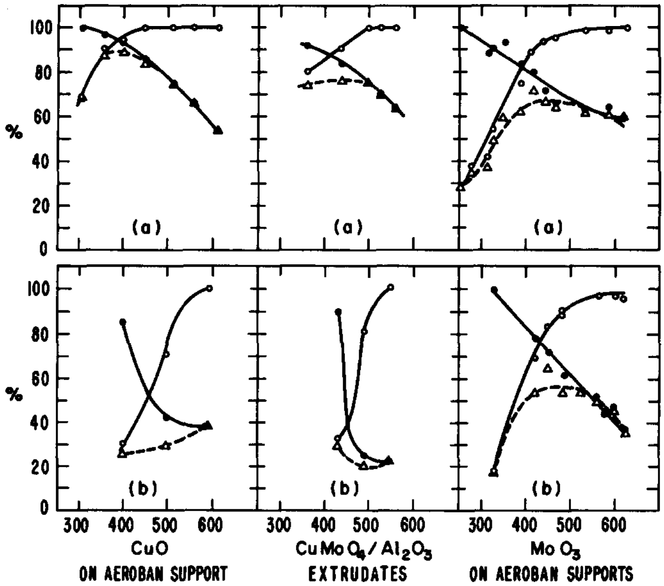

FIG. 1. Ammonia oxidation activity and selectivity over CuO, $CuMoO_4$ and MoO_3: (a) dry conditions; (b) with 10% H_2O; (○) total NH_3 converted; (●) N_2 as % of converted NH_3; (△) N_2 as % of inlet NH_3.

is midway between that of its components. In a wet system the selectivity of the copper-containing catalyst is drastically suppressed, while in the case of the MoO_3 the decrease in the selectivity is much less pronounced.

Table 2 summarizes the results of activity and selectivity for N_2 formation for all the catalysts employed in this work, at two representative temperatures, with and without water addition. It is again clearly seen that the water effect is weakest on the MoO_3 catalyst with respect to both the suppression of activity and selectivity. The cobalt and iron molybdates are considerably less active than either the copper molybdates or MoO_3.

Using the ion-scattering spectrometer (ISS) (*10*) an examination was made of the surface of the two mixed copper molyb-

TABLE 2

CATALYST ACTIVITY AND SELECTIVITY FOR N_2 FORMATION IN NH_3 OXIDATION[a]

		Conversion of NH_3 (%)				N_2, (as % of NH_3 converted)			
	T (°C):	450		550		450		550	
Catalyst	H_2O (%):	10	0	10	0	10	0	10	0
Cu_2MoO_5 (P)		38	97.5	83.5	100	74	79.5	28	68
$CuMoO_4$ (P)		37.5	93	100	100	43	82	22	65
$CuMoO_4$ (M)		N.M.	73	N.M.	95	N.M.	93	N.M.	73
$CoMoO_4$ (M)		0	47	44	92.5	0	91	69.5	77
$FeMoO_4$ (M)		0	20	17.5	76	0	70	36	69.5
CuO		47.5	100	95	100	26.5	85	38.5	66.5
MoO_3		82	94.5	96.5	99.5	73	73.5	51.5	63.0

[a] Experimental conditions: space velocity, 40,000 hr^{-1}; inlet gas composition: NH_3, 500 ppm; O_2, 3%; H_2O, 0.0 or 10.0% in N_2 carrier gas.

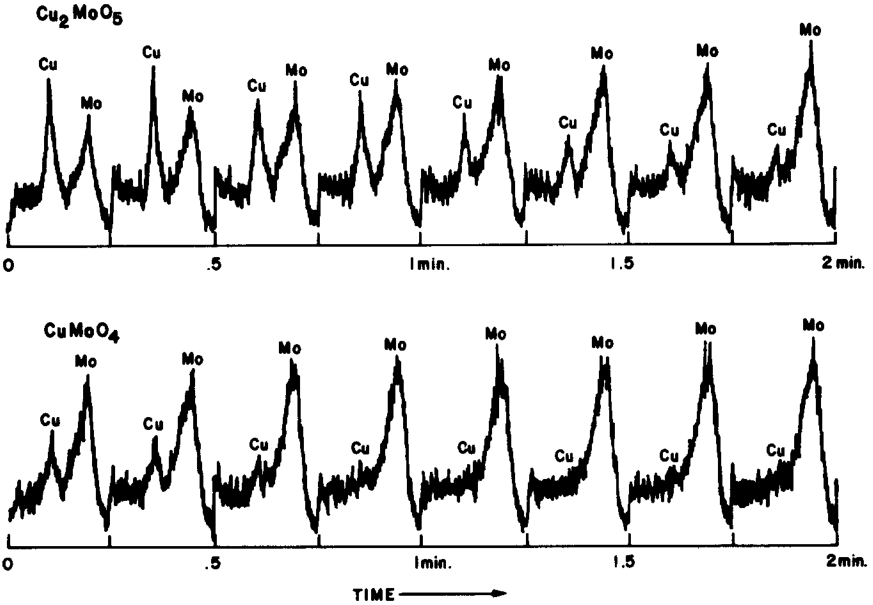

FIG. 2. Sequential ion scattering spectra of Cu_2MoO_5 and $CuMoO_4$. Incident beam: $^{20}Ne^+$ at 2000 eV.

date powders, Cu_2MoO_5 and $CuMoO_4$, as shown in Fig. 2. The spectrum at zero time is most representative of the relative population of the ions on the surface, while the successive scans represent scattering from subsurface layers, made accessible by sputtering away the top layers by the incident beam of $^{20}Ne^+$ accelerated to an energy of 2000 eV. Since the object was to explore only the relative abundance of Cu and Mo ions, only this part of the spectrum was scanned. One scan took approximately 15 sec. It should be borne in mind that no quantitative significance is attached to the relative peak heights of Cu and Mo besides the observation, that both Cu and Mo ions are present on the surface of both molybdates. Further observations are: (a) there is more Cu on the surface in the Cu-rich molybdate which reflects the bulk composition and (b) with progressive sputtering the Cu signal decreases while the Mo signal increases in both samples. The surface composition of both molybdates is in agreement with their catalytic behavior, which falls in between that of the pure oxides. Although there is considerable difference in the ISS surface spectrum between the two molybdates, the catalytic data from the integral reactor do not possess sufficient resolution for meaningful discrimination to confirm differences in catalytic behavior.

The conclusion from the catalytic results is that the selectivity of mixed molybdenum oxide catalysts for producing nitrogen in ammonia oxidation at low temperatures is neither unique nor surprising. Indeed, Ilchenko and Golodets (*11*) stated that, under their experimental conditions, nothing but N_2 and N_2O (and water) is formed below 400°C over MnO_2, Co_3O_4, CuO, Fe_2O_3 and V_2O_5. This is also in agreement with the results of Krauss (*9*). Even on platinum catalysts at low temperatures, oxidation of NH_3 produces mainly products with $N{\equiv}N$ bonds at low temperatures, if the NH_3 pressure is not very low (*8,12,13*).

Both Krauss (*9*) and Ilchenko and Golodets (*11*) have considered independently the mechanism of this reaction over transition metal oxides and their schemes bear also some resemblance to earlier formulations (*8*). Apart from a slight difference in the primary act of NH_3 adsorption on a surface oxygen ion, both mechanisms are very similar: interaction of two surface (HNO) groups releases an N_2O molecule and a water molecule and interaction of an imide group (NH) with an (HNO) group releases an N_2 molecule and a water molecule. It is worth noting that this formulation is almost analogous to the surface steps in the $NH_3 + NO$ reaction which were experimentally verified by tracer experiments (*14*). Ilchenko and Golodets (*11*) have developed a kinetic equation from their mechanism of NH_3 oxidation over transition metal oxides, which adequately represents the experiment.

By analogy to partial oxidation of hydrocarbons, Wise (*3*) considered N_2 and N_2O to be products of partial oxidation of NH_3 and NO the product of complete oxidation. Ilchenko and Golodets expressed a similar view. We wish to point out that conceptually this analogy is erroneous, since it is always assumed, tacitly in some cases, that the products of partial oxidation can be further oxidized completely. Not so in the case of nitrogen-containing species. Once the extremely stable double bond between nitrogen atoms is formed, it can be oxidized only under extreme conditions such as in high-intensity electric discharges in air, or in flames. Thus, the oxidation of NH_3 to N_2 or N_2O on one side and to NO on the other occurs in two separate paths, one involving the pairing of N-atoms and the other not, and only the pairing probability will determine the selectivity. At high surface coverages by N-containing species, one can expect mostly pairing (N_2 and N_2O). In the case of NH_3 oxidation in dry systems, the pairing is predominant even at low partial pressures of NH_3 in the gas as opposed to NO reduction under similar dry conditions (4). Apparently, the coverage of the catalyst surface at reaction temperatures by NH_3 (or fragments derived therefrom) is much higher than by NO at corresponding partial pressures. While the chemisorption of NO on oxide surfaces has been measured in the last several years on many oxides (*2*), data on NH_3 chemisorption needed for this comparison are not available.

In comparing further the NH_3 oxidation by oxygen with the NO reduction by hydrogen it is necessary to point out that whereas in the first case lower temperatures favor the formation of $N{\equiv}N$ bonds in the latter case it takes place mostly at the higher temperatures. The reason for this behavior lies in the very slow NO decomposition in the presence of oxygen on oxidized catalysts even at high temperatures while at sufficiently high temperatures over reduced metals (in contact with excess hydrogen) the mobility of N-containing fragments derived from NH_3 is fast and thus also the pairing of N-atoms.

The sharp drop in surface coverage by NH_3 can be expected in the presence of large amounts of water. Water does compete with NH_3 for the adsorption sites as has been shown convincingly by Blyholder and Richardson (*15*) in the case of activated α-Fe_2O_3. There is every reason to expect that, due to the similarity of both adsorbents, this behavior will prevail also over the mixed transition metal oxides used in this work. As the H_2O/NH_3 ratio, in the runs with water present was 200-fold, the sharp drop-off in activity and the narrowing of the temperature range in which pairing of N-atoms prevails, can both be explained by the exclusion of NH_3 from the surface by the preponderance of water. Obviously, there are differences between the oxides in their relative affinity for NH_3 or H_2O adsorption and thereby also in the relative degree of the suppression of NH_3 oxidation activity and selectivity for $N{\equiv}N$ bond formation in the presence of water vapor. Confirmation of this premise for the case of MoO_3 vs CuO for instance, as suggested by the present results, would require further adsorption measurements.

Owing principally to the chemisorptive competition between small amounts of NH_3 and large amounts of H_2O in exhaust stream, with the resultant narrow range of the desired selectivity, it appears that such approaches to prevent NH_3 reoxidation to NO in dual catalytic systems using mixed molybdates are not practical. This is quite apart from other considerations such as susceptibility of base metal oxides to sulfur-poisoning, and other modes of deactivation.

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