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NO reduction by CH_4 over rare earth oxides

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Abstract

NO reduction by methane was studied between 773 and 973 K. All the REO catalysts tested were active for this reaction in both the absence and presence of O_2. Activities increased continuously with reaction temperature and no deactivation or bend-over was observed at high temperatures except for Sm_2O_3, over which complete combustion of CH_4 occurred in the presence of O_2. The specific activities for NO reduction to N_2 by CH_4 were higher than those for NO decomposition, showing that CH_4 enhances NO conversion. CH_4 reduction of NO gave selectivities to N_2 that were near 100% for all the catalysts except Sr/La_2O_3, Sm_2O_3 and Sr/Sm_2O_3, over which 5–20% N_2O was formed. Except for CeO_2, the presence of O_2 promoted the rate of NO conversion to N_2. Overall, Sr/La_2O_3 had the highest specific activity for NO reduction by CH_4 in either the absence or presence of O_2, with respective values of 4.6×10^{-3} and 13×10^{-3} μmole $N_2/s/m^2$ at 773 K. Turnover frequencies (TOFs) under these two sets of conditions, based on NO adsorption at 300 K, were $0.78 \times 10^{-3}\ s^{-1}$ and $2.3 \times 10^{-3}\ s^{-1}$, respectively. Activation energies fell between 22–32 kcal/mole for all the REOs. The best REO catalysts correlated with those best for the oxidative coupling of methane. On either a specific activity or a TOF basis, the best REO catalysts were comparable to Co-ZSM-5.

Keywords: Nitrogen oxide; Methane; Rare earth oxides

1. Introduction

Metal ion-exchanged ZSM-5 catalysts have been shown to be active for selective reduction of NO by CH_4 and the presence of excess oxygen actually enhanced activities for NO reduction [1]. However, the zeolite-based catalysts showed a volcano-like activity dependency on temperature and at higher temperatures NO reduction was severely decreased, which could limit the suitability of these zeolite catalysts for some applications. We have successfully prepared and characterized two non-zeolitic catalyst systems (Li/MgO and La_2O_3) for NO reduction by CH_4 [2,3]. Li/MgO and La_2O_3 were chosen because they were two of the best catalyst systems for the methane oxidative coupling (MOC). The results showed both Li/MgO and La_2O_3 were active for NO reduction by CH_4. Unlike the zeolites, the activities of these catalysts continuously increased with reaction temperature. In this paper we present the results of NO reduction by CH_4 in both absence and presence of O_2 over a series of rare earth oxide (REO) catalysts. In order to make comparisons, the corresponding results obtained over Li/MgO and Co-ZSM-5 are also included and discussed.

2. Experimental

The pure rare earth oxide samples, La_2O_3, CeO_2, Nd_2O_3, Sm_2O_3, Tm_2O_3, Lu_2O_3, were pre-

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pared by calcining the corresponding commercial oxides at 1023 K for 10 h under flowing dry air (~ 50 sccm) [4]. The doped samples of 4 wt.-% Sr/La_2O_3 and 4 wt.-% Sr/Sm_2O_3 were prepared by following the preparation of the Li/MgO samples [2].

All the activity measurements and kinetic studies were made at atmospheric pressure under steady-state reaction conditions in a quartz microreactor. The microreactor system has been described in detail in a previous paper [2]. A typical gas mixture, unless otherwise specified, of 2% NO and 0.5% CH_4 in He at a stoichiometric ratio of $NO:CH_4 = 4:1$, according to the reaction: $4NO + CH_4 \rightarrow 2N_2 + CO_2 + 2H_2O$, was passed through the reactor which contained ca. 100 mg catalyst. All the gases used were from MG Ind., UHP Grade, except for the NO mixed with He, which was 99.0^{+}% with major mixture impurities of N_2 (ca. 600 ppm), N_2O (ca. 100 ppm) and CO_2 (ca. 100 ppm). The reactor effluent was analyzed with a gas chromatograph (Perkin-Elmer Sigma-2B) equipped with a Carboxen^{1000} column (Supelco) and a P-E Nelson 1020S integrator [2]. During the Arrhenius runs, a period of 30 min on stream was allowed at each temperature before any gas sample was taken. An ascending–descending temperature sequence from 773 to 973 K was typically used to check for any deactivation during these measurements. Runs with no catalyst verified that no reaction occurred over this temperature range. The conversions were generally kept below 20% to ensure differential reactor operation.

3. Results

The reaction of NO reduction by CH_4 over these rare earth oxides was studied between 773 and 973 K using a stoichiometric NO/CH_4 ratio of 2.0% NO, 0.51% CH_4 in He at a total flow rate of 40 ml/(STP)/min (20 ml/min for La_2O_3). All the REO catalysts were active for NO reduction by CH_4 at 773 K, the activities continuously increased with temperature, and no deactivation was observed over a period of 30 h. The corresponding activation energies are presented in Table 1. N and C mass balances were within ±2.5% thus indicating that little or no NO_2 was formed although the GC column used did not separate NO_2 as a well-defined peak [2]. Except for a small amount of N_2O in the product stream whose concentration was routinely near that of the impurity N_2O level in the feed (ca. 100 ppm), dinitrogen was essentially the only N-containing product detected over La_2O_3 [2], Lu_2O_3, CeO_2, Nd_2O_3, and Tm_2O_3. Therefore, the net rate of N_2O formation was near zero and the selectivities of NO conversion to N_2 were close to 100%. However, noticeable amounts of N_2O were observed over Sr/La_2O_3, Sm_2O_3 and Sr/Sm_2O_3, particularly at low temperature and selectivity to N_2 dropped to 80–95% at lower temperatures but increased with temperature.

Table 1
NO Reduction by CH_4 at 773 K (No O_2), $P_T = 1$ atm, $P_{NO} = 15.4$ Torr and $P_{CH4} = 3.8$ Torr

Catalyst	E_a (kcal/mol)	Rate of N_2 Formation ($\mu mol/s/g \times 10^3$)	Specific Activity ($\mu mol/s/m^2 \times 10^3$)	TOF ($s^{-1} \times 10^3$)
La_2O_3	24	5.3	1.5	0.39
Sr/La_2O_3	26	7.8	4.6	0.78
CeO_2	28	1.3	0.54	0.31
Nd_2O_3	22	4.9	1.4	0.54
Sm_2O_3	32	15	2.1	0.46
Sr/Sm_2O_3	28	11	1.6	0.51
Tm_2O_3	28	1.0	1.1	0.19
Lu_2O_3	22	6.8	2.8	0.56
Li/MgO	31	1.8	0.50	0.67
Co-ZSM-5	–	332	1.7	0.59

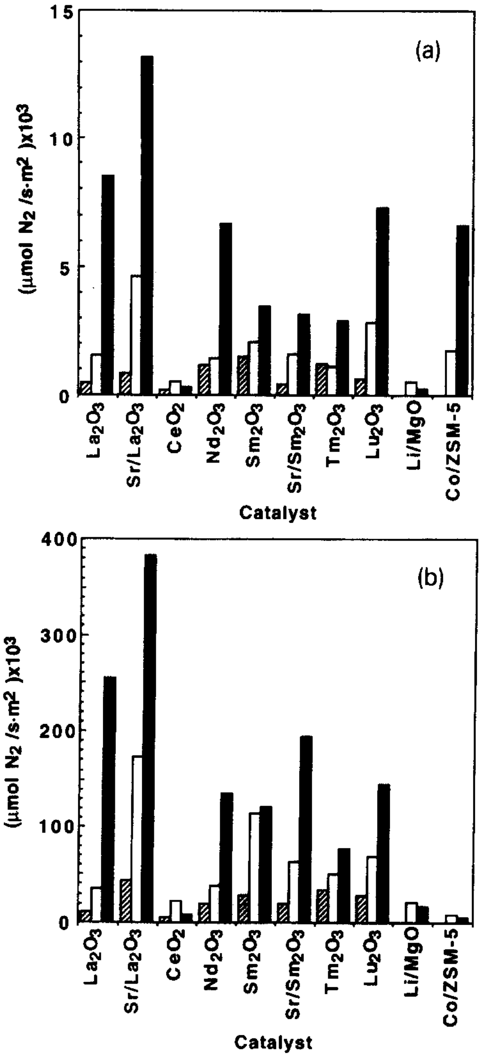

Fig. 1. Specific activities: (shaded square) NO decomposition (from Ref. [4]), (□) NO reduction by CH_4 and (■) NO reduction by CH_4 in the presence of O_2; (a) $T = 773$ K and (b) $T = 973$ K, partial pressure as stated in results section.

Table 1 also summarizes the rates, specific activities and turnover frequencies (TOFs) at 773 K for N_2 formation during NO reduction by CH_4 in the absence of O_2 over the REOs as well as Li/MgO and Co-ZSM-5. The TOFs (molecules N_2/s/site) are based on the number of NO molecules irreversibly adsorbed at 300 K [4]. The specific activities obtained at both 773 K and 973 K are presented in Fig. 1. On a gram basis, Sr/La_2O_3, Sm_2O_3 and Sr/Sm_2O_3 were the most active catalysts at both 773 and 973 K, although they were much less active than Co-ZSM-5 at 773 K. When specific activities and TOFs are compared, Sr/La_2O_3 was clearly the most active and was even more active than Co-ZSM-5. Li/MgO had a low specific activity, but the TOFs on all these surfaces, including Li/MgO and Co-ZSM-5, are remarkably similar, with the possible exception of Tm_2O_3. Every rate of N_2 formation via CH_4 reduction was higher than the corresponding rate for direct NO decomposition [4], as shown in Fig. 1a, indicating CH_4 enhances the activity for NO conversion to N_2.

The effect of dioxygen on the activity and selectivity of NO reduction by CH_4 on the REOs was also investigated between 773 and 973 K using a mixture of 1.8% NO (2.0% for La_2O_3), 0.45% CH_4 (0.51% for La_2O_3) and 1.0% O_2 in He at a total flow rate of 44.5 ml(STP)/min (40 ml/min for La_2O_3). Again it was found that all the REOs were active at 773 K, the rates of N_2 formation continuously increased with temperature up to 973 K, and no bend-over behavior was observed except for Sm_2O_3 after all the CH_4 had combusted. The corresponding activation energies, presented in Table 2, varied from 22 to 29 kcal/mol and were quite similar to those in the absence of O_2. Because of NO_2 formation downstream from the reactor due to the gas-phase reaction between NO and O_2, the selectivity of NO conversion to N_2 could not be quantitatively determined in these experiments.

The effect of dioxygen on the activity and selectivity of NO reduction by CH_4 on the REOs was examined and Table 2 also summarizes the rates, specific activities, and TOFs at 773 K for N_2 formation via NO reduction by CH_4 in the presence of O_2, while specific activities obtained at 773 K and 973 K are presented in Fig. 1. On a gram basis, La_2O_3 was the most active catalyst while CeO_2, much less active than all the other REOs, and Co-ZSM-5 was again 1–2 orders of magnitude more active. However, the specific activities of all the REOs except CeO_2 were comparable to that of Co-ZSM-5, with Sr/La_2O_3 having the highest value, which was double that of Co-ZSM-5. A

Table 2
NO Reduction by CH_4 at 773 K in the presence of 1% O_2, $P_T = 1$ atm, $P_{NO} = 13.8$ Torr and $P_{CH4} = 3.5$ Torr

Catalyst	E_a (kcal/mol)	Rate of N_2 Formation (μmol/s/g × 10^3)	Specific Activity (μmol/s/m^2 × 10^3)	TOF (s^{-1} × 10^3)
La_2O_3	26	30	8.5	2.2
Sr/La_2O_3	26	22	13	2.3
CeO_2	28	0.75	0.30	0.17
Nd_2O_3	22	23	6.7	2.5
Sm_2O_3	23	25	3.5	0.77
Sr/Sm_2O_3	29	21	3.2	1.0
Tm_2O_3	25	2.7	2.9	0.49
Lu_2O_3	22	18	7.3	1.4
Li/MgO	35	0.84	0.24	0.32
Co-ZSM-5	–	1280	6.6	2.3

comparison of TOFs shows almost identical values on La_2O_3, Sr/La_2O_3, Nd_2O_3 and Co-ZSM-5 at 773 K. Specific activities and TOFs in this reaction were higher in the presence of O_2 than in its absence, thus indicating that O_2 facilitates NO reduction to N_2 except for the two worst catalysts (CeO_2 and Li/MgO) whose activities were somewhat lower in the presence of O_2.

In the presence of O_2, methane can react not only with nitric oxide but also with O_2 via combustion as follows:

$$4NO + CH_4 \rightarrow 2N_2 + CO_2 + 2H_2O \quad (1)$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad (2)$$

Total methane conversion frequently increased rapidly with temperature and the selectivity of CH_4 reacting with NO, i.e., the fraction of CH_4 reaction with NO vs. the total CH_4 reacted, typically decreased as temperature increased before reaching a nearly constant value. Fig. 2 shows an example of total NO and CH_4 conversion, and the selectivity of CH_4 reacting with NO vs. O_2. No higher hydrocarbons due to the oxidative coupling of methane were detected in the presence of O_2 under any circumstances.

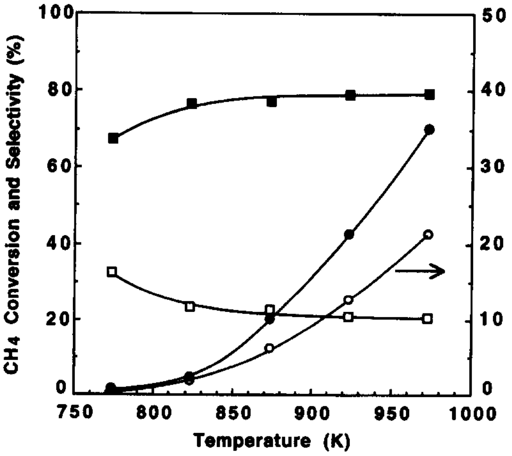

Fig. 2. NO conversion (○), CH_4 conversion (●), selectivity for CH_4 reacting with NO (□) and with O_2 (■) over Sr/La_2O_3.

4. Discussion

This study has confirmed that certain REOs and promoted REOs are quite active for NO_x reduction. For comparison, the activity of each REO for NO conversion to N_2 in this study is expressed in three different ways: (1) a rate, μmol N_2/s/g; (2) a specific activity, μmol N_2/s/m^2; and (3) a turnover frequency (TOF), molecule N_2/site/s. Tm_2O_3 had a very low BET surface area and CeO_2 had a very low irreversible NO uptake which could have led to a high specific activity and a high TOF, respectively, although their rates are among the lowest. At these high temperatures, activities over Co-ZSM-5 become much less favorable in comparison with REOs because they severely decrease with increasing temperature above 700–800 K [1,4]. At lower temperatures the zeolite catalysts are more active.

A comparison of the rates for NO reduction by CH_4 (see Table 1 and Table 2) and those for direct NO decomposition [4] shows that CH_4 clearly enhances the NO conversion, as illustrated in Fig. 1a, for example, the activity over Sr/La_2O_3 increased by a factor of 5.5 while the respective activation energies for these two reactions remained quite similar. CeO_2, Sm_2O_3 and Lu_2O_3 showed a somewhat larger variation in E_a values. The promotional effect of CH_4 on NO conversion to N_2 might be expected on the basis that CH_4 can facilitate the removal of surface oxygen left behind by the decomposition of nitrogen oxide species. This would be particularly apparent if the rate-determining step were the removal of surface oxygen. Indeed, CO_2 was observed instead of O_2 in the presence of CH_4, indicating an interaction between CH_4 and surface oxygen. CO was not detected in these experiments, partly because its peak overlaps with NO in the chromatogram so that even if some CO were formed it would be obscured by the large NO peak. On the other hand, CO, once formed, could rapidly react with NO to produce N_2 and CO_2. The selectivity of NO conversion to N_2, rather than N_2O, was essentially 100% over La_2O_3, Lu_2O_3, CeO_2, Nd_2O_3 and Tm_2O_3. However Sr/La_2O_3, Sm_2O_3 and Sr/Sm_2O_3 produced noticeable amounts of N_2O under the same conditions, i.e., 5 to 20% of the product was N_2O. The N mass balance indicated that there were only small amounts, if any, of other N-containing compounds such as NO_2. As proposed previously, N_2O could be an intermediate during NO reduction by methane [3]; thus the amount of N_2O in the products would depend on the relative rates of NO conversion and N_2O decomposition to N_2. Interestingly, N_2O was observed only with the most active catalysts for NO reduction. Over these catalysts the rate of N_2O decomposition may not be significantly higher than that of NO reduction thus resulting in some undecomposed N_2O, while over other catalysts the rate of N_2O decomposition was presumably much higher than the rate of NO reduction, which resulted in no N_2O detected in the reaction products [3].

Perhaps of greater importance, the presence of excess O_2 promotes NO reduction by CH_4 over all the catalysts except CeO_2 and Li/MgO (see Table 1 and Table 2), and the magnitude of the activity increase differs. For example, the activity on La_2O_3 at 773 K increased by a factor of about 6 in the presence of dioxygen, while that of Sm_2O_3 increased less than 2-fold. As discussed in a previous paper [2], the role of dioxygen in NO reduction by CH_4 over the rare earth oxides is not likely due to the formation of NO_2 as an intermediate, as suggested for zeolite catalysts [5,6], rather it is presumed to promote the activation of methane via the formation of methyl radicals, which are presumed to remain on the surface at these lower temperatures. Chajar et al. recently reported that as reduction of NO_2 by propane occurred over a Cu/MFI zeolite catalyst, a partial decomposition of NO_2 created O_2 which was responsible for an increase in activity via the partial oxidation of propane [7]. It is not known why the presence of excess dioxygen inhibits NO conversion to N_2 over CeO_2 and Li/MgO under the same conditions; however, CeO_2 is not a good methane oxidative coupling catalyst. Total CH_4 conversion on CeO_2 varied from ca. 1% at 773 K to ca. 35% at 973 K, which was much lower than CH_4 conversions over other REOs. Therefore, the activity decrease in the presence of O_2 is not due to a much lower CH_4 concentration caused by combustion. It is perhaps surprising that CeO_2 has the lowest activity for both direct NO decomposition and reduction by CH_4 in the absence of oxygen as CeO_2 has been widely used as a promoter in three-way automotive exhaust catalysts [8].

Correlations between catalytic activity and properties of the rare earth oxides have always been interesting subjects because of gradual changes caused by the lanthanide contraction. Takasu et al. found similarities between activity for NO oxidation to NO_2 and that for isotopic oxygen exchange suggesting that the rate-determining process of each reaction was closely related [9]. In a study of CO hydrogenation over REO-supported Pd, Vannice et al. found the CH_4 turnover frequency decreased as the activation energy for electrical conductivity increased in the REO support, whereas the CH_3OH turnover frequency was dependent on the atomic number of the REOs and decreased with the lanthanide contraction [10]. In the present work no correlation could be found between any catalytic activity and a given property of the REOs, such as electron configuration, covalent and ionic radii, or activation energy for electron conductivity. However, we have found that, in general, good methane oxidative coupling catalysts are also good NO reduction catalysts. For example, La_2O_3 and Sm_2O_3 are two of the best catalyst systems reported for methane oxidative coupling [11,12]. Doping La_2O_3 with strontium improves both activity and selectivity for oxidative coupling [12], and our study has shown it also provides a significant increase in specific activity for NO reduction by CH_4. Nd_2O_3 is a moderately active catalyst for this reaction [13], while CeO_2 is completely non-selective for C_2 hydrocarbon formation, although it is active for total oxidation to CO_2 [12]. The conversion to N_2 over Li/MgO is lowered because of the high selectivity to N_2O [2]. All these observations are consistent with the present results for NO reduction by CH_4 over these REOs and support our belief that these two reactions are closely related in terms of methane activation, presumably involving methyl radicals [2].

It is well known that methyl radicals can be generated on the surface of Li/MgO catalysts during methane oxidative coupling [14]. Control experiments performed over both Li/MgO and La_2O_3 [2,3] verified that the catalysts prepared in this study are indeed methane oxidative coupling catalysts, which implies that they can generate methyl radicals under appropriate conditions. However, no C_2 hydrocarbons were detected over the REOs under any circumstances during NO reduction by CH_4 in the presence of O_2. The absence of any detectable amount of C_2 hydrocarbons may imply one of several possibilities: (1) once generated, all methyl radicals on the surface react rapidly with NO before they can desorb into the gas phase and couple to form C_2H_6, (2) methyl radicals do desorb but react rapidly with NO in the gas phase and (3) any C_2 hydrocarbons formed by coupling of methyl radicals react further with NO, as it has been reported that higher hydrocarbons are more reactive with NO than CH_4 during NO reduction over zeolite catalysts [15]. The first explanation is preferred.

It is important to compare these REO catalysts with other catalysts which can also reduce NO to N_2 by CH_4. A number of zeolite catalysts have been studied, and Co-ZSM-5, Ga-H-ZSM-5 and Ga/H-mordenite have been found to be the most active for NO reduction by CH_4 in the presence of O_2 [1,16,17]. When the reaction was conducted at 773 K in a gas mixture of 1610 ppm NO, 1000 ppm CH_4 and 2.5% O_2 at a GHSV of 30 000 h^{-1}, the rates of N_2 formation over Co-ZSM-5 and Ga-ZSM-5 were 0.18 and 0.20 μmol/s/g, respectively, which are about 1–2 orders of magnitude higher than those of the REO catalysts at the same temperature after correction for the NO pressure dependence [1]. The rate of N_2 formation over Co-ZSM-5 is enhanced at higher NO concentrations [3]. When compared in terms of either specific activity or TOF, the REOs are comparable to Co-ZSM-5 for NO reduction by CH_4 in the presence of O_2, as shown in Table 2 and Fig. 1. Furthermore, the activity of each REO continuously increased with reaction temperature, except for Sm_2O_3, and the activities at 973 K are about 20–30 times higher than those at 773 K, whereas both Co-ZSM-5 and Ga/H-ZSM-5 showed a decrease in activity above 773 K, particularly for Co-ZSM-5 [1]. It was suggested that the decrease in NO conversion did not happen until almost all the CH_4 was combusted, thus this behavior can be attributed to CH_4 depletion [17]; our results support this explanation [4]. Nevertheless, dioxygen promotes NO reduction to N_2 by CH_4 on both the zeolite and REO catalysts (except for CeO_2) which may indicate similar chemistry associated with the formation of reaction intermediates involving oxygen.

5. Summary

This study has shown that NO reduction by CH_4 can occur readily on both pure REOs and Sr-promoted REO surfaces. Furthermore, the rate of NO reduction by CH_4 was enhanced 2- to 6-fold by the presence of O_2 over all the REOs examined except CeO_2. In the absence of O_2, the relative specific activities for NO reduction by CH_4 are: Sr/La_2O_3 > Lu_2O_3 > Sm_2O_3 > Sr/Sm_2O_3, La_2O_3, Nd_2O_3 > Tm_2O_3 > CeO_2. However, the TOF values are all rather similar, except possibly for Tm_2O_3. In the presence of 1% O_2, a much wider variation (over 40-fold) in specific activity occurred for NO reduction by CH_4 and the relative order at 773 K was Sr/La_2O_3 > La_2O_3 > Lu_2O_3 > Nd_2O_3 > Sm_2O_3 > Sr/Sm_2O_3 > Tm_2O_3 > CeO_2. The addition of O_2 had little effect on the apparent activation energy except for Sm_2O_3. These results have been discussed in greater detail elsewhere [4]. The surface chemistry associated with these catalytic processes is not yet understood and studies are underway in our laboratory to gain additional insight; however, the positive influence of both promoters and O_2 coupled with the capability to determine both specific activities and TOFs provides optimism that further improvements are possible.

Acknowledgements

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