Catalysis Letters 61 (1999) 131–138

Influence of homogeneous decane oxidation on the catalytic performance of lean NO_x catalysts

C.C. Cheung and M.C. Kung

Department of Chemical Engineering, Northwestern University, Evanston, IL 60208, USA

Received 12 April 1999; accepted 14 June 1999

Extensive homogeneous gas-phase reactions were observed when decane was used as the hydrocarbon reductant for the selective reduction of NO_x. The catalytic performance of a $SnO_2/CoO_x/Al_2O_3$ catalyst was found to be strongly dependent on the extent of the homogeneous reaction in the pre-catalytic volume. The effect of the homogeneous reaction on the catalytic performance also depended on whether SO_2 was present in the feed. By filling the pre-catalytic volume with 25–35 mesh irregularly shaped quartz chips, gas-phase reaction was suppressed significantly. This methodology was used to evaluate the inherent catalytic performance of $SnO_2/CoO_x/Al_2O_3$ and SnO_2/Al_2O_3 catalysts with decane as a reductant. It was found that in the absence of SO_2, SnO_2/Al_2O_3 was a better catalyst than $SnO_2/CoO_x/Al_2O_3$, but in the presence of 30 ppm of SO_2 the latter was a far better catalyst.

Keywords: homogeneous reaction, decane, selective NO_x reduction, $SnO_2/CoO_x/Al_2O_3$, SnO_2/Al_2O_3

1. Introduction

Homogeneous reactions of alkanes have been studied as early as the 1930's [1]. Rice [1] has observed that the reaction is initiated by the breaking of the carbon–carbon bond as this is the weakest bond in the molecule. The radicals formed subsequently may react with other molecules, or decompose, or adsorb onto the walls of the reactor [1]. Thus, the reaction scheme is rather complex, and the products and conversions are highly dependent on process variables such as temperature, pressure, wall conditions and the presence of other reactants such as O_2. In the low-temperature regime and in the presence of oxygen, the primary stable products are oxygenates like alcohols and aldehydes [2]. In the high-temperature regime ($T > 500\,^\circ C$), the ease of an alkane to undergo homogeneous reactions increases with its molecular weight [4].

Small alkanes such as propane and isobutane have been used extensively as model reductants in the study of lean NO_x catalysis [5]. No significant homogeneous reactions were observed below 500 °C when a lean NO_x feed containing these small alkane reductants was passed through an empty reactor [6,7]. However, larger molecules such as decane appear to be more representative reductants for the evaluation of catalysts for the abatement of diesel engine exhaust [8]. Since decane is a large alkane, the temperature for the initiation of oxidative pyrolysis reaction is significantly lower than those of the light alkanes. It has been well demonstrated that the effectiveness of a lean NO_x catalyst at a particular temperature is strongly dependent on the nature of the reductant [9]. For example, Cu-ZSM-5 is an effective catalyst with C_3H_6 but not with CH_3OH as the reductant; whereas a less active catalyst such as H-ZSM-5 is a more effective catalyst when CH_3OH is the reductant [9]. Thus, the product distribution in the oxidative pyrolysis of decane could profoundly affect the effectiveness of lean NO_x catalysts.

Since the initiation of this work, a publication by Kharas et al. detailing the deleterious role of the homogeneous oxidation reactions of hydrocarbons on the performance of high-temperature lean NO_x catalysts has appeared [8]. However, it is conceivable that homogeneous gas-phase reactions can be used advantageously to broaden the temperature window of operation, particularly toward lower temperatures. This may be accomplished by the initiation of the alkane homogeneous reaction at low temperatures in the pre-catalytic region to produce molecules, such as oxygenated hydrocarbons, that are more reactive than alkanes. These molecules can subsequently react catalytically with NO_x to produce N_2.

In order to design a catalytic system that operates in the presence of both homogeneous and catalytic reactions, it is important to compare and understand the catalytic behavior in the presence and absence of the gas-phase reactions. Thus, this is the focus of our investigation of the $SnO_2/CoO_x/Al_2O_3$ catalyst. It has been reported in the literature that significant suppression of the gas-phase reaction is possible when the void space in a reactor is filled with quartz chips as the latter are highly effective free-radical quenchers [10]. Martin et al. [11] have observed that the rate of propane pyrolysis in the presence of oxygen can be significantly suppressed at large surface to volume ratio and attributed this to the effectiveness of surface ions in destroying oxygenated free radicals. Thus, catalytic results obtained in reactors with void space filled with quartz chips are taken to be representative performance characteristics of a catalyst. With quartz-chips-filled reactors, the negative impact of SO_2 on catalytic performance of two highly reactive catalysts $SnO_2/CoO_x/Al_2O_3$ and SnO_2/Al_2O_3 are also examined.

2. Experimental

2.1. Catalyst preparation

γ-Al_2O_3 was prepared with a method similar to that of Maeda et al. [12], by hydrolysis of alumina isopropoxide (Aldrich) dissolved in 2-methyl-2,4-pentanediol (Aldrich). It was calcined to 700 °C in flowing air at a heating rate of 1 °C/min. The temperature was maintained at 700 °C for 2 h. 1.6% H_2O was introduced into the calcination feed at 500 °C and the H_2O concentration was increased to 6% at 700 °C.

The $SnO_2/CoO_x/Al_2O_3$ catalyst was prepared as follows. A sample of CoO_x/Al_2O_3 was first prepared by stepwise impregnation of a cobalt nitrate (Aldrich) solution onto α-Al_2O_3 in a manner similar to the procedures of Chung et al. [13]. Five sequential steps of impregnating 1 wt% Co each time was used. The sample was calcined at 500 °C overnight after each impregnation, and at 800 °C for 2 h after the last one. Then, this CoO_x/Al_2O_3 catalyst was impregnated with an ethanolic $SnCl_2$ (Aldrich) solution to achieve a final loading of 5 wt% Sn. The sample was subsequently dried and calcined for 4 h at 500 °C. The BET surface area was 155 m^2/g.

The SnO_2/Al_2O_3 catalyst was prepared by incipient wetness impregnation of γ-Al_2O_3 with ethanolic $SnCl_2$ solution. The sample was dried and calcined at 500 °C for 4 h and 800 °C for 2 h. The BET surface area was 197 m^2/g.

2.2. Reaction tests

The reaction tests were conducted with either feed A or B. Feed A was composed of 11% O_2, 7% H_2O, 0.03% decane, 0.1% NO, and balance He. Feed B was composed of 10% O_2, 6% H_2O, 0.03% decane, 0.1% NO, 0.003% SO_2, and balance He. The desired decane and water concentrations were obtained by flowing He through the respective saturators. The decane saturator was at room temperature, while the H_2O saturator was maintained at 56.7 °C. The total flow rate was 386 ml in the absence of SO_2 and 415 ml when SO_2 was added. The reaction products were analyzed with a Hewlett–Packard 5890 gas chromatograph. O_2, N_2, CO, and CO_2 were separated with a molecular sieve 5A column (with temperature programming up to 200 °C to elute the CO_2 peak). O_2, CO_2, and decane were separated with a Porapak P column. The O_2 peak areas from both columns were used to relate the decane peak area from the Porapak P column to the CO and CO_2 areas from the molecular sieve 5A column. Although the separation of O_2 and CO_2 was poor in the Porapak P column, the large excess in O_2 concentration relative to CO_2 rendered the error in calculating the O_2 concentration insignificant. The catalyst was heated in 10% O_2 in He to 350 °C and the remaining components of the feed were introduced at that temperature. Since there was little or no reaction at that temperature, the O_2 and decane gas chromatography areas were regarded as representative of the unreacted feed. This calibration procedure was necessary because the pressure of the system above 350 °C was 5 psig higher for feed going through than by-passing the catalyst.

The catalytic reaction was performed in a fused silica U-tube and the catalyst was sandwiched between two layers of quartz wool. The inside diameter of the reactor upstream of the catalyst bed was 0.265 inches and was 0.153 inches downstream from the bed. A thermocouple was placed contiguous to the reactor wall next to the catalyst bed. The blank tests were conducted using either an empty reactor (volume = 7.1 ml in the heated zone), or a reactor packed with 3 mm glass beads (void volume = 3.9 ml) or 25–35 mesh quartz chips (void volume = 2.8 ml). The catalytic tests were performed with the pre-catalytic volume filled with either 3 mm glass beads or 25–35 mesh quartz chips. The post-catalytic void volume was always packed with 25–35 mesh quartz chips. The total catalyst weight was 0.2 g, which translated to a space velocity of 57,900 h^{-1} for experiments without SO_2 and 62,400 h^{-1} for experiments with SO_2.

3. Results

Figure 1 shows the temperature profile in the furnace when the thermocouple used to control the furnace temperature registered 425 °C. The thermocouple was 5.5 inches and the bottom of the reactor was 6.5 inches from the top of the furnace.

Decane was very reactive even in the absence of a catalyst. Around 440 °C, decane was completely consumed when feed A was passed into an empty reactor at a flow rate of 200 ml/min. No attempt was made to identify the products of the gas-phase reaction as it was difficult to separate the many small GC peaks that overlap with the large water peak. The decane conversion was considerably suppressed when the total flow rate was increased to 386 ml/min and the total void volume reduced to 3.9 ml by loading the reactor with 3 mm glass beads (figure 2, curve (a)). There was no formation of N_2. When the 3 mm glass beads were replaced with irregularly shaped 25–35 mesh quartz chips in what would be the post-catalytic volume in a catalytic run, the gas-phase decane conversion was further reduced (curve (b)). When the whole reactor was filled with 23–35 mesh quartz chips, only a small amount of gas-phase reaction was observed at temperatures as high as 470 °C (curve (c)). In the experiment where the reactor was filled with glass beads, adding SO_2 to the feed did not change the extent of gas-phase reaction significantly.

Since only gas-phase reactions in the pre-catalytic void volume would influence the catalytic performance, the effect of homogeneous reaction on the activities of the $SnO_2/CoO_x/Al_2O_3$ catalyst was examined with the reactor

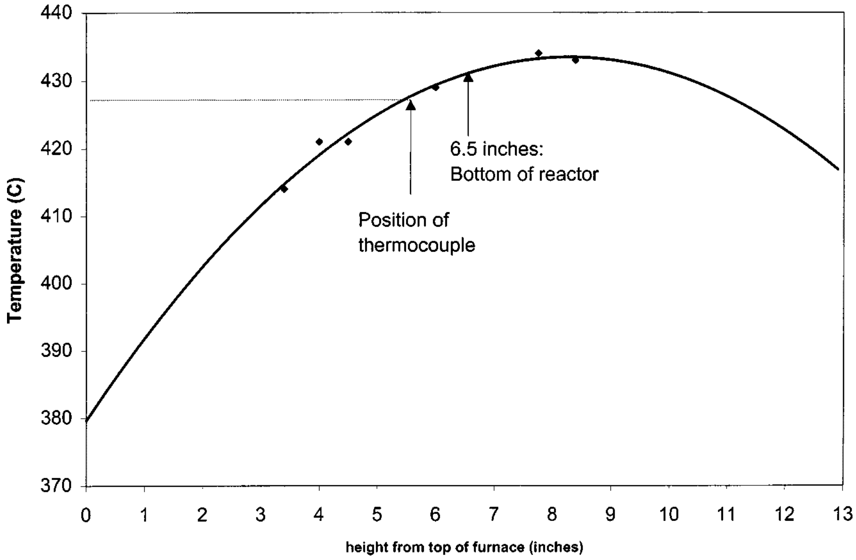


Figure 1. Temperature profile of furnace, when the thermocouple that controlled the furnace registered 425 °C, and placed at 5.5 inches from the top.

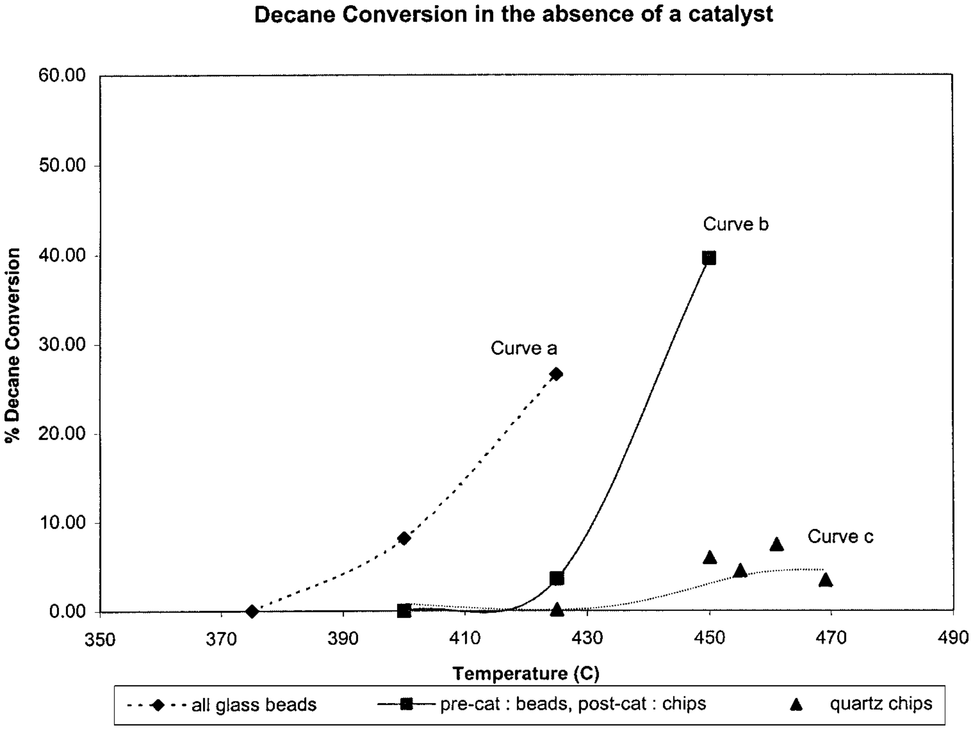
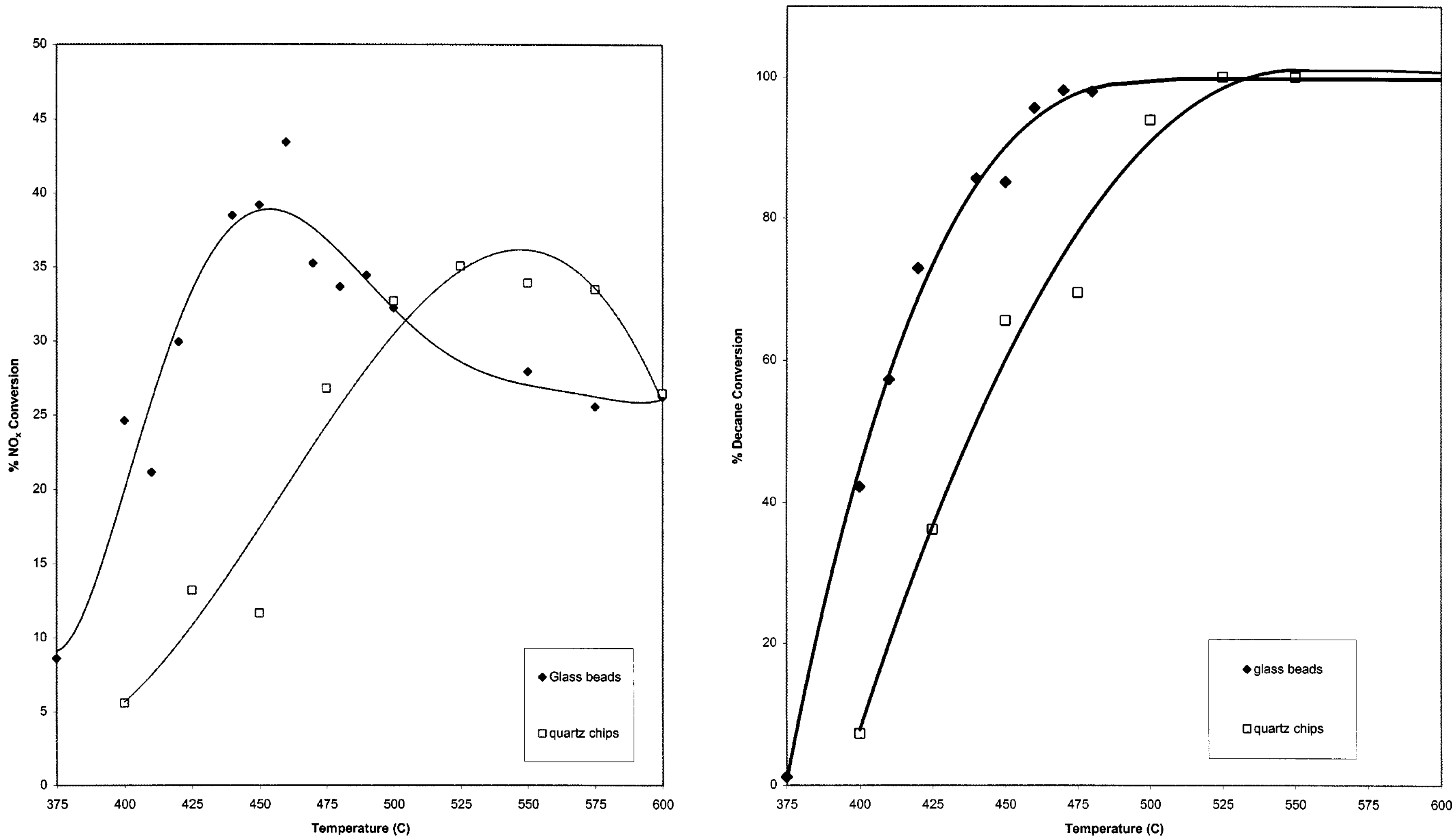


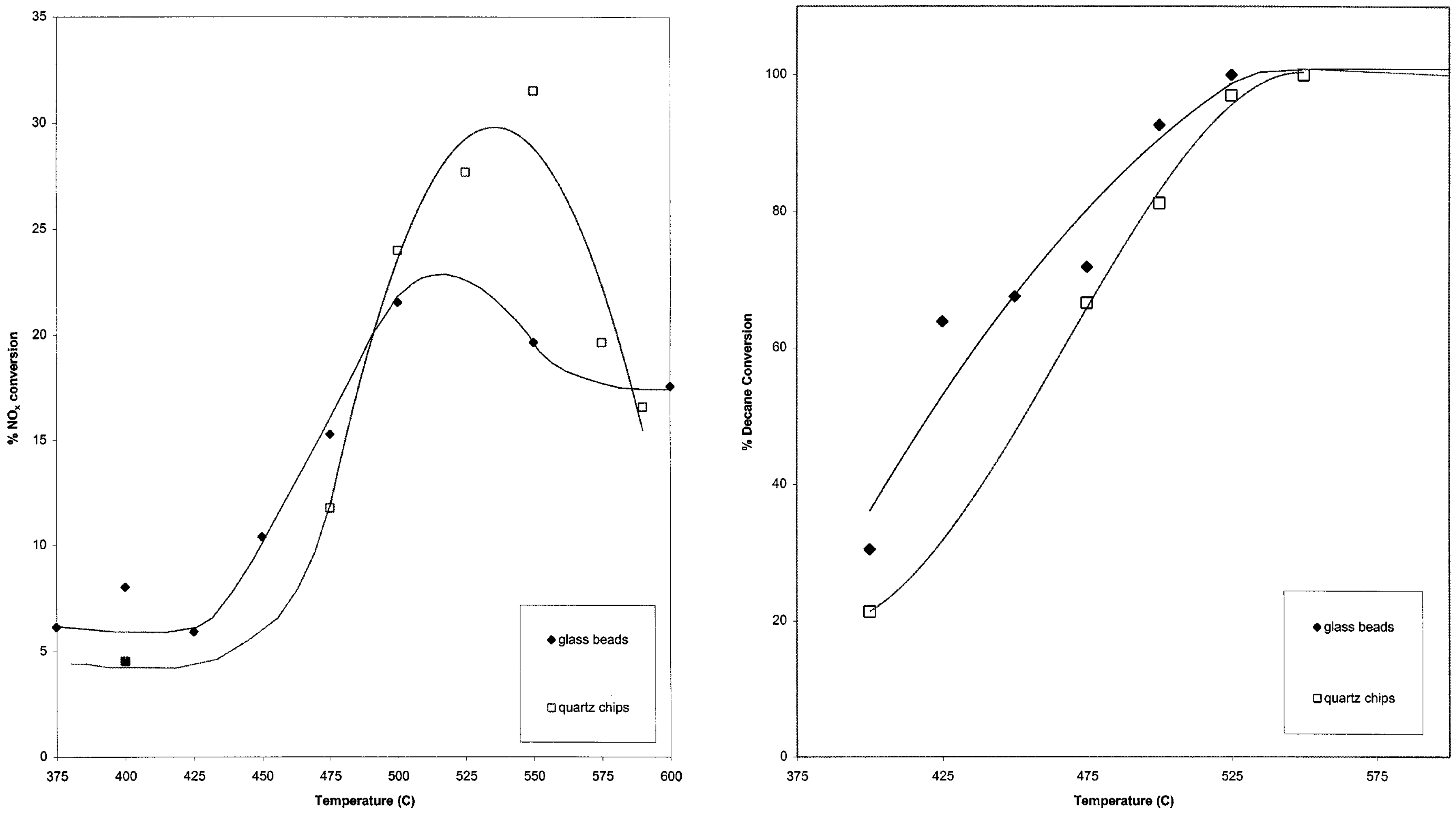
Figure 2. Decane conversion activity in a reactor (a) packed with 3 mm glass beads (reactor void volume 3.96 ml); (b) packed with 3 mm glass beads in the "pre-catalytic volume" and separated from the 25–35 mesh quartz chips in the "post-catalytic volume" by a layer of quartz wool; (c) packed with 25–35 mesh quartz chips. Feed composition: 10% O_2, 270 ppm decane, 933 ppm NO, 28 ppm SO_2, 10% H_2O, balance He, 440 °C.

pre-catalytic volume filled with either glass beads or quartz chips. Figure 3(a) compares the NO_x conversions to N_2, in the absence of SO_2, over the $SnO_2/CoO_x/Al_2O_3$ catalyst in a reactor with its pre-catalytic volume charged with either glass beads or quartz chips, and the post-catalytic volume filled with quartz chips. For the reactor packed with 3 mm glass beads, the highest NO_x conversion of around 40% was observed at a temperature of 450 °C. For the reactor packed with quartz chips, the NO_x conversion was the highest at 35% at a temperature of 550 °C. At temperatures below 475 °C, the decane conversions were also substantially lower for the reactor packed with quartz chips (figure 3(b)). When SO_2 was introduced into the feed, the NO_x conversions were suppressed significantly over the catalyst with glass beads packed upstream (figure 4(a)). For the reactor charged with quartz chips, the decrease in the maximum NO_x conversion was minor, but the temperature window was noticeably narrowed. The effect of SO_2 on the decane conversions was much less pronounced for catalysts in either of the reactor configurations (figure 4(b)).



(a) (b)

Figure 3. Comparison of reactant conversion over $SnO_2/CoO_x/Al_2O_3$ in reactors with the pre-catalytic volume filled with glass beads (◆) or quartz chips (☐). Feed composition: 11% O_2, 1040 ppm NO, 7% H_2O, 300 ppm decane, balance He. (a) NO_x conversion to N_2; (b) decane conversion.



(a) (b)

Figure 4. Comparison of reactant conversions in the presence of SO_2 over $SnO_2/CoO_x/Al_2O_3$ in reactors with the pre-catalytic volume filled with glass beads (◆) or quartz chips (□). Feed composition: 10% O_2, 270 ppm decane, 933 ppm NO, 28 ppm SO_2, 10% H_2O, balance He. (a) NO_x conversion to N_2; (b) decane conversion.

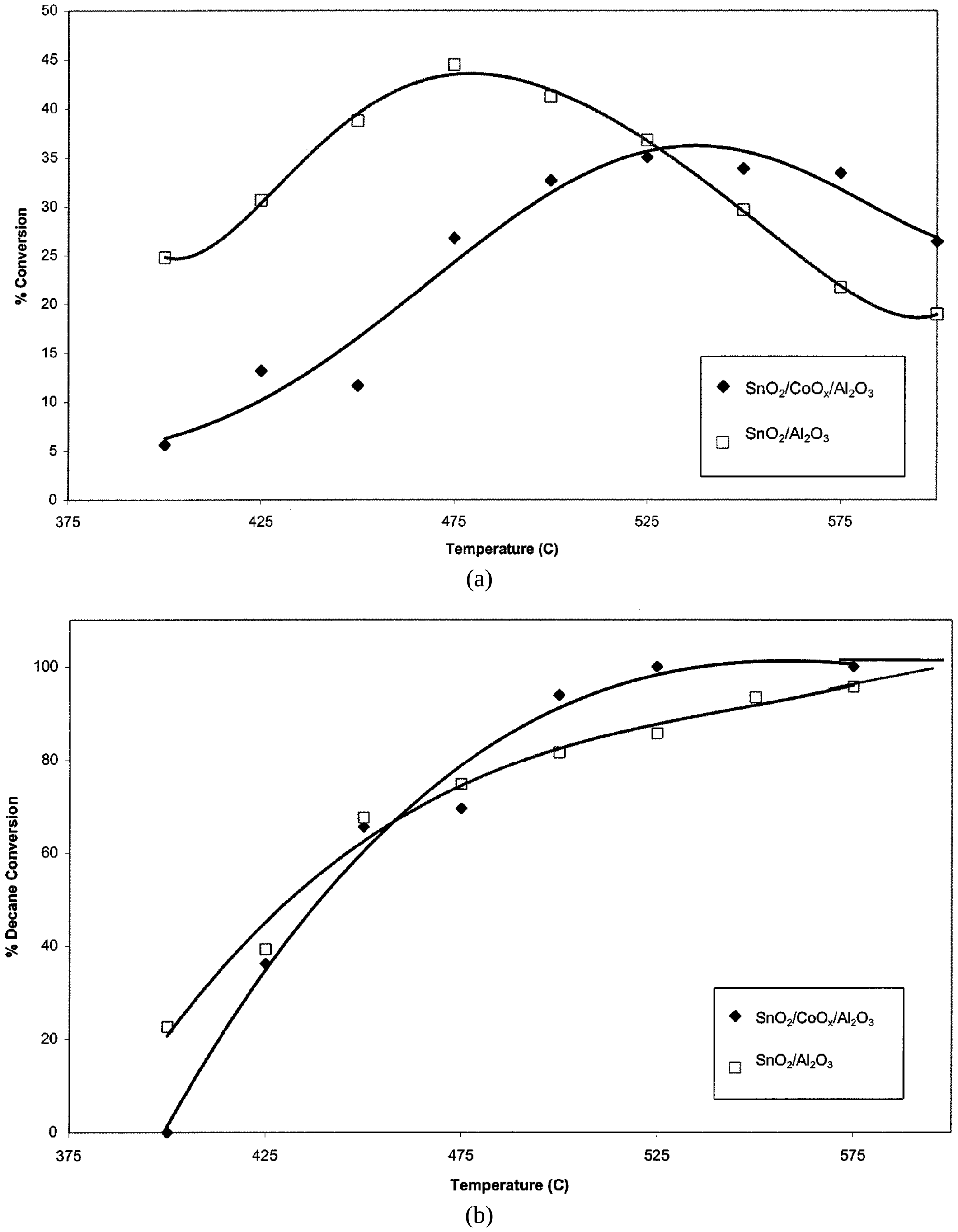


Figure 5. Comparison of reactant conversions of $SnO_2/CoO_x/Al_2O_3$ and SnO_2/Al_2O_3 in a feed composition of 11% O_2, 1040 ppm NO, 7% H_2O, 300 ppm decane, balance He. The void volume of the reactor was filled with quartz chips. (a) NO_x conversion to N_2; (b) decane conversion.

Figure 5(a) compares the differences in NO_x conversion between the SnO_2/Al_2O_3 catalyst and the $SnO_2/CoO_x/Al_2O_3$ catalyst when the reactor void volume was filled with quartz chips and SO_2 was absent from the feed. The maximum NO_x conversion over the SnO_2/Al_2O_3 was about 45% at a temperature of 475 °C. Over the $SnO_2/CoO_x/Al_2O_3$, it was about 35% at 525 °C. The decane conversion profiles of the two catalysts were rather similar (figure 5(b)). The SnO_2/Al_2O_3 catalyst was very ineffective for the selective reduction of NO_x by decane with 30 ppm of SO_2 in the feed. The maximum NO_x conversion was less than 15% and this occurred at a low temperature of 425 °C. The activity decreased with time on stream. Since the complete feed was introduced into the reactor at 350 °C, it was suspected that substantial deactivation had already occurred at that low temperature.

4. Discussion and conclusions

Decane readily undergoes homogeneous reactions in an empty reactor in the presence and absence of SO_2. When glass beads or quartz chips are loaded into the reactor, the extent of the homogeneous reaction is greatly reduced. This is in part due to the reduction of the void volume, but more importantly, it is because the surface to volume ratio in the heated zone is greatly increased. The difference in the void volumes is small for reactors filled with glass beads and quartz chips, but the surface area of the irregularly shaped quartz chips is much greater than that of the glass beads. This larger surface area is important in quenching oxygenated free radicals formed in the gas phase, as proposed by Martin et al. [11]. The extent of the gas-phase reaction for the whole reactor filled with quartz chips is very low, even at 470 °C. Hence a reactor configuration where the pre-catalytic volume is filled with quartz chips is taken as one where the catalytic performance is not affected significantly by gas-phase reactions.

With the $SnO_2/CoO_x/Al_2O_3$ catalyst, the occurrence of homogeneous reaction in the pre-catalytic volume substantially lowers the temperature when decane reaction begins (see figure 3(b)). Concomitantly, the temperature at which N_2 formation is detected is also lowered. Since N_2 is not a product of the gas-phase reaction, its formation must result from the reaction of gas phase generated reactive species with NO on the surface of $SnO_2/CoO_x/Al_2O_3$. It is well documented that the homogeneous reaction of an alkyl radical with O_2 will result in the formation of an alkyl peroxy (RO_2) radical [14]. Under the conditions used here, the concentration of hydrocarbon in the feed is low. Therefore, bimolecular reactions, such as RO_2+RH or RO_2+RO_2, are probably not important. Instead, the isomerization of the RO_2 radical, the proposed dominant pathway for hydrocarbons with carbon numbers greater than 5, may be important [14–16]. This reaction occurs via intramolecular hydrogen migration to form hydroperoxyalkyl radicals which subsequently decompose either into alkenes or O-heterocyclic compounds. The hydroperoxyalkyl radical can also react with O_2 and then decompose to form non-cyclic oxygenated hydrocarbons [14]. The relative importance of the different decomposition pathways, and hence the product distribution, is strongly dependent on the oxygen and hydrocarbon partial pressures as well as temperature. However, it is important to note that all of the products are more reactive than the original alkane and this may account for the decrease in the temperature for N_2 production when pre-catalytic homogeneous reaction is present. Reactions with NO_x is another additional pathway for the radicals generated in the homogeneous reaction. For C_3H_6 at high temperatures, we have observed that the extent of the gas-phase reaction is greatly enhanced by the presence of a small concentration of NO_x in the feed [17]. Kharas et al. [8] have observed decrease in the NO_x concentration at the inlet of their reactor and have proposed the formation of R–NO_2-like species.

In the presence of pre-catalytic homogeneous reaction, the $SnO_2/CoO_x/Al_2O_3$ catalyst is quite effective for the selective reduction of NO_x by decane, with a broad temperature window of operation and respectable N_2 yields at a high space velocity of 60,000 h^{-1}. The benefit of the homogeneous reaction is negated when 30 ppm of SO_2 is introduced into the feed. Since the loss in N_2 conversion is significantly more than the decrease in decane conversion, it appears that the effect of SO_2 alters the catalytic process such that the hydrocarbons generated by the homogeneous reaction can no longer be utilized effectively. The results also suggest that the effect of SO_2 is highly dependent on the nature of the reductant, since its effect on the selective reduction of NO_x by decane in the absence of homogeneous reaction is much more moderate.

The results here are in contrast to those reported by Kharas et al. [8]. Under their test conditions, homogeneous reaction has a deleterious effect on the lean NO_x reaction. This is in part due to the fact that a significant fraction of the hydrocarbon is depleted via non-productive combustion to CO_x. However, another important parameter is the effect of the speciation of the decane in the gas phase on the catalytic performance. As mentioned in section 1, the product distribution from the homogeneous reaction depends greatly on the process variables such as pressure and reactor geometry and catalysts differ in their efficiency in promoting NO_x conversions for a given reductant. Therefore it is not surprising that our observation on the effects of homogeneous reactions on catalyst performance differs from those of Kharas' group. Our result, however, suggests that it may be possible to take advantage of gas-phase reaction by tailoring the reactivity of the catalyst to the products of the homogeneous reaction.

Finally, figure 5 shows a comparison of SnO_2/Al_2O_3 and $SnO_2/CoO_x/Al_2O_3$ in the absence of pre-catalytic homogeneous reaction. It shows that SnO_2/Al_2O_3 is better than $SnO_2/CoO_x/Al_2O_3$ in the absence of SO_2. The SnO_2/Al_2O_3 catalyst promotes the selective reduction of NO_x by decane at a much lower temperature and the overall N_2 yield is noticeably better. However, the suppression effect of SO_2 is much more severe. The serious loss in activities for the SnO_2/Al_2O_3 catalyst due to SO_2 is unexpected, because the effect of SO_2 is much milder when C_3H_6 is the reductant [18]. Thus, the effect of SO_2 is highly dependent on the reductant and the catalyst.

Acknowledgement

A grant in aid from the Caterpillar Company is gratefully acknowledged. We would also like to thank Professor Harold Kung for in depth discussions of this paper.

References

[1] F.O. Rice, J. Am. Chem. Soc. 53 (1931) 1959.

[2] J.H. Knox and A.F. Trotman-Dickenson, Trans. Faraday Soc. I 54 (1970) 161.

[3] J.H. Knox, Adv. Chem. Ser. 76 (1968) 10.

[4] H.H. Kung, Adv. Catal. 40 (1994) 1.

[5] F. Witzel, G.A. Sill and W.K. Hall, J. Catal. 149 (1994) 229.

[6] M. Sasaki, H. Hamada, Y. Kintaichi and T. Ito, Catal. Lett. 15 (1992) 297.

[7] D.B. Lukyanov, G. Sill, J.L. d'Itri and W.K. Hall, J. Catal. 153 (1995) 265.

[8] K.C.C. Kharas, M.J. Miller and J.-Y. Yan, SAE paper #982604 (1998).

[9] H. Hamada, Y. Kintaichi, M. Sasaki and I. Takehiko, Appl. Catal. 70 (1991) L15.

[10] K.T. Nguyen and H.H. Kung, J. Catal. 122 (1990) 415.

[11] R. Martin, M. Dzierzynski and M. Niclause, J. Chem. Phys. 61 (1964) 790.

[12] K. Maeda, F. Mizukaini, S.I. Newa, M. Toba, M. Watanake and K. Masuda, J. Chem. Soc. Faraday Trans. 88 (1992) 97.

[13] K.S. Chung and F.E. Massoth, J. Catal. 64 (1980) 332.

[14] R.D. Wilk, R.S. Cohen and N.P. Cemansky, Ind. Eng. Chem. Res. 34 (1995) 2285.

[15] A.D. Walsh, in: *9th Symp. (International) on Combustion*, Pittsburgh, 1962, p. 1046.

[16] A. Fish, Quart. Rev. Chem. Soc. (London) 18 (1964) 243.

[17] Y. Zheng and M.C. Kung, unpublished result.

[18] M.C. Kung, P.W. Park, D.W. Kim and H.H. Kung, J. Catal. 181 (1999) 1.