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LETTER TO THE EDITOR

Emphasizing the Mechanistic Importance of Intermediate $N_2O + CO$ Reaction in Overall $NO + CO$ Reaction System (Reply to Comments by V. P. Zhdanov)

In response to the interesting comments made by Zhdanov (1) on our recent publications (2–4), we carefully examined both his arguments and our previous findings/conclusions in those papers. We could find neither adequate justifications for his claims nor any need for modifications in our earlier findings and conclusions. However, we felt it necessary to elaborate on our findings and conclusions reported in those papers. It is hoped that this additional explanation will help him and others to better understand our contributions to the literature.

1. Regarding Zhdanov's statement that our interpretation (3) is misleading, it is important to recognize that the intermediate $N_2O + CO$ reaction over Rh/Al_2O_3 involves the $N_2O_a + CO_a$ reaction on the Rh surface which proceeds via the elementary reaction steps [5], [6], and [8] in (4), where the subscript "a" denotes the adsorbed species on the catalytic surface. The fact that the $N_2O_a + CO_a$ is an integral part of the intermediate $N_2O + CO$ reaction was clearly spelled out in our previous publications (2, 4). Furthermore, we specifically noted [p. 698, Ref. (4)] that "the gas phase intermediate (N_2O) and the surface intermediate (N_2O_a) cannot be treated separately due to the exchange process occurring between them through adsorption and desorption," in order to emphasize the fact that any discussion of the intermediate $N_2O + CO$ reaction should include both N_2O and N_2O_a.

Turning to Zhdanov's "total" rate of N_2 formation in the $NO + CO$ reaction, we point out that his "total" rate is equivalent to our rate of N_2 formation via N_2O intermediates which include both N_2O_a on the surface and N_2O in the gas phase. Also, *his "direct channel" is nothing but the formation of* N_2 *via the intermediate* N_2O_a *on the surface*. Here, we recall our statement on this direct nature [p. 706, Conclusion 2, Ref. (4)], "... particularly when N_2O_a reacts *directly* as a surface intermediate." In light of the above explanation, Zhdanov's reinterpretation—*that the overall* $NO + CO$ *reaction occurs primarily via the direct channel*—is nothing new, and it is already properly embedded in our conclusion on the kinetic importance of the intermediate N_2O_a.

2. Regarding Zhdanov's claim that our conclusion about the importance of the $N_2O + CO$ reaction is not supported by our kinetic analysis (3), it is well known that the apparent rate of the isolated $N_2O + CO$ reaction under stoichiometric steady-state conditions is very slow. However, the intrinsic rate of the $N_2O_a + CO_a$ reaction on the surface can be much faster than the apparent rate of the $N_2O + CO$ reaction, as shown in our kinetic analysis (3). This is due to the fact that the rate limiting process of the isolated $N_2O + CO$ reaction under stoichiometric steady-state conditions is the adsorption of gas-phase N_2O to form N_2O_a on the surface, as revealed in our previous study (4).

The importance of the intermediate $N_2O + CO$ reaction can be verified by showing that the $N_2O_a + CO_a$ reaction on the Rh surface is very fast under the overall $NO + CO$ reaction conditions. However, direct experimental demonstration of this is rather tricky due to the difficulties in providing the surface with N_2O_a. A simple addition of gas-phase N_2O to the $NO + CO$ reaction system, such as that employed in Ref. (6), is not adequate for this purpose in view of the unfavorable conditions for N_2O adsorption when the surface coverage is near saturation. Our approach was to create highly favorable conditions for N_2O adsorption through transient operation of the catalyst. This idea was demonstrated in the cyclic experiments [Fig. 4 in Ref. (4)], the results of which were shown in Fig. 6 of Ref. (4). In this highly favorable environment for N_2O adsorption (i.e., almost clean Rh surface at the beginning of the $N_2O + CO$ half-cycle), the rate of the isolated $N_2O + CO$ reaction can closely approximate the rate of the $N_2O_a + CO_a$ reaction on the surface. Figure 6 in Ref. (4) shows that complete conversion of N_2O is achieved in the $N_2O + CO$ reaction during the first 4 s of the $N_2O + CO$ half-cycle, even though the steady-state conversion is only 8% for the isolated $N_2O + CO$ reaction (4). This high activity of the $N_2O + CO$ reaction during the short transient period translates to a turnover frequency (TOF) of $0.25\ s^{-1}$ [based on the Rh dispersion of 28% (2)]. This TOF is about the same as the rate of the $NO + CO$ reaction (5) and is faster than the rate of the isolated $N_2O + CO$ reaction reported by McCabe and Wong (5) by about two orders of magnitude. We believe this is a clear indication of the importance of the $N_2O_a + CO_a$ reaction on the surface, which is the essential part of the intermediate $N_2O + CO$ reaction. This is exactly what our previous kinetic analysis (3) has predicted.

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3. Regarding our assumption (3) of negligible N_2 formation via $N_a + N_a$ on the surface, we have shown that its validity can be checked by the use of a criterion presented in Eq. (22) in Ref. (3). This criterion is satisfied under typical exhaust conditions as illustrated in Ref. (3). However, for UHV systems, it must be checked carefully before the results of the kinetic analysis in Ref. (3) can be directly applied to such systems, as we have already cautioned (3).

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