

NO₂-catalyzed deep oxidation of methanol: Experimental and theoretical studies

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Abstract

The NO₂-catalyzed deep oxidation of methanol has been studied by both experimental and theoretical techniques. On-line infrared (IR) and in situ IR investigations show that a trace amount of NO_x (for example, 600 ppm NO and/or NO₂) can dramatically promote the oxidation of methanol as manifested by the reduced reaction temperature together with significantly enhanced CO₂ selectivity. The reactions of methanol and nitrogen dioxide are investigated by theoretical calculations at the CBS-Q//B3LYP/6-311++G(2d,p) level of theory. Seven channels are found totally. The calculated reaction barriers of the controlling steps of the two lowest channels are 20.5 and 21.1 kcal mol⁻¹, which are in good agreement with the reported experimental value of 21.4 kcal mol⁻¹. The reaction rate constants are also calculated by the microcanonical variational transition state theory (μ VT) with tunneling corrections. The three-parameter fitting expression for the overall forward rate constant is $1.72 \times 10^{-22} T^{3.38} \exp(-10153 T^{-1}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The theoretical simulation of methanol conversion is in satisfactory agreement with the experiment. A reaction mechanism for the CH₃OH–O₂–NO_x system has been proposed based on the experimental and theoretical studies. © 2006 Elsevier B.V. All rights reserved.

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1. Introduction

Although the reactions involved in the CH₄–O₂–NO_x co-feed system have been comprehensively investigated [1–7], those in the related CH₃OH–O₂–NO_x system have not yet been so widely studied. The reactions in the latter system are related to at least three important areas, i.e., selective oxidation of methane to oxygenates including methanol [1–7], complete combustion of methanol as a gasoline additive [8], and selective reduction of NO by methane [9]. The three areas are relatively independent and are not routinely well cross-referenced in the literature.

The selective oxidation of methane promoted by NO_x (NO and/or NO₂) has been shown to give a variety of oxygenates (mainly methanol and formaldehyde) [1–7]. Methanol is the

desired product in such a process but the yield is normally far from being satisfactory [1–4]. The best yield of oxygenates as reported by Tabata et al. [1] and Otsuka et al. [2] is lower than 7% at a temperature of 873 K with an NO_x concentration of 0.5%. Deep oxidation of methanol, which is more active than methane, is a key factor responsible for the low yield. What role NO_x plays in the deep oxidation still has not been clearly characterized, however. Understanding the mechanism, in particular, the mechanistic difference between the conversion of methane and methanol, is thus of great value in finding a process that can make selective oxidation of methane more feasible.

Methanol is nowadays considered as an alternative to gasoline for transport on environmental grounds. In combustion processes such as in automobile engines, NO_x is formed from thermal fixation of molecular nitrogen at high temperatures. The NO_x concentrations are typically 10–1000 ppm. Yano [8] has found that NO can considerably accelerate the oxidation of residual methanol to formaldehyde in the exhaust of methanol-fueled engines. Incomplete combustion of these oxygenates may cause further environmental problems. Furthermore, from a mechanis-

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tic view of point, it is not clear whether or not NO_x reacts with alcohols stoichiometrically [10,11].

The catalytic reduction of NO_x to N_2 with methane is a potentially useful strategy for the remediation of exhaust from natural gas-fired power plants and lean-burn natural-gas engines [9]. However, methanol may be formed in this process via the intermediate CH_3NO as reported by Ying [9]. As mentioned above, even a low level of methanol in the exhaust may result in external environmental problems, and the formation of methanol should be avoided via deep oxidation.

It is worthwhile noting that NO_x -promoted gas phase oxidation of methanol has many advantages as far as performing in situ IR or theoretical studies are concerned. The absence of a solid catalyst, together with the high IR sensitivities of the different products, means that in situ observations can be carried out with either very low or very high methanol concentrations, over a very wide temperature range. In our previous paper [5], by comparison of the in situ IR spectra with the on-line results we have shown that the HONO species, which is observed only by in situ measurements, is a key intermediate in the NO_x -promoted gas-phase oxidation of methane. In this paper we report on-line reaction studies, in situ IR experiments, and theoretical calculations that allow us to conclude that deep oxidation of methanol to carbon oxides can be catalyzed by NO_2 .

2. Experimental details

The procedure used a conventional gas flow reactor system. Three separate streams of NO/N_2 (1880 ppm NO, or 1.56% NO alternatively, N_2 balanced), O_2 (99.995%) and N_2 (99.999%) were used. Flow rates were adjusted by mass flow controllers. Three streams were premixed (typical composition: 600 ppm NO, 5% O_2 and 95% N_2 , respectively) prior to being bubbled through liquid methanol (>99.5%, dipped in ice water). Then, the gas mixture flowed through a quartz tube (heating length 20 cm, i.d. 5.8 mm, flow rate 40 ml min^{-1}), which was heated at temperatures ranging from room temperature to 873 K. The exit mixture was analyzed by on-line FT-IR using a Bruker Vector 22 infrared spectrometer with a gas cell (length 10 cm, KBr windows). In the case of NO concentration measurement, the exit mixture flowed through a P_2O_5 drier prior to the quantitative analysis, in order to exclude the water interference. The concentrations of the products were computed automatically with the OPUS quantitative method using calibration curves. On-line mass spectrometer (HIDEN HPR-20 gas analyzer) was used to further check the low concentration compounds (NO_2 , CH_3NO_2 , etc.) in the exit mixture.

The in situ experiments were carried out in a homemade quartz infrared cell (i.d. 10 mm, length 15 cm). KBr windows cooled by flowing water were attached to both sides of the cell. A 7.5 cm heating element wrapped around the cell allowed collection of in situ spectra at elevated temperatures. The temperature was monitored by a thermocouple located on the outside of the cell (and near the heating element) and was calibrated by another thermocouple put in the cell under the same conditions. In situ infrared spectra were collected using a Bruker Vector 22 spectrometer with a resolution of 2 cm^{-1} .

3. Computational details

3.1. Electronic structure calculations

The electronic structure calculations were performed using the Gaussian 98 program package [12]. The geometries of all the stationary points were optimized by employing the hybrid density functional B3LYP method (Becke's three-parameter nonlocal exchange functional [13] with the correlation functional of Lee, Yang and Parr [14,15]) with the 6-311++G(2d,p) basis set. To obtain more accurate energies, the complete basis set method CBS-Q [16] was employed to refine the energies based on the geometries optimized at the B3LYP/6-311++G(2d,p) level of theory. All the transition states were confirmed by frequencies and IRC (intrinsic reaction coordinate) calculations with the B3LYP/6-311++G(2d,p) method. All the energies in this study were corrected with the ZPE (zero point energy) except those pointed out explicitly. The ZPE and frequencies were not scaled due to the use of triple-zeta basis sets.

3.2. Rate constant calculations

Within the framework of microcanonical variational transition state theory (μVT), the thermal rate constant at a given temperature T can be expressed as:

$$k^{\mu\text{VT}}(T) = \sigma \frac{\int_0^\infty \min_s \{N^{\text{GTS}}(E, s)\} e^{-E/k_B T} dE}{h Q_R}$$

where σ is the statistical factor of the reaction, and h and k_B are the Planck and Boltzmann constants, respectively. Q_R is the total reactant partition function, which is the product of electronic, rotational and vibrational partition functions. The relative translational partition function was calculated classically. However, the rotational and vibrational partition functions of the reactant were calculated quantum mechanically within the rigid rotor and harmonic oscillator approximations. $N^{\text{GTS}}(E, s)$ is the sum of states of electronic, rotational and vibrational motions at energy E of the generalized transition state located at the reaction coordinate s . $N^{\text{GTS}}(E, s)$ along the minimum energy path were also calculated quantum mechanically using the rigid rotor and harmonic oscillator approximations. Since all the channels involve hydrogen transfer, the tunneling effects were calculated and included in $N^{\text{GTS}}(E, s)$ using the Eckart potential. The forward and reverse symmetry factors are 6 and 2 for channels 1–3, and 3 and 2 for channel 4, respectively. All the rate constant calculations were carried out with the VKLab 1.0 program [17].

4. Results and discussion

4.1. Spontaneous oxidation of methanol

The results of one pass oxidation of methanol in the absence of NO are shown in Table 1. It can be seen that the temperature required for initiating the spontaneous oxidation of methanol is at least 773 K.

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