Comment

Rebuttal to the Comment on “The role of methyl radicals in the reduction of NO by CH_4 over a Ba/MgO catalyst”

[by A.Yu. Gladky, V.K. Ermolaev and V.N. Parmon]

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In several studies, we have used a technique known as variable ionization energy mass spectrometry (VIEMS) to detect methyl radicals that were formed during either the decomposition of azomethane or the catalytic reaction of methane with oxygen over metal oxides that promote the oxidative coupling of methane [1–3]. Gas phase $CH_3\cdot$ radicals have independently been shown to be intermediates in both types of reactions [4–7]. The VIEMS method takes advantage of the fact that the appearance potential for $CH_3\cdot$ (9.8 eV) is much less than that of CH_4 (12.8 eV); thus, $CH_3\cdot$ radicals can be detected in the presence of a large excess of CH_4, provided the electron impact energy of a mass spectrometer is adjusted so that $CH_3\cdot$ radicals are preferentially ionized.

Gladky et al. [8], in the accompanying paper, have criticized our interpretation of the VIEMS results shown in figure 1 of their note (also figure 1 of [3]), and questioned whether the peak at 15 amu in spectrum (c) results from methyl radicals. Their interpretation is based on ionization cross sections for the reactions

$$CH_3\cdot \rightarrow CH_3^+ + e^- \tag{1}$$

$$CH_4 \rightarrow CH_4^+ + e^- \tag{2}$$

$$CH_4 \rightarrow CH_3^+ + H + e^- \tag{3}$$

They argue that at an electron impact energy of 19 eV, the ionization cross sections for reactions (2) and (3) would be so large that one could not detect methyl radicals in a gas mixture containing 1% $CH_3\cdot$ in CH_4, as we claim [3]. Furthermore, they conclude that the actual electron impact energy is close to 19 eV, as indicated by the ratio of the 15 and 16 amu peaks in figure 1(A), spectrum (b).

We disagree with both conclusions of Gladky et al. In our papers, we were careful to point out that only *nominal* electron energies were reported, i.e., the values reported could have differed from the actual energies by several eV. Stair and co-workers [4] carried out a similar experiment on the C_1 fragments derived from pyrolysis of azomethane, and they used the appearance potentials of methyl radicals and argon to calibrate their system. Although not specifically stated, we relied on the occurrence of reaction (2) to calibrate our system. The presence of significant peaks in figure 1(A), spectrum (c), at 18 and 32 amu, due to H_2O (12.6 eV) and O_2 (12.1 eV), respectively, but only a weak peak at 16 amu due to CH_4 (12.8 eV), indicates that the *actual* electron impact energy was ca. 13 eV. Methane, of course, was the major component. Based on the results shown in figure 2 of [8], one would expect that the cross section for $CH_3\cdot$ radical ionization would be >20 fold that of CH_4 ionization at 13 eV.

The implications of using a *nominal* electron impact energy are further apparent when one compares the results of figure 1 in [8] with those of figure 2 in [2]. In the former case the nominal energy was reported to be 19 eV and in the latter case it was 16 eV. At 16 eV the ratio of the 15 amu peak to 16 amu peak was larger, which may indicate a slightly smaller actual impact energy or it may reflect the fact that the Sr/La_2O_3 catalyst is particularly effective in generating $CH_3\cdot$ radicals. Nevertheless, in both cases, the ratio of the 15 amu peak to the 16 amu peak was large. The nominal electron energy that was required to produce acceptable signal levels with a large mass 15-to-mass 16 ratio increased slowly with usage of the mass spectrometer, presumably due to the formation of a carbonaceous residue on the filament. The argument of Gladky et al. that the electron impact energy cannot be as small as 13 eV is based on their interpretation of figure 1(A), spectrum (b). Since the amplitude of the peak at 15 amu is about 80% of the amplitude of the peak at 16 amu, they conclude from the cross sections shown in their figure 2 that the impact energy must actually be about 19 eV. They fail to recognize, however, that there is a significant background peak at 15 amu, of unknown origin, when no CH_4 is present in the system. The intensity of this peak, shown in spectrum (a), is comparable to that in spectrum (b), but it is small compared to the peak at 15 amu of $CH_3\cdot$ radicals in spectrum (c). The contribution at 15 amu in spectrum (b) is, therefore, a result of this background contribution and is not an indication of a large impact energy.

Finally, the case against the detection of $CH_3\cdot$ radicals by this method is unsupportable based on chemical evidence. The reaction of CH_4 and O_2 over these catalysts has definitively been shown by us and other investigators to produce $CH_3\cdot$ radicals. The radicals have been detected using matrix isolation electron spin resonance techniques [6,7,9] and photoionization together with mass spectrometry [5]. Under the conditions used in the studies under consideration, gas-phase $CH_3\cdot$ radicals would definitely be formed if CH_4 and O_2 were passed over these catalysts at elevated temperatures, and the *growth* of the peak at 15 amu in figure 1, spectrum (c), confirms their presence. According to the arguments of Gladky et al., based on ionization cross sections for CH_4, it is not possible to explain why the intensity of the mass 15 peak would increase dramatically (spectrum (c)) when the temperature of the catalytic reactor was increased from 25 to 775 °C. Moreover, mixtures of CH_4 and $CH_3\cdot$ radicals, derived from the decomposition of azomethane, and CH_4 produce the expected results. That is, one can observe a large ratio for the 15 amu-to-16 amu peaks, even when the $CH_3\cdot$ radicals are diluted in CH_4. Admittedly, the VIEMS method is not highly quantitative, but it does allow one to detect $CH_3\cdot$ radicals and to evaluate their relative concentrations in a semiquantitative manner.

References

[1] M. Xu, T.H. Ballinger and J.H. Lunsford, J. Phys. Chem. 99 (1995) 14494.

[2] S. Xie, T.H. Ballinger, M.P. Rosynek and J.H. Lunsford, Stud. Surf. Sci. Catal. 101 (1996) 711.

[3] S. Xie, M.P. Rosynek and J.H. Lunsford, Catal. Lett. 43 (1997) 1.

[4] G.H. Smudde, X.D. Peng, R. Viswanathan and P.C. Stair, J. Vac. Sci. Technol. 9 (1991) 1885.

[5] Y. Feng and D. Gutman, J. Phys. Chem. 195 (1991) 6558.

[6] D.J. Driscoll, W. Matir, J.-X. Wang and J.H. Lunsford, J. Am. Chem. Soc. 107 (1985) 58.

[7] M. Xu and J.H. Lunsford, Catal. Lett. 11 (1991) 295.

[8] A.Yu. Gladky, V.K. Ermolaev and V.N. Parmon, Catal. Lett. 60 (1999) 99.

[9] J.H. Lunsford, Langmuir 5 (1989) 12.