Catalysis Letters Vol. 111, Nos. 3–4, November 2006 (© 2006)
DOI: 10.1007/s10562-006-0144-5

A note on the statistical distribution of labeled and unlabeled oxygen atoms from N_2O decomposing on Fe-zeolites and the equilibrium constant between dioxygen isotopomers

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Received 16 May 2006; accepted 29 June 2006

Pirngruber and Roy [1,2] claim that the statistical distribution of ^{18}O atoms during the decomposition of nitrous oxide over Fe-MFI labeled by ^{18}O leads to the release of dioxygen species in equilibrium (or, in some transient experiments, out of equilibrium). The equilibrium constant $Q = [^{16}O^{18}O]^2/([^{16}O_2]*[^{18}O_2])$ is equal to 4 at temperatures common in catalyzed decomposition of nitrous oxide. In paper [2] both denominator terms are squared, probably by a printing error The (non) equilibration state has led Pirngruber and Roy to speculations on the reaction mechanism. However, we would like to point out that the recombination of statistically distributed ^{18}O and ^{16}O does not lead to the desorption of dioxygen isotopomers in equilibrium. Let us consider that there are, e.g., 3 atoms of ^{18}O and 7 atoms of ^{16}O; the probability of the release of $^{18}O_2$ is 0.06, of $^{16}O^{18}O$ 0.47 and the same for the release of $^{16}O_2$. The Q value is clearly far off 4, similarly as for different $^{16}O/^{18}O$ ratios. The interaction of dioxygen species with active oxygen atoms in the zeolite has to be clearly involved. The authors [1,2] have not found such a reaction, most probably because of impropriate dioxygen and ^{18}O ratios. Contrary to this, we have reported on a rapid equilibration between oxygen from nitrous oxide labeled by ^{18}O and unlabeled dioxygen over Fe-ferrierites below 300 °C [3]. As the isotopic exchange of only $^{18}O_2$ with Fe-ferrierite does not proceed below at least 500 °C, dioxygen molecules in the mixture with labeled N_2O must react with active oxygen atoms formed from nitrous oxide. Similarly, the equilibrium in isotopomers of dioxygens released from decomposing $N_2{}^{18}O$ (without additional dioxygen in the gas phase, which does not affect the reaction rate) is also rapidly established. We have therefore suggested that this equilibration proceeds between primarily released $^{18}O_2$ and oxygen of the zeolite by a single mechanism – the isotope exchange of 1 atom from the dioxygen molecule for one atom in the surface in one reaction step – for details see [4].

References

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