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C-centered paramagnetic species generated radiolytically in molecular sieves.

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Radicals play an important role in many radiolytic and catalytic reactions. However, their structure and properties are difficult to study because of extremely high reactivity. Matrix isolation technique in noble gas matrices and trapping in zeolites are the methods of choice for studying electronic structure and geometry of radical ions in solids.

We present the study of paramagnetic carbon centers generated radiolytically in molecular sieves with adsorbed carbon oxide. The combinations of Electron Paramagnetic Resonance technique and quantum chemical computation have been applied in order to identify the radical centers and define their geometry and reactivity.

All samples after degassing and dehydration on vacuum line were exposed to 13CO and γ-irradiated in 60Co source at 77 K with dose of 5 kGy. The EPR spectra were measured in temperature range 100 −370 K. In all samples slightly anisotropic doublets with different 13C hyperfine splittings were recorded just after irradiation. We assigned them to carbon centered radicals stabilized in different lattice sites.

Based on the EPR measurements and DFT calculations we found that zeolite samples with high silica alumina ratio as: ZSM-5/13CO: Si/Al=38÷200, FAU Y/13CO: Si/Al=30÷80 and MOR/13CO: Si/Al=8 stabilize three type of carbon centres. In the first one (center A) •+CO radical cation interacts with oxygen located between Si and Al atoms -[≡Si-O-Al≡]•+CO. In the second one (center A‘) it is bounded to oxygen located between two Si atoms [≡Si-O-Si≡]•+CO. For last carbon center we proposed the structure in which CO is attached to oxygen of terminal silanol group forming center B: [≡Si-O]•CO. In zeolites with Si/Al<5.1 as: LTA/13CO or FAU /13CO only centre A is stabilized.

The values of 13C hyperfine splitting for centre A in various zeolites differ from Aiso=25.4 mT to Aiso=27.8 mT. In zeolites with stronger acid sites the higher A(13C) values were observed than in molecular sieves with weaker acid sites. We linked this change to the character of bonding between carbon and lattice oxygen. According to DFT calculations this bonding changes the character from covalent one in zeolites with weak acid sites to ionic in lattices with stronger acid centers. Our results show that the hyperfine splittings of +•13CO EPR doublet might be useful tool for probing the active sites in zeolite catalysts.

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