^{93}Nb NMR CHEMICAL SHIFT SCALE FOR NIOBIA COMPOUNDS

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Introduction

Nb-containing mixed metal oxide catalysts exhibit high activity and selectivity in light alkane conversion. At the present time, however, there is a lack of fundamental structure-activity relationships which could be critical for development of efficient catalysts. Solid state ^{93}Nb NMR spectroscopy is expected to be effective tool for characterization of Nb-containing catalysts since ^{93}Nb (I=9/2) is the one of the most sensitive quadrupolar nuclei (0.482 relative sensitivity to ^{1}H respectively) with sufficiently favorable qudrupole moment (-0.28x10^{-28} m^{2}). The lack ^{93}Nb NMR studies [1, 2] is partly a result of a relatively large value of quadrupolar constant and relatively small value of chemical shielding anisotropy. Here we use ultra high magnetic fields and magic-angle spinning technique to measure chemical shift and quadrupolar tensor parameters for a number of Nb compounds with known structure. According to these data and the previous ^{93}Nb NMR studies, the chemical shift scale for Nb-O compounds is proposed.

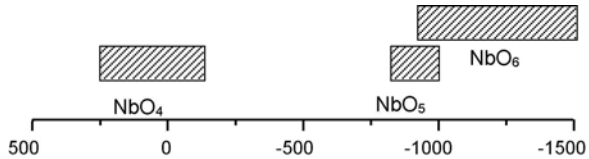
Experimental

^{93}Nb static and MAS spectra at rotation frequencies 20 – 35 kHz were obtained in different 9.4T, 11.75 T, 19.5T and 21.2T magnetic fields. The ^{93}Nb chemical shifts were referenced externally to saturated solution of $NbCl_5$ in acetonitrile. The compounds $LaNbO_4$, $YNbO_4$, Na_5NbO_5, Li_3NbO_4, $BiNbO_4$, $LiNbO_4$, $NaNbO_3$, $KNbO_3$, $AlNbO_4$, $SnNb_2O_4$, $NbVO_5$, VNb_9O_{25}, $LaNb_5O_{14}$, $CaNb_2O_6$, $Ca_2Nb_2O_7$, $Ba_4Ca_2Nb_2O_{11}$, La_3NbO_7, Nb_2O_5, $Te_3Nb_2O_{11}$, $ScNb_2VO_9$ were synthesized according to literatures.

Results and Discussion

The coordination number in Nb-containing compounds varies from 4 to 8. To get Nb NMR chemical shift scale a series of samples with different Nb environment were synthesized: 4 coordinated ($LaNbO_4$, $YNbO_4$), 5 – coordinated (Na_5NbO_5), 6 – coordinated (Li_3NbO_4, $BiNbO_4$, $LiNbO_3$, $NaNbO_3$, $KNbO_3$, $AlNbO_4$, $SnNb_2O_6$, $NbVO_5$, and ones with several types of coordination: La_3NbO_7, $LaNb_5O_{14}$, $LaNbO_4$, VNb_9O_{25}, Nb_2O_5). The structures of these compounds are known from the literature. NMR parameters were determined from 9.4T and 21.2T spectra (static and MAS) using NMR5 program developed by A.Shubin [3]. For 4 - coordinated Nb sites isotropic chemical shift (with the second order corrections) varies from 225 to -150 ppm, Q_c from 29 to 43 MHz, For 5 - coordinated Nb (we have only one compound) δiso = 920 ppm. Q_c ~ 10 MHz, For 6 - coordinated Nb δiso varies from -900 ppm to -1400 ppm and Q_c from 13 to 23 MHz, For compounds with several Nb sites the NMR parameters can be obtained for each site using STMAS method (work under progress). In Fig.1 the Nb chemical shift range is shown for Nb compounds. The literature data for the 6- coordinated Nb sites are in agreement with the scale proposed here.

Fig.1 ^{93}Nb chemical shift range.



Conclusions

^{93}Nb NMR chemical shift scale was proposed for niobia compounds. These results will be the base for further studies of different Nb- containing systems and catalysts.

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