Modulated excitation Raman spectroscopy of V_2O_5-TiO_2 and V_2O_5-WO_3-TiO_2

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Raman spectroscopy is the technique of choice to obtain the structure of atomically and nanodispersed metal oxides of transition elements [1] supported, e.g. on Al_2O_3, SiO_2 and TiO_2 that are active for a number of catalytic industrial processes. Nevertheless, when used under reaction conditions, it becomes difficult to isolate the contribution of that fraction of M=O and M-OH species that are effectively involved in adsorption and reaction from that of the overall phase constituted by the transition metal oxide. We have applied the modulated excitation (ME) approach [2] to increase our sensitivity to such species in the case of typical catalysts used for the selective catalytic reduction of NO_x by NH_3, e.g. V_2O_5-TiO_2 and V_2O_5-WO_3-TiO_2. ME consists in subjecting the sample to repeated pulses, e.g. alternate reducing and oxidizing conditions, while acquiring spectroscopy data with sufficient time resolution. Finally, the spectroscopic data are processed by phase sensitive detection (PSD) to eliminate the contribution of species not responding to the perturbation of the gas phase applied to the sample.

Here, we show that in simple ME experiments where water is repeatedly added to an O_2 feed on V_2O_5-TiO_2 V=O and V-O-V signals are greatly enhanced. These signals represent only a small fraction of the overall time-resolved signals suggesting that only a fraction of the available V is perturbed and can be detected with high sensitivity upon PSD: the fwhm of the V=O signal at 1024 cm^{-1} was of only 14 cm^{-1} after PSD. Additionally, we show by the same approach that NH_3 adsorption can be monitored on V_2O_5-TiO_2 and V_2O_5-WO_3-TiO_2 when pulsing NH_3 in various feeds also by the perturbation of the TiO_2 signal at 700-300 cm^{-1}. This region is otherwise omitted when experiments are performed under steady state conditions because of the strong intensity and the subtle changes. Comparison between V_2O_5-TiO_2 and V_2O_5-WO_3-TiO_2 clearly demonstrated that PSD enables a careful differentiation of the contribution of the responsive V=O (1028 cm^{-1}) and W=O (1012 cm^{-1}) species within the broad signal of unresponsive species.

The sensitivity obtained by the ME approach potentially defines new frontiers for the application of Raman spectroscopy to the characterization of dispersed transition metal oxide catalysts. Moreover, it calls for combination with detailed theoretical simulation in order to understand precisely the origin of signal shifts.

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