

Abstraction of Oxygen from Stable Oxides via a Mechanochemical Route toward Functional Nanocomposites

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Metal oxides with their oxidation number lower than the highest often exhibit attractive functional properties. However, conventional chemical or thermal reduction of the stable oxides is complicated and laborious in many instances. Therefore, we here try to explore non-conventional, simple reduction methods via a solid-state. Unique features of reduction processes of SiO_2 toward suboxides, SiO_x ($1 \leq x < 2$) were found by milling fumed silica nanoparticles with polyolefins (POL), i.e., poly (propene) (PP) or poly (methylene) (PE) and a fluorine-containing POL, poly (1,1-difluoroethylene) (PVDF). We mainly examined the electronic and coordination states of Si by Si2p XPS spectra and ^{29}Si MAS NMR, respectively.

They significantly differ from those experienced a thermal route. Judging from the degree of reduction of SiO_2 from the changes in the coordination of SiO_4 , which parallels the chemical shift of ^{29}Si MAS NMR, the function of POL as a reductant is in the order $\text{PP} \approx \text{PE} > \text{PVDF}$. Since the present solid-state reduction does not involve the unstable gaseous SiO as an intermediate, the products are free from Q^0 state close to that of metallic Si. From these results we conclude that the main mechanism of the present solid-state reduction is the oxygen abstraction from the SiO_4 units by POL, with simultaneous oxidative decomposition of the latter up to the state of carbon. The present process paves a way to controlled introduction of oxygen vacancies to stable metal oxide without passing through a high-temperature process.