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Featured Letter

New insights into oxygen defects, Lewis acidity and catalytic activity of vanadia hybrid nanomaterials

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ABSTRACT

Structural defects in both MCM–41 (Mobil Composition of Matter No. 41) framework and V_2O_5 nanocrystals and surface acid sites of the V_2O_5/MCM–41 hybrid nanomaterials were quantitatively determined. Oxygen defects were found to be related to Lewis acid sites in the materials. In the oxidative desulfurization of a model diesel, dibenzothiophene conversion was almost proportional to the number of Lewis acidity and generally correlated with the oxygen defects concentration in V_2O_5. This work confirmed that increasing surface Lewis acidity and oxygen defect concentration is an effective route to improve the catalytic activity in the oxidation of sulfur compounds.

1. Introduction

There are many structural defects or lattice vacancies in the surface of solid materials [1,2]. From the surface sciences and catalysis points of view, these cationic or anionic defects usually take as active centres for reactants adsorption and surface reactions [3,4]. Investigation on structural vacancies and their correlation with surface reaction activity may provide new insight into the understanding of catalytic properties. Unfortunately, to day, a rather limit number of papers dealing with structural defects and catalytic properties were reported due to the difficulty in the quantitative determination and characterization of such nanocrystalline features [5–8].

It is well known that MCM-41 (Mobil Composition of Matter No. 41) is a mesoporous silicate solid material that consists of a highly ordered arrangement of cylindrical mesopores with a one-dimensional pore system, a sharp pore distribution (2–6 nm), a big surface area (500–1000 m^2/g) and a large pore volume (0.8–1.2 cm^3/g). In this work, we used MCM-41 as catalyst support and vanadia nanoparticles as active phase to synthesize a series of V_2O_5/MCM–41 mesoporous hybrid nanomaterials. Their structural defects in both the support MCM-41 and V_2O_5 were quantitatively determined by Rietveld refinement method and solid state ^{29}Si MAS-NMR spectroscopic technique. For the first time, correlations of structural defects with Lewis acidity and catalytic activity in V_2O_5 dispersed catalysts in the oxidation of dibenzothiophene in a model diesel were investigated.

2. Experimental

MCM-41 support was synthesized according to reference [9]. For preparing V_2O_5/MCM-41 hybrid nanomaterials, a proper amount of ammonium metavanadate (NH_4VO_3 Aldrich 99%) aqueous solution was impregnated on the MCM-41 solid. After evaporating the water, the wet solid was dried at 60 °C for 12 h and then was calcined at 550 °C for 4 h under static air atmosphere. They termed Xwt%V_2O_5/MCM-41 nanocatalysts where X represented weight percentage of V_2O_5.

Surface acidity, morphological features, crystalline structures of catalysts were characterized by *in situ* Fourier-transform infrared (FTIR) spectra of pyridine adsorption method, X-ray diffraction analyses (XRD), solid state ^{29}Si MAS-NMR, and X-ray photoelectronic spectroscopy (XPS). Experimental details were reported in Supplementary Documents. The crystalline structure of V_2O_5 was refined with the Rietveld method using the JAVA based MAUD software [10]. The crystallite size was determined using Scherer equation. The oxygen deficiency in the crystalline structure of V_2O_5 was obtained from the refinements of oxygen occupancy. The theoretical occupational number can be determined by multiplicity of the corresponding atom divided by the total number of the multiplic-

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ity. For refining V_2O_5 structure, the atomic fractional coordinates were reported in Supplementary Documents SD Table 1. After the Rietveld refinement, this number may be changed by fitting the experimental data, the oxygen defects can be calculated by:

$$\%\,\text{Oxygen deficiency} = \frac{OT - OE}{OT} \times 100$$

OT: Theoretical occupational number of oxygen calculated by multiplicity of the corresponding atom divided by the total number of

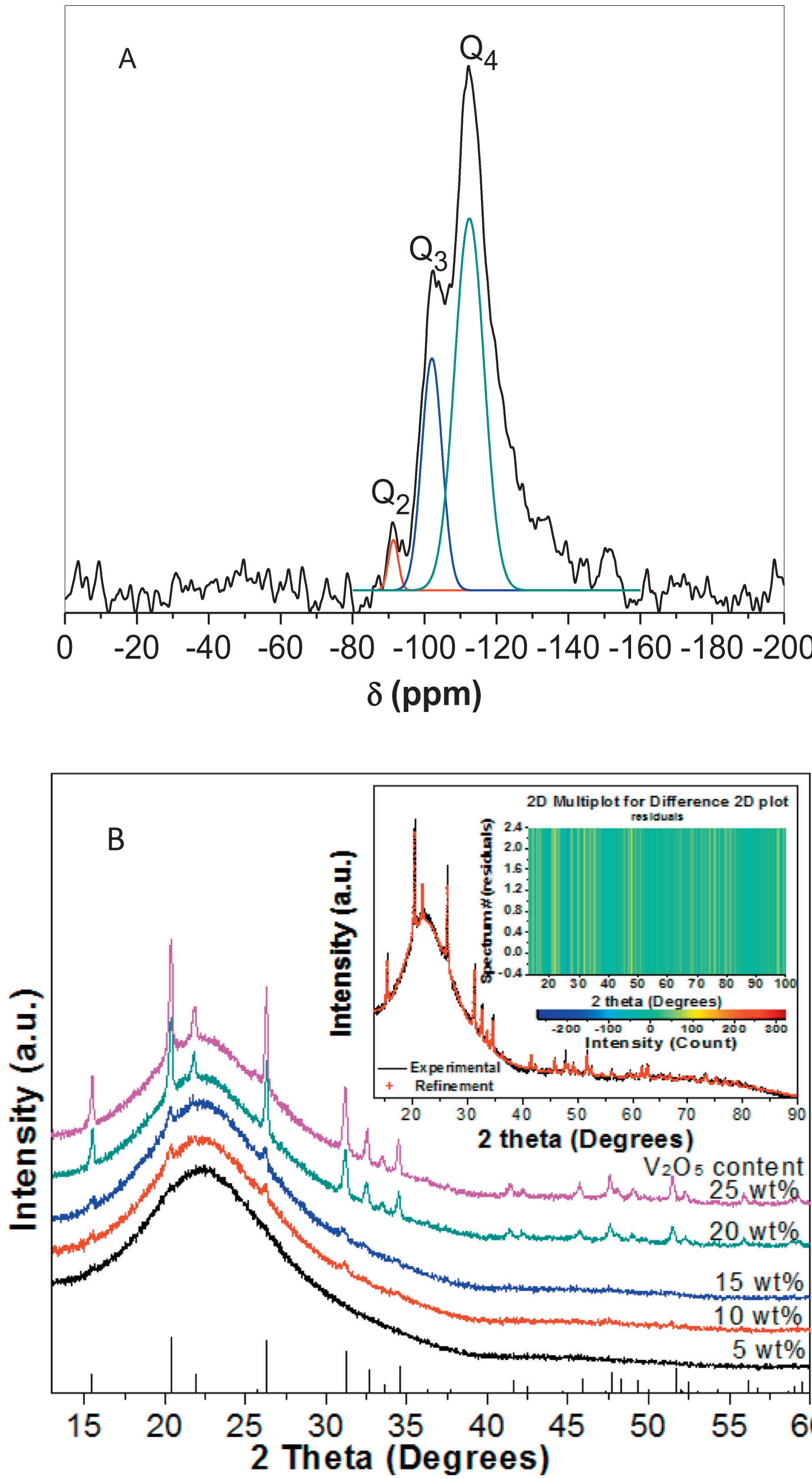

Fig. 1. (A) [31]Si-MAS-NMR spectrum of pure MCM–41 solid; (B) X-ray diffraction patterns of V_2O_5/MCM–41 hybrid nanomaterials and a Rietveld refinement plot of the 25 wt% V_2O_5/MCM-41. The marks in the bottom corresponded to the orthorhombic V_2O_5. The inset 2D plot indicates the difference between the experiment and simulation.