RKCL4654

INFLUENCE OF PREPARATION METHOD ON THE STRUCTURE AND CATALYTIC ACTIVITY OF SUPPORTED SOLID SULFURIC ACID

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Abstract

FT-IR and ^{29}Si-NMR studies suggested the interaction of H_2SO_4 with the SiO_2 support in the material synthesized by the sol-gel method. ^{1}H-NMR results showed that the acid strength of solid sulfuric acid was almost the same as that of liquid sulfuric acid. The catalyst showed higher catalytic activity and stability than that prepared by impregnation method.

Keywords: Supported solid sulfuric acid, sol-gel method, impregnation method

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INTRODUCTION

Sulfuric acid is used in a variety of reactions such as alkylation, esterification and isomerization as a liquid acid. In spite of the high activity, many drawbacks exist in the process of using, such as a large amount of sulfuric acid waste, the difficulty of continuous process and the difficult separation of the catalyst from the products. Those drawbacks induced studies for the solid acid which can substitute for liquid sulfuric acid with the same activity.

Sato reported the synthesis of supported solid sulfuric acid catalyst by impregnation for the vapor phase nitration of benzene [1]. The results demonstrated

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that silica was the most efficient for supported sulfuric acid catalyst and the catalyst showed high activity. However, the catalyst prepared by impregnation method deactivated quickly with the reaction time on-stream. The reason of deactivation was attributed to the leaching of sulfuric acid [2]. Therefore, finding a method that can prevent the leaching of sulfuric acid is certainly a problem.

The synthesis of supported catalysts by sol-gel method has been developed in recent years as an alternative to the traditional methods (impregnation, co-precipitation). The uniqueness of the method is that one starts with the molecular precursor of the supported material and then goes all the way to the final catalyst with greater degree of homogeneity and purity compared with the traditional methods [3, 4].

Hirata reported the synthesis of the supported phosphoric acid catalyst on silica by sol-gel method [5]. Prompted by this paper, here we synthesized the solid sulfuric acid catalyst by sol-gel method. The properties and the structure of the materials were characterized by different methods. The supported solid sulfuric acid catalyst was also prepared with impregnation method for comparison. Aldol condensation of cyclohexanone was performed to study the effect of preparation method on the catalytic performance.

EXPERIMENTAL

Catalyst preparation

28.3 g of tetraethyl silicate, 19.5 g of water and 6 g of HCl (0.04 mol/mL) were thoroughly mixed in a rotavapor to form a sol under stirring. 20 g of H_2SO_4 (V/V=1/1) was slowly added into the sol under stirring to form gel and was maintained for 2 h. The white resulting material was heated at 373 K for 4 h. This material is referred to as H_2SO_4/SiO_2(SG).

28.3 g of tetraethyl silicate, 19.5 g of water and 6 g of HCl (0.04 mol/mL) were introduced in a rotavapor to form sol under stirring. The sol was maintained for 24 h at room temperature to form a gel and then was heated at 373 K for 4 h. This material is referred to as SiO_2-gel.

The sample prepared by impregnation method was described in the paper [1] and the material is termed as H_2SO_4/SiO_2(IM).

Catalysts characterization

X-ray diffraction (XRD) was carried out in a Shimadzu RD-6000 diffractometer operated at 40 kV and 30mA, using Cu Kα radiation ($\lambda = 0.1542$ nm). IR spectra were obtained with a Nicolet Impact 410 spectrophotometer

using KBr pellet technique. High-resolution NMR spectra were collected using a Varian INOVA-500 Spectrometer, operating at the ^{1}H-NMR frequency of 400.1 MHz and at the ^{29}Si-NMR frequency of 79.5 MHz. The acquisition parameters for all spectra were set to 30° flip angle with a recycle delay of 4 s between scans.

Catalytic tests

The reactions were carried out in a fixed bed tubular reactor using 0.5 g catalyst at 453 K. The stream of nitrogen and cyclohexanone was introduced at a constant rate into the upper zone of the reactor, which was packed with SiO_2 pellets maintaining the reaction temperature for preheating and vaporization. The products were analyzed by gas chromatography (Shimadzu GC-14B).

RESULTS AND DISCUSSION

X-ray diffraction

The X-ray diffraction patterns of all the materials are shown in Fig. 1. All XRD patterns show an amorphous phase. The sample obtained by impregnation method shows two diffraction peaks. The first peak may be attributed to the coked
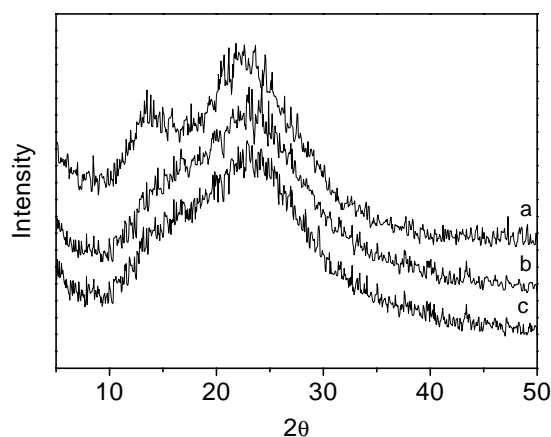
Fig. 1. XRD patterns of the materials
a: H_2SO_4/SiO_2(IM); b: SiO_2-gel; c: H_2SO_4/SiO_2(SG)

coked material synthesized in the drying process, and the second one can be due to amorphous SiO_2. The sample obtained by sol-gel method shows the same diffraction peak as SiO_2-gel, suggesting the uniform distribution of H_2SO_4 into the matrix of SiO_2.
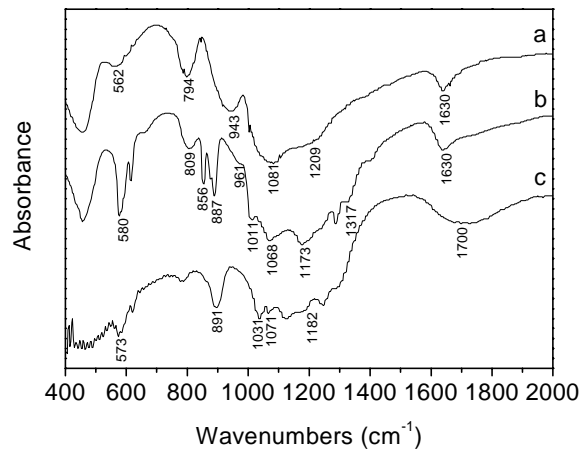
Fig. 2. FT-IR spectra of the samples
a: SiO_2-gel; b: H_2SO_4/SiO_2(SG); c: H_2SO_4/SiO_2(IM)

IR spectroscopy

Figure 2 shows the IR spectra of the samples. Seen from the spectrum of SiO_2-gel (Fig. 2a), the adsorption band at 1081 cm^{-1} is typical of a stretching mode of silica, accompanied by a shoulder at 1209 cm^{-1} [6]. The band at 1630 cm^{-1} corresponds to HOH bending of physically adsorbed water, and the two bands at 943 cm^{-1} and 562 cm^{-1} are due to the Si-OH vibration of the gel surface. For the sample prepared by impregnation method (Fig. 2c), the broad adsorption band at about 1700 cm^{-1} corresponding to bending of molecular water indicates that a large amount of water was absorbed in the sample. In the impregnation process most of H_2SO_4 distributed on the external surface, which resulted in a large amount of water adsorbed on the surface. Meanwhile, the vibration adsorption peak of Si-OH changed markedly. The vibration band at 943 cm^{-1} disappeared, and the band at 562 cm^{-1} shifted to 573 cm^{-1}. This can be attributed to the pulling off of Si-OH band from the surface of SiO_2 by H_2SO_4 during the drying process. The characteristic bands of SO_4^{2-} observed at 1182, 1071, 891 and 573 cm^{-1} are in agreement with the literature [2,7], which indicates that the basic structure of H_2SO_4 did not change after supporting on

SiO_2. In the case of the sample synthesized by sol-gel method (Fig. 2(b)), the characteristic adsorption bands of H_2SO_4 are observed at 1173, 1068, 887 and 580 cm^{-1}. The band at 794 cm^{-1} shifts to 809 cm^{-1}, and new bands appear at 1317, 1011 and 856 cm^{-1}. The results show that the basic structure of H_2SO_4 has changed to some extent. Moreover, the vibration band of Si-OH at 943 cm^{-1} shifts to 961 cm^{-1}, and the intensity decreases markedly. In the sol-gel process, the distribution of H_2SO_4 and the formation of SiO_2 matrix proceed simultaneously, which result in the uniform distribution of H_2SO_4 throughout the matrix of SiO_2. Some Si-OH bands on the surface of silica gel still exist for this reason. On grounds of the above results, we concluded that a new chemical bond was formed by the interaction of H_2SO_4 and SiO_2, which induced the anchoring of H_2SO_4 on the matrix of SiO_2.

^{29}Si MAS NMR results

In order to make clear the structure difference of the samples synthesized by different methods, ^{29}Si-NMR characterization of the samples was carried out. Table 1 showed the chemical shifts of ^{29}Si-NMR of the samples. For SiO_2-gel, the first chemical shift at -101.221 ppm is assigned to silicon atoms bearing one hydroxyl group (Si-O)$_3$*Si*-OH, and the second one at -111.012 ppm is due to silicon atoms without hydroxyl groups *Si*(Si-O)$_4$ [7]. In the case of H_2SO_4/SiO_2(SG), the first peak shifts to -102.833 ppm, and the second one shifts to -111.819 ppm. The results suggest interaction between H_2SO_4 and SiO_2-gel. In the case of H_2SO_4/SiO_2(IM), the two chemical shift peaks all shift to higher degree, but show much lesser extent than that of H_2SO_4/SiO_2(SG).

Table 1

^{29}Si-NMR chemical shifts of the samples

Sample	δ1	δ2
SiO_2-gel	-101.221	-111.012
H_2SO_4/SiO_2(SG)	-102.833	-111.819
H_2SO_4/SiO_2(IM)	-102.102	-110.529

^{1}H MAS NMR results

To characterize the molecular interaction between H_2SO_4 and SiO_2, the ^{1}H-NMR spectra of the samples have been recorded. The chemical shift is one of the main spectral parameters. For ^{1}H-NMR spectra, the chemical shifts depend

on the electronic depletion of the acid hydrogen nucleus, consequently the value of chemical shift may be considered as a measure of acid strength [2].
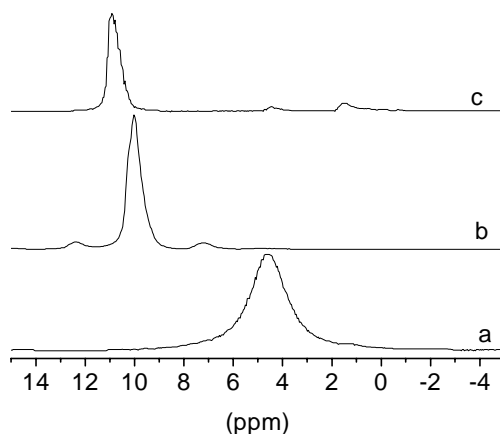
Fig. 3. ^{1}H-NMR spectra of the samples
a: SiO_2-gel; b: H_2SO_4/SiO_2(IM); c: H_2SO_4/SiO_2(SG)

The ^{1}H-NMR spectra of the SiO_2-gel, H_2SO_4/SiO_2(SG) and H_2SO_4/SiO_2(IM) are shown in Fig. 3. As seen in Fig. 3(a), two peaks of chemical shifts are observed, suggesting the presence of two kinds of H-bond on the surface of SiO_2-gel. The chemical shift peak at 4.271 ppm is attributed to the absorbed water molecule, and the chemical shift at 1.016 ppm is related to Si-OH. Three bands are observed in the spectrum of H_2SO_4/SiO_2(SG) (Fig. 3(c)). The peak at 4.271 ppm decreases markedly, suggesting only a little water on the surface. The peak at 1.016 ppm disappeared, and a new peak at 1.344 ppm appears. The peak at 10.791 ppm corresponds to the H adsorption of H_2SO_4. It is known that the chemical shift peak of liquid H_2SO_4 (95%) is at 10.85 ppm. The results suggest that the acid strength of H_2SO_4 is maintained after deposition on SiO_2. In the spectrum of H_2SO_4/SiO_2(IM) (Fig. 3b), the chemical shift peak of Si-OH disappeared, suggesting that the Si-OH was pulled off from the surface of silica by H_2SO_4 in the drying process. The result is in agreement with the IR results. The chemical shift at 9.737 ppm is attributed to the H adsorption of H_2SO_4. In the impregnation process, most of H_2SO_4 on the surface of silica absorbed a large amount of water, which result in great decrease of acid strength. It is concluded from above results that the acid strength of the sample prepared by sol-gel method is much larger than that prepared by impregnation method. Because most H_2SO_4 entered the matrix of silica, instead of only absorbed on the surface of silica for the sample prepared by sol-gel method. The results are consistent with the literature [8].

Reaction study

Table 2 lists the catalytic results of cyclohexanone condensation over the two supported sulfuric acid catalysts. It can be seen that H_2SO_4/SiO_2(SG) shows higher cyclohexanone conversion and selectivity to 2-(1-cyclohexenyl) cyclohexanone than that of H_2SO_4/SiO_2(IM) at 2 h-on-stream. Moreover, the H_2SO_4/SiO_2(IM) catalyst deactivated rapidly with running time, which can be attributed to the leaching of sulfuric acid absorbed on the external surface [2]. While the cyclohexanone conversion on H_2SO_4/SiO_2(SG) just decreased slightly and the selectivity to 2-(1-cyclohexenyl) cyclohexanone kept steady at around 92% for 70 h of time on stream. The higher stability may be due to the presence of the relatively strong interaction between H_2SO_4 and the matrix of SiO_2 in the catalyst synthesized by sol-gel method.

Table 2

The catalytic activity and stability results of cyclohexanone condensation on H_2SO_4/SiO_2(SG) and H_2SO_4/SiO_2(IM) catalysts [a]

Time (h)	H_2SO_4/SiO_2(SG)		H_2SO_4/SiO_2(IM)	
	Conv. (%)	Sel. (%)[b]	Conv. (%)	Sel. (%)[b]
2	46.4	92.1	38.9	73.5
5	46.1	92.2	29.5	73.4
10	45.5	92.0	10.1	73.5
20	45.2	91.9	0.8	73.2
30	44.6	92.1		
50	43.8	92.3		
70	42.5	92.0		

[a] Reaction conditions: T = 453 K, P = 1 atm and LHSV = 1.0 h^{-1}
[b] Selectivity to 2-(1-cyclohexenyl) cyclohexanone

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