Preparation of SO_4^{2}-/ Fe_2O_3-TiO_2-Nd_2O_3 Solid Acid and its Activity for the Synthesis of Menthyl Acetate

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(Received on 25th November 2010, accepted in revised form 6th September 2011)

Summary: This paper reports the preparation of SO_4^{2-}/ Fe_2O_3-TiO_2-Nd_2O_3 (designated as SFTN) by combustion method, which were characterized by FT-IR and NH_3-TPD techniques respectively. The results showed that SFTN kept the typical covalence S=O bond structure of SO_4^{2-}/M_xO_y(SM) solid acids, and both Lewis and Brønsted acid sites existed; SFTN exhibited higher activity for the esterification of acetic acid and menthol, with 98.30% yield of menthyl acetate. The higher activity was attribute to the enhancement of acidic properties of the catalyst by the addition of Nd_2O_3 to SO_4^{2-}/ Fe_2O_3-TiO_2 (SFT).

Introduction

Menthyl acetate is a monoterpene with the smell and flavor of peppermint. It is often used as a tobacco flavor, as it possesses long-lasting flavor. In the conventional approach for Menthyl acetate production , sulfuric acid [1] is always used as catalyst, resulting in serious environment pollution and equipment corrosion problems, and the flavor and color of the menthyl acetate product is not satisfactory, it is necessary to develop new and environmentlly benign catalysts for the production of menthyl acetate.

SO_4^{2-}/M_xO_y solid super acid catalysts show high activity and selectivity in many acid catalytic reactions, including acetalation [2], light alkanes isomerization [3], acylation [4] and esterification [5]. In addition, as a solid super acid, SM may alleviate corrosion of apparatus and thus avoid environmental pollution. Therefore, it has been used as a new catalyst in a variety of acid catalytic reactions [6-8].

Although more attention has been paid to the promotion effects of different lanthanide oxides on SM in the esterification, the Nd-promoted SM used as catalyst in the esterification of acetic acid and menthol has not been reported. This paper is to report a new solid super acid catalyst prepared by doping SFT with Nd, and the catalytic activity for the preparation of menthol acetate was tested.

Results and Discussion

The effect of the Nd_2O_3 content of SFT on the catalytic activity was shown in Fig. 1. The results showed that when the Nd_2O_3 was 2 wt %, the catalytic activity of SFTN was the highest with the yield of menthyl acetate being 98.30%.

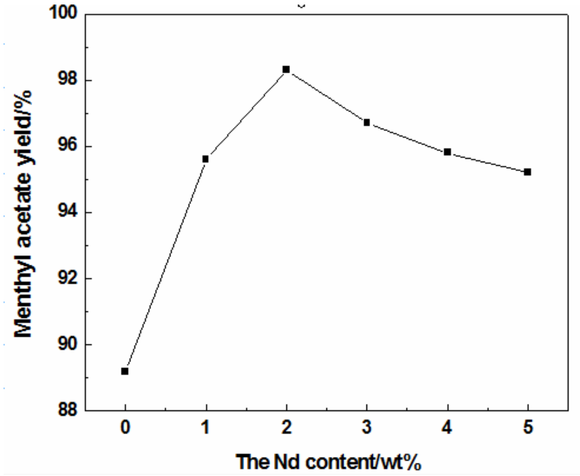

Fig. 1: Menthyl acetate yield as a function of the Nd content of SFT.

FT-IR of Samples

It was reported that when the sample was heated at higher temperature, the sulfate species structure on the surface of the catalyst would be changed in the process of dehydration, namely, forming strong Lewis acid sites (Scheme 1) [2]. It is essential that the sulfate species must contain strong covalence S=O bond that has a strong ability of inducing electron for the formation of solid super acid, which will enhance Lewis acidity of metal center ion.

From Fig. 2, it was shown that there were two characteristic bands between 800 and 1450 cm^{-1}

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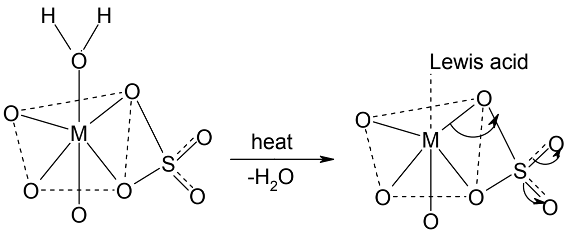
in SFTN and SFT spectrum respectively, that was 1122 and 1386 cm^{-1}, which indicated that there were sulfate species in both samples [9]. The band at 1122 and 1386 cm^{-1} could be attributable to the asymmetry stretch and shrink vibration of S=O bond, and these S=O bonds had the similar character with the covalence bond. Therefore, the strong acidic center was formed on the surface of catalyst.



Scheme 1: The forming process of the catalysts

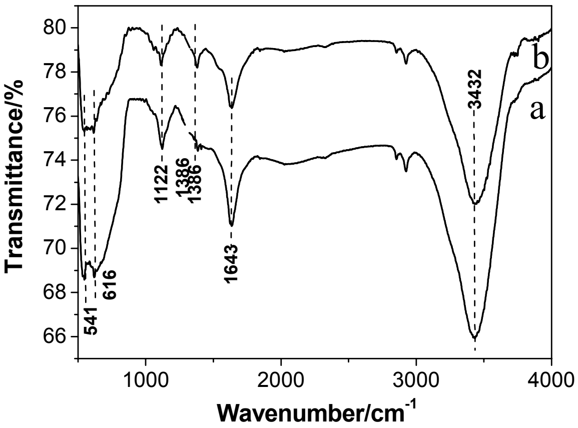


Fig. 2: The FT-IR spectrum of the samples (a SFT; b SFTN)

According to the literature [10], before TiO_2 was impregnated with SO_4^{2-} , the vibration peak of Ti-O was at 650 cm^{-1}, but after impregnating with SO_4^{2-}, this peak shifted to a lower frequency, 616 cm^{-1} as illustrated in SFT spectrum of Fig. 2. The band at 541 cm^{-1} in SFT spectrum was the stretching vibration of Fe-O bond [11]. However, it has been seen small peaks in the region of 541~616 cm^{-1} in SFTN shown in the spectrum of Fig. 2, instead of peaks both 541 and 616 cm^{-1}, from which it could deduce that those small peaks were attribute to the introduction of Nd_2O_3 into the SFT.

The strong absorption peak at 3432 cm^{-1} and peak at 1643 cm^{-1} might be assigned to the dissociative hydroxyl of H_2O absorbed on the solid super acid (shown in Fig. 2), indicating that the prepared solid super acid catalysts could both act as Bronsted acid and Lewis acid in the catalytic reaction [12].

NH_3-TPD of Samples

The NH_3-TPD technique is used to compare the acidic characteristics of the SFT and SFTN catalysts. In Fig. 3, two desorption peaks can be observed in the samples: the first broad low-temperature (LT) desorption peak at 200-300□, which is attributed to NH_3 adsorbed on weak Lewis acid sites [11]; and there is a distinct high-temperature (HT) peak(at the range of 700-1200□), which is attributed to the presence of Brønsted acid sites [11, 13]. T. Riemer. *et. al.* [14] have studied that the 'very strong' acid sites found in solid acid are mostly due to the presence of Brønsted acid sites. Moreover, there is an obvious difference in the strength of the acid sites between both samples. The peaks at both LT and HT for SFTN are higher than that for SFT, and the peak areas in the TPD profiles of SFTN are larger than that of SFT, which suggested that the strength of acid sites of SFTN was stronger than that of SFT, indicating that the addition of Nd_2O_3 to SFT resulted in an increase of the acidity of the catalyst, being responsible for the better esterifiation reaction activity.

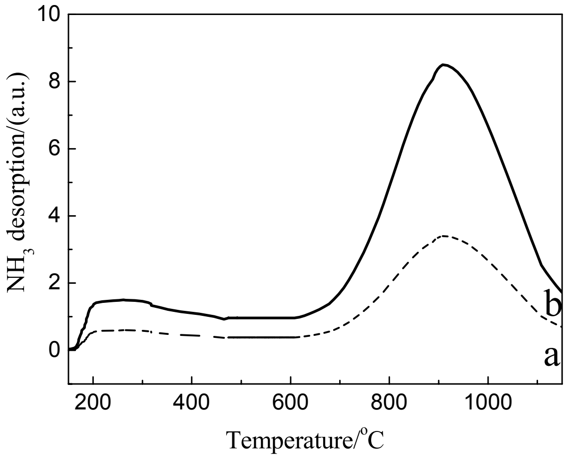


Fig. 3: The NH_3-TPD of the samples(a SFT; b SFTN).

Reuse of the Catalysts

It can be seen from Fig. 4 that the yield of methyl acetate over SFT catalyst quickly decreased with the increasing of the catalyst reuse times. After the fifth time for the catalyst reuse cycle, the menthyl acetate yield reduced to 49.50%, which was approximately half of the yield (89.20%) achieved on the fresh catalyst.

As for SFTN, the menthyl acetate yield

showed only a mild change after five times reuse cycle, it decreased only from 98.30% to 96.80% after the sixth of the catalyst reuse, the menthyl acetate yield was rapidly decreased and it reached 49.90% at the tenth of reuse. These results indicated that the catalytic activity got decayed after several times of catalysts reuse. However, the SFTN catalyst shows more stable activity than SFT catalyst does□and it can be reused 5 times effectively.

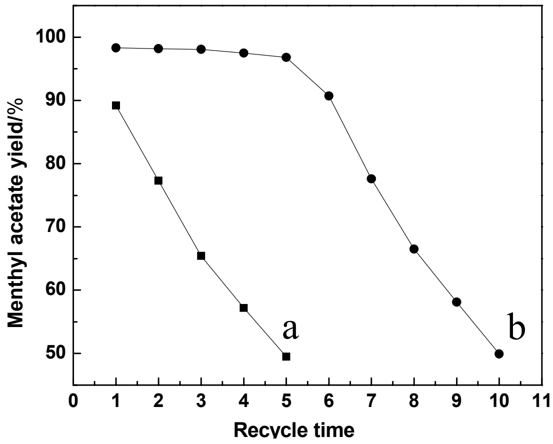


Fig. 4: Menthyl acetate yield as a function of time of the catalyst reuse cycle (a SFT; b SFTN).

Experimental

Preparation of SFT and SFTN

SFTN was obtained by heating the homogeneous solution of $Nd(NO_3)_3{\cdot}6H_2O$, $[CH_3(CH_2)_2O]_4Ti$, $Fe(NO_3)_3{\cdot}9H_2O$, $C_6H_8O_7{\cdot}H_2O$ and C_2H_5OH to combustion on the electric stove, collecting the ash followed by impregnating in 1.5mol/L $(NH_4)_2SO_4$ solution for 18 h and calcining at 600□ temperature for 3 h. The Nd loading was changed by changing the amount of $Nd(NO_3)_3{\cdot}6H_2O$ added. SFT was prepared according to the above-mentioned method.

Synthesis of Methyl Acetate

The esterification of acetic acid and menthol in a molar ratio of 3:1 was performed in a three-necked flask with a thermometer reflux condenser and magnetic stirrer at 405 K for 6 h .The liquid product was obtained by separating the catalyst from the reaction mixture. The catalyst could be reused. The liquid product was analyzed by using a gas chromatograph with a flame ionization detector (GC-FID, Simadzu 8A) and a Porapak QS column.

FT-IR spectra of the samples in KBr disk were obtained in the range 4000-400cm^{-1}. NH_3-TPD profiles were carried out by ramping the temperature from 393 to 873K at a rate of 10K/min.

Conclusion

A SFTN solid super acid catalysts were prepared by combustion method. Effect of Nd_2O_3 content on the catalytic activity was investigated. The results indicated that the introduction of Nd_2O_3 improved the acidic properties of the catalysts. When the Nd_2O_3 content was 2wt%, the catalytic activity of sample was highest, with the yield of menthyl acetate being 98.3%. The introduction of Nd_2O_3 to SFT made the acid strength of catalyst be stronger, which increases its catalytic activity. Moreover, SFTN can be easily separated from reaction mixture and reused, it will be a desirable catalyst for the green synthesis of menthyl acetate [15-17].

Acknowledgments

The author (C.Y.) acknowledges financial support from Department of Education of Jilin Province for the "the Eleventh Five" Scientific and Technological Research Projects (2007-444).

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