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Effect of additives doping on catalytic properties of $Mg_3(VO_4)_2$ catalysts in oxidative dehydrogenation of cyclohexane

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ABSTRACT

Effects of additives comprising alkali and alkaline earth metals (Li, Na, K and Ca) introduced to $Mg_3(VO_4)_2$ on their structures, physicochemical properties and the catalytic behaviors in the oxidative dehydrogenation of cyclohexane were investigated. The characterization and the experimental results showed that the additive does not affect markedly the structure of the catalyst, but blocks the active sites and hinders the reducibility of the active species thus decreasing the catalytic activity. Moreover, the additive could enhance the selectivity to cyclohexene by enhancing the nucleophilicity, the redox property as well as the type and number of the oxygen species on the catalyst surface. The doped catalysts could give the catalytic activity and selectivity to cyclohexene in the orders of K- < Na- ≈ Ca- < Li- < non-doped and non-doped < Li- < Na- < K- < Ca-, respectively. Among the doped catalysts, Ca–$Mg_3(VO_4)_2$ catalyst demonstrated a yield of cyclohexene of 8.2%, which was a promotion compared with 6.4% of $Mg_3(VO_4)_2$.

1. Introduction

The oxidative dehydrogenation (ODH) of cyclohexane to cyclohexene is a challenging pursuit in both economic and scientific terms. Previous investigations of the catalysts used in the ODH reaction of cyclohexane demonstrated $Mg_3(VO_4)_2$ has been considered as a favorite catalyst for producing a promising yield of cyclohexene [1–3]. However, a major challenge in the commercial development of cyclohexane ODH is further improvement in cyclohexene yield since the main cause of the selectivity limitation arises from the conversion–selectivity relationship [4,5].

One of the solutions for the catalyst is to ensure easy desorption of intermediate product cyclohexene from the catalyst surface. While, the difficulty or the ease of cyclohexene desorption depends on the properties of the catalyst surface. Therefore, an effective way for improving the selectivity is to modify the catalyst surface by the introduction of additive, especially the alkali/alkaline earth metal [6–11]. The introduction of alkali/alkaline earth metal to V_2O_5/Al_2O_3 [6,7], V_2O_5/TiO_2 [8,9], V_2O_5/SiO_2, V_2O_5/MgO [10,11] and V—Mg—O catalysts [12] has been carried out in the ODH of lower alkanes to produce the corresponding alkenes. Most of the additives, such as Ca, Li, Na and Cs, played a promoting effect on the selectivity to the objective alkene which could be explained by modification of acid–base properties and the reducibility of the active phases by alkalis. While the other additive, such as K, was found to decrease the selectivity to the objective product since K was found to inhibit the formation of $Mg_3(VO_4)_2$ from a mixture of MgO and NH_4VO_3 and/or trace K was segregated onto the surface of magnesium vanadates [13–16]. Compared with the ODH of lower alkanes, Patcas et al. [17,18] only investigated the effect of alkali metal addition on the catalytic activity in the ODH of cyclohexane. They first modified NiO/Al_2O_3 catalyst by alkali (Na, K and Cs) and found no promotion effect owing to a lower active species content and a larger amount of bulk nickel aluminate leaded by the modification. Then they modified the egg-shell NiO/Al_2O_3 catalyst by Li and proposed Li could enhance the catalytic activity and the selectivity to cyclohexene by decreasing the formation of bulk nickel aluminates. Besides, it is a pity that few or no studies have been reported on the influence of alkali/alkaline earth metal doping on catalytic property of $Mg_3(VO_4)_2$ in the ODH of cyclohexane.

In this work, the catalytic performance of the alkali/alkaline metal (Li, Na, K and Ca) doping on $Mg_3(VO_4)_2$ was studied in the ODH of cyclohexane. N_2-adsorption, XRD, H_2-TPR and XPS techniques were applied to give further information on the structural, the reducibility of active species as well as the type and distribution of the surface oxygen species of the catalyst. Furthermore, the relationship among the reducibility of the active species, the type and

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distribution of the surface oxygen species and the catalytic behavior of the catalysts were investigated in detail.

2. Experimental

2.1. Catalyst preparation

$Mg_3(VO_4)_2$ was synthesized via the citrate complexation method, which has been described in detail in the literature [2,3]. First, a transparent solution of $Mg(NO_3)_2{\cdot}6H_2O$ and NH_4VO_3 with Mg/V atomic ratio of 3/2 was prepared. Then citric acid was added in the mixing solution with a 20% excess over the number of ionic equivalents of cations. Subsequently, ammonia was added to adjust the pH value of 4.8. The solution obtained was evaporated at 343 K to form a gel, and the gel was dried subsequently in a vacuum oven overnight at 343 K. Finally, the resulting solid was ground and heated up to 673 K for 18 h at a constant rising rate of 1 K/min to decompose the gel precursor, then calcined in the air at 823 K for 6 h. The final sample was crushed and sieved to obtain a particle size of 20–40 mesh.

The doped samples were denoted as A-, where A were Li, Na, K and Ca, respectively. In this work, the atomic ratio A/V of 0.1 was adopted, which was based on the following aspects [19]: (1) the K/V ratio of 0.1 was shown in previous studies as optimal for V-based catalysts; (2) the A/V ratio of 0.1 can avoid formation of mixed A—V—O bulk compounds and/or trace A onto the catalyst surface; (3) the evident modification of the catalytic properties can be observed at the A/V ratio of 0.1. The doped samples were prepared by incipient impregnation. The additive was introduced by adding the appropriate amount of the corresponding nitrate solution onto $Mg_3(VO_4)_2$ particles. After impregnation, the obtaining sample was dried at 393 K overnight and calcined in the air at 823 K for 6 h.

2.2. Catalyst characterization

BET surface area of the as-prepared sample was measured by N_2 physisorption at 77.3 K (ASAP 2010, Micromeritics). The XRD pattern was measured using Cu Kα radiation (D/MAX 2550 X-ray diffractometer) at 40 kV and 40 mA. Actual composition of the sample was determined on an ICP-AES equipment (Varian 710 ES). XPS measurements were carried out on a PHI 5300/ESCA system with Al Kα as a radiation source (Perkin-Elmer), the correction of the surface charge electricity effect was using C_{1s} (284.60 eV) and the range of the spectrum of scanning energy was from 0 to 1200 eV. XPSPEAK software was used for the deconvolution and analysis the XPS characterization results.

The temperature-programmed reduction (H_2-TPR) was measured on a Micromeritics AutoChem II 2920 apparatus. Before reduction, about 0.20 g sample was pre-treated in air at 423 K for 40 min to remove the adsorbed water, followed by cooling to 313 K under Ar flow (30 ml/min). Subsequently, the sample was reduced with a 10 vol.% H_2/Ar mixture (30 ml/min) by temperature programming from 313 to 1273 K at a rate of 10 K/min.

2.3. Catalytic test

The catalyst activity test was carried out isothermally at atmospheric pressure in a fixed-bed microreactor made of stainless steel with an inner diameter of 9 mm. About 0.5 g of as-prepared catalyst diluted with inert quartz sands at a mass ratio of 1:4 was loaded into the reactor so as to ensure a uniform catalyst distribution. In each run, the catalyst was first pretreated in an air stream of 50 ml/min at 773 K for 1 h, and then adjusted to the reaction conditions. The system was allowed to stabilize for 1.5 h before the first product sample was taken for analysis. The liquid products were analyzed by a HP 6890 gas chromatography equipped with a PEG 20,000 column.

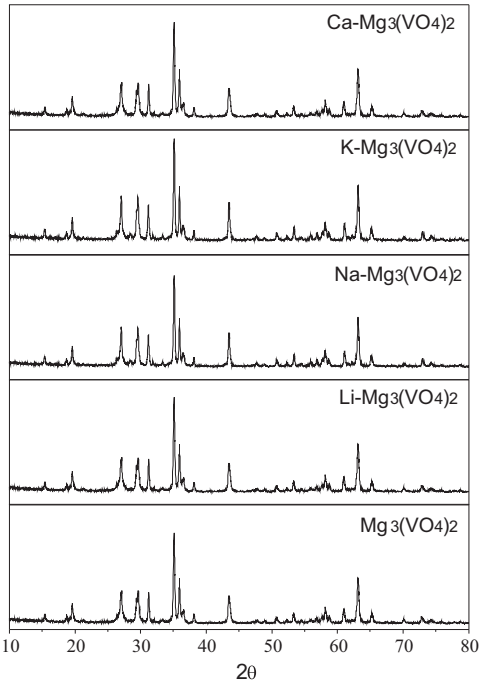

Fig. 1. XRD patterns of the catalysts.

3. Results and discussion

3.1. Textural and structural properties

Examination of the surface areas of the samples reveals that the doping treatment produces a modification during the preparation procedure. The doped catalysts show a lower BET surface area with respect to the non-doped one (Table 1); meanwhile, the results show that the surface area decreases along with the ion size increasing, which could be explained by the formation of $-O^-A^+$ on the catalyst surface [20,21].

As shown in Fig. 1, no features of crystalline additive vanadates or additive metal involving material can be observed in the doped catalysts, which is different from the research of Kung and Kung [13,14]. The XRD characterization result suggests that the additive coordinates with the surface active species in modifying its structure instead of forming bulk compounds.

3.2. Characterization results of TPR

As shown in Fig. 2, the temperature of maximum hydrogen consumption (T_{max}) is 970 K for $Mg_3(VO_4)_2$, while it shifts to 979 (Li-), 1002 (Na-), 1054 (K-), and 1023 K (Ca-) for the doped catalysts, respectively. The shift to higher temperature could be due to the stronger interaction between the active species and the additive, which is in agreement with the views of Valenzuela et al. [12], and Balderas-Tapia et al. [22]. It is obviously that the reducibility of the active species decreases in the order of $Mg_3(VO_4)_2$ > Li- > Na- > Ca- > K-. In addition, based on the previous researches [24,25], T_{max} ranged from 873 to 973 K is responsible for the adsorption of the incompletion reduction oxygen $O^{\delta-}$ ($0 < \delta < 2$), and the value ranged from 973 to 1173 K is involved in the adsorption of lattice oxygen. Therefore, the oxygen species on the doped-catalysts surface are the mixture of the lattice oxygen and $O^{\delta-}$ ($0 < \delta < 2$) species.