

硅烷化 TS-1 对环己烷均相氧化反应的促进作用

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摘要: 考察了钛硅分子筛 (TS-1) 以及硅烷化钛硅分子筛 (TS-1-S) 上环烷酸钴 (Co-nap) 催化环己烷氧化反应性能。结果表明, TS-1 和 TS-1-S 对该反应均具有显著的促进作用, 环己烷转化率由无 TS-1 时的 3.6% 分别提高至 6.4% 和 7.9%, 产物选择性保持在 80% 左右, 反应时间由 300 min 可缩短为 130 min。进一步的研究表明, 随着 TS-1 的加入, Co-nap 在其表面发生了吸附, 使得均相反应变成了“类多相催化反应”, 这是反应性能显著提高的主要原因。

关键词: 钛硅分子筛; 环己烷; 均相氧化; 吸附; 硅烷化

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Silanized Titanium Silicate (TS-1) Molecular Sieve for Promoting the Homogeneously Catalyzed Oxidation of Cyclohexane

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Abstract: The promoting effect of titanium silicate (TS-1) molecular sieve and silanized TS-1 (TS-1-S) on the homogeneous liquid oxidation of cyclohexane catalyzed by cobalt naphthenate (Co-nap) with oxygen as oxidant was investigated. Both TS-1 zeolites were efficient promoters. The conversion of cyclohexane was 7.9% with a selectivity of 83.7% when it was catalyzed by Co-nap/TS-1-S, and the reaction time was reduced to 130 min as compared to 300 min with Co-nap as the catalyst. The adsorption of Co-nap on TS-1-S, which transformed a homogeneous reaction into a “quasi-heterogeneous” reaction, was the reason for the better catalytic performance.

Key words: titanium silicate sieve; cyclohexane; homogeneous oxidation; adsorption; silylation

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烃的液相选择氧化在石油化工和精细化工领域占据非常重要的地位, 其中环己烷催化氧化是一个有代表性的反应, 其氧化产物环己醇和环己酮 (俗称 KA 油) 是生产己二酸和己内酰胺的重要原料^[1]。早期工业生产采用以羧酸钴为催化剂的均相工艺^[2],

目前工艺以非催化氧化过程为主, 相比而言, 它存在着操作温度和压力都偏高等缺点。近几十年来, 由于环境问题日益突出, 固体催化剂因分离简便而广泛用于环己烷氧化的研究中, 其中包括金属氧化物^[3]、含过渡金属或贵金属/分子筛^[4~8], 但反应活性

还不够高、活性组分易流失等,限制了它们的工业化应用,仍停留在实验室阶段.

Taramasso 等^[9]发现,在较温和的反应条件下,以 H_2O_2 或有机过氧化物为氧化剂时,钛硅分子筛 (TS-1) 可催化多种有机底物. Schuchardt 等^[10,11]详细地研究了以 H_2O_2 为氧化剂,TS-1 为催化剂的环己烷氧化过程,认为 TS-1 中存在两种活性中心:一种是非选择性的,位于分子筛的外表面;另一种具有选择性,位于分子筛的孔道中.因此,本文以环烷酸钴为主催化剂、TS-1 为助催化剂进行环己烷氧化反应.为了增加 TS-1 的疏水性,将其置于含 0.5% 六甲基二硅胺烷的甲苯溶液中回流 2 h,得到硅烷化 TS-1 (TS-1-S).作为对照,同法硅烷化处理 H- β 样品,记作 H- β -S.

图 1 为 TS-1 和 TS-1-S 以及从反应溶液中分离出的 Co-nap/TS-1 和 Co-nap/TS-1-S 的红外光谱 (FT-IR).可以看出,TS-1 除出现其自身特征峰外,还有明显的吸附水特征峰 (~ 3500 和 $\sim 1700\text{ cm}^{-1}$),这说明 TS-1 表面具亲水性.硅烷化后 TS-1-S 样品上水的特征峰明显减弱,同时在 2975 cm^{-1} 处出现一个弱的 $-\text{CH}_3$ 特征伸缩振动峰,说明 TS-1 已被硅烷化,其水接触角为 127° ,进一步证实了这一点 (TS-1 的水接触角为 0°),也表明经硅烷化后,TS-1 表面疏水性显著增加.当吸附 Co-nap 后,Co-nap/TS-1 和 Co-nap/TS-1-S 均出现了羰基 (1713 cm^{-1}) 的特征吸收峰和亚甲基 (2854 和 2928 cm^{-1}) 的特征吸收峰,说明环烷酸钴吸附在 TS-1 和 TS-1-S 上.另外,吸附水的特征峰进一步减弱,表明 Co-nap 的吸附使得

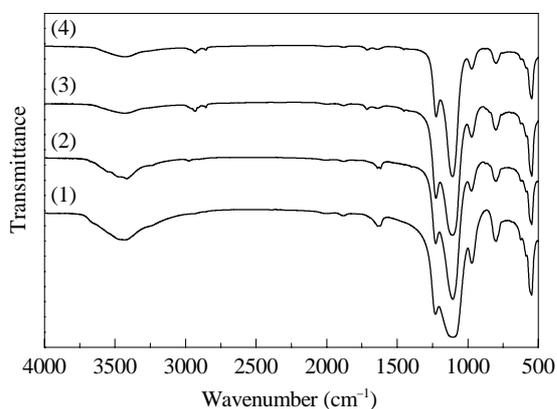


图 1 TS-1 吸附环烷酸钴前后的 FT-IR 谱

Fig. 1. FT-IR spectra of the TS-1 samples. (1) TS-1; (2) TS-1-S; (3) Co-nap/TS-1; (4) Co-nap/TS-1-S.

TS-1 和 TS-1-S 表面疏水性增加.

表 1 为不同样品上环己烷氧化反应结果.可以看出,TS-1 或 TS-1-S 本身并无催化活性,但将它们加到 Co-nap 中,环己烷转化率从 3.6% 分别增加到 6.4% 和 7.9%,KA 油的选择性变化不大,可以保持在 80% 左右.可见 TS-1-S 的促进效应更为显著,特别是反应时间从 300 min 缩短到 130 min.另外,碳纳米管 (CNTs) 加入 Co-nap 后,除 KA 油比例稍有变化外,其活性和选择性变化不明显,而 H- β 的加入则抑制了反应的进行.

表 1 不同催化剂对环己烷氧化反应的催化性能

Table 1 Catalytic performance of the different catalysts for oxidation of cyclohexane

Catalyst	Reaction time (min)	Conversion (%)	Selectivity (%)	
			Cyclohexanol	Cyclohexanone
TS-1	300	—	—	—
TS-1-S	300	—	—	—
Co-nap	300	3.6	46.6	35.5
Co-nap ^a	300	—	—	—
Co-nap ^b	300	—	—	—
Co-nap/TS-1	270	6.4	42.7	44.2
Co-nap/TS-1-S	130	7.9	42.1	41.6
Co-nap/CNTs	300	3.3	57.6	21.9
Co-nap/H- β	300	1.1	53.7	32.0
Co-nap/H- β -S	300	1.0	53.5	33.0

Reaction conditions: cyclohexane 5 g, Co-nap 0.001%, TS-1 50 mg, temperature 130°C , $p(\text{O}_2) = 1.0\text{ MPa}$.

^aSolution after filtering off TS-1. ^bSolution after filtering off TS-1-S.

采用 ICP-AES 测定了加入 TS-1 或 TS-1-S 前后环己烷溶液中 Co-nap 的浓度,发现其浓度从 $7.7\text{ }\mu\text{g/g}$ 分别下降至 $0.036\text{ }\mu\text{g/g}$ 和 $0.035\text{ }\mu\text{g/g}$,表明溶液中 Co-nap 基本上吸附在 TS-1 或 TS-1-S 上.分离 TS-1 后环己烷溶液不能发生氧化反应,也证实了这一点. Co-nap 吸附于 TS-1 后,活性中心则从液相转移到 TS-1 的表面,反应也从均相变成多相.为了区别固体催化剂的多相催化反应,我们将这种活性组分吸附在载体 (助剂) 上而进行的称为“类多相催化反应”.

活性中心周围微环境的改变可能是反应性能提高的主要原因.在均相反应中,由于反应产物 KA 油具有一定的极性,从活性中心区域扩散至溶液中的速度比较慢,容易发生过氧化,从而导致反应选择性下降.对于多相反应,产物的扩散与催化剂表面疏水性密切相关:疏水性越强,极性产物越易离开,

这已被我们前期工作所证实^[12]. TS-1 硅烷化及其吸附 Co-nap 后, 催化剂表面疏水性增强, 因此环己烷反应活性和选择性增加, 可见载体的疏水性对环己烷氧化反应的影响至关重要.

Drago 等^[13]的研究认为, TS-1 在环氧化反应中的优异性能缘于其表面存在弱酸性中心. Sun 等^[14]认为, H- β 的中等强度的 B 酸中心是环己基过氧化氢分解的主要活性中心. Co-nap 催化的环己烷氧化是一个自由基反应^[15], 包含链引发、链增长、链终止等过程, 而 H- β 高效分解环己基过氧化氢使其浓度大幅降低, 从而抑制了链增长. 由表 1 还可以看出, 尽管硅烷化可增加 H- β 的疏水性, 但是仍抑制了反应的进行, 说明硅烷化处理对 H- β 分子筛酸性中心影响不大, 不能降低其分解环己基过氧化氢的活性.

综上所述, 将 TS-1 尤其是 TS-1-S 加入到 Co-nap 催化环己烷氧化的均相体系中, 能够显著提高反应性能. 这可归因于 Co-nap 在 TS-1 表面的吸附、催化剂表面的强疏水性以及其强酸性中心的缺失. 这种“类多相催化反应”具有较高的反应速率和选择性, 因而有可能应用于环己烷氧化反应中, 也可作为其它类似反应的研究提供借鉴.

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英 译 文

English Text

Liquid phase selective oxidation of hydrocarbon is important in petrochemical and fine chemical production. The oxidation of cyclohexane is especially important due to the wide application of its products, cyclohexanone and cyclohexanol (the so-called KA-oil), which are key intermediates for adipic acid and caprolactam in the manufacture of nylon-66 and nylon-6 polymers [1]. Industrially, the production of KA-oil from the oxidation of cyclohexane was first carried out by homogeneous catalytic liquid phase oxidation using a salt of carboxylic acid as catalyst. Subsequently, a non-catalytic oxidation process became the dominant process because a higher temperature and pressure could be used compared to the homogeneous catalytic process [2]. In view of the convenient separation and recyclability of heterogeneous catalysts and increasing environmental concerns over the homogeneous process, extensive studies have focused on heterogeneous catalytic liquid phase oxidation of cyclohexane, and catalysts based on metal oxides [3], redox molecular sieves containing transition metals and noble metals [4–8] have been developed. However, most heterogeneous catalysts used in the oxidation of cyclohexane are still under laboratory research because as compared to the homogeneous catalyst, the reaction rate of the oxidation of cyclohexane catalyzed by a heterogeneous catalyst is not yet satisfactory. Moreover, the leaching of the active component of the catalysts also hinders the industrialization of the heterogeneous catalytic oxidation processes.

Taramasso et al. [9] reported the synthesis of titanium silicalite (TS-1), which is known to be a selective catalyst for a variety of important oxidation reactions, using aqueous H₂O₂ or organic peroxide as oxidant under relatively mild conditions. Schuchardt et al. [10,11] studied the oxidation of cyclohexane catalyzed by TS-1 with H₂O₂ as oxidant, and proposed that there were two types of active centers on the TS-1: one type is very selective and exists inside the pore system, and the other type is very unselective and on the external surface. This work is based on the homogeneous liquid phase catalytic oxidation system that uses cobalt naphthenate (Co-nap) as catalyst, and is an investigation of the effect of TS-1 as a cocatalyst. In order to enhance the hydrophobicity of TS-1, it was silanized by suspending the samples in a 0.5% (m/m) hexamethyl disilazane solution of toluene. The product was denoted as TS-1-S. For comparison, H- β was also silanized using the above method. The

silanized H- β was denoted as H- β -S. When TS-1, especially TS-1-S, was introduced into the cobalt naphthenate system, significantly enhancement of the catalytic performance was obtained. The improvement is suggested to be related with the hydrophobic nature of TS-1.

Figure 1 shows the FT-IR spectra of TS-1, TS-1-S and TS-1, TS-1-S after these were separated from the solution of cobalt naphthenate. Apart from the characteristic peak of TS-1, the characteristic peaks of adsorbed water (3500 and 1700 cm^{-1}) were also observed, which indicated that TS-1 had some hydrophilic character. In the spectrum for TS-1-S, which is shown in Fig. 1(2), both the weakening of the characteristic peaks of adsorbed water and the appearance of the stretching vibration of $-\text{CH}_3$ at 2930 cm^{-1} indicated that the TS-1 was successfully silanized. The increase of the water contact angle of TS-1 from 0° to 127° confirmed this. The characteristic frequency of carbonyl groups at 1713 cm^{-1} and the frequency of $-\text{CH}_2$ at 2854 and 2928 cm^{-1} were observed for Co-nap/TS-1 and Co-nap/TS-1-S, which indicated that adsorption of Co-nap onto the surface of TS-1 and TS-1-S had taken place. At the same time, the further weakening of the characteristic peaks of adsorbed water also suggested that the adsorption of Co-nap on TS-1 and TS-1-S enhanced the hydrophobicity of TS-1 and TS-1-S.

The data of Table 1 showed that TS-1 and TS-1-S had no catalytic activity for the oxidation of cyclohexane. However, when TS-1 or TS-1-S was added into the Co-nap catalyst system, a remarkable increase in conversion with fairly good selectivity to KA-oil was obtained. As compared with the use of only Co-nap, the conversion of cyclohexane catalyzed by Co-nap/TS-1 was increased from 3.6% to 6.4% with a selectivity of 86.9%, which was slightly higher than with only Co-nap as catalyst. In the case of Co-nap/TS-1-S as catalyst, a better promoting effect was achieved, with the conversion increasing to 7.9%, and with almost the same selectivity. Furthermore, the reaction time was reduced from 300 min to 130 min by the addition of TS-1-S. In contrast, some commonly used carriers that have been tested were not productive. For example, with Co-nap/CNTs, besides a change in the proportion of alcohol and ketone in the product, there were no obvious changes in conversion and selectivity. However, H- β had a negative effect on the catalytic performance.

ICP-AES characterization was carried out to determine the concentration of Co-nap before and after the adding of TS-1 and TS-1-S. The concentration of Co-nap decreased from 7.7 $\mu\text{g/g}$ to 0.036 $\mu\text{g/g}$ with TS-1 and to 0.035 $\mu\text{g/g}$ with TS-1-S, which indicated that the Co-nap in the solution was totally adsorbed on the surface of TS-1. As can be seen from Table 1, after filtrating out TS-1 or TS-1-S, the filtrate gave no conversion to KA-oil, which confirmed that the

filtrate contained no Co-nap. Due to the adsorption of Co-nap on TS-1-S, the catalytic characteristic of the reaction was changed, and a homogeneous catalytic process was changed into a heterogeneous-like process. We call this heterogeneous-like catalyst, caused by the adsorption of the active component onto the carrier, a “quasi-heterogeneous” catalyst to differentiate it from genuine heterogeneous catalysts.

The change in the microenvironment of the catalytic active centers was possibly the reason for the better catalytic performance. In a homogenous process, the polarity of KA-oil caused it to diffuse slowly away from the active center in the solution, and it was thereby liable to over-oxidation, which gave poor selectivity. For the quasi-heterogeneous process, the diffusion of products also depended on the hydrophilic-hydrophobic property of the support. For a heterogeneous process, the diffusion of product is related to the hydrophobicity of the surface of the catalyst. The product can easily diffuse from a more hydrophobic surface, which was shown in our previous work [12]. The benefit from the super hydrophobicity of TS-1-S was that the reaction rate was increased significantly. This indicated that the hydrophobic property of the support was a key factor in the improvement of catalytic performance.

Drago et al. [13] reported that the absence of strong acid sites resulted in the outstanding performance of TS-1 in epoxidation. There are only weak acid sites on TS-1. In Sun et al.'s work [14], they suggested the medium strength Brønsted acid sites of H- β as the main active centers for the decomposition of cyclohexyl hydroperoxide. The oxidation of cyclohexane catalyzed by Co-nap is considered to follow a free radical chain mechanism [15]. The facile decomposition of cyclohexyl hydroperoxide by H- β hindered the chain propagation of the free radical reaction of cyclohexane by sharply decreasing the concentration of cyclohexyl hydroperoxide. Moreover, the silanized H- β (H- β -S) also hindered the reaction. It was probable that silylation had little influence on the acidity of H- β , and H- β -S maintained a high activity for the decomposition of cyclohexyl hydroperoxide.

In summary, in the homogeneous liquid phase catalytic oxidation of cyclohexane with cobalt-naphthenate as catalyst, when titanium silicate TS-1 or especially silanized TS-1 was introduced, there was a significantly better catalytic performance. The improvement was due to the adsorption of Co-nap on the surface of TS-1, the hydrophobicity of the surface and the absence of strong acid sites on TS-1. This quasi-heterogeneous catalyst is promising for use in the industrial liquid oxidation of cyclohexane.

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