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Short communication

Esterification of benzoic acid using Ti_3AlC_2 and SO_4^{2-}/Ti_3AlC_2 ceramic as acid catalysts

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Abstract

A novel catalyst of SO_4^{2-} over Ti_3AlC_2 ceramic was prepared by an impregnation method. The resulting catalyst exhibited high catalytic activity and selectivity for the esterification of benzoic acid to ethyl benzoate. This study realized 80.4% conversion for benzoic acid and $>99\%$ selectivity for ethyl benzoate under 120 °C at 34 h. Various characteristics of the reaction were studied, such as performance of Ti_3AlC_2 and SO_4^{2-}/Ti_3AlC_2, the influence of bases, reaction temperature, reaction time, and recycling of the catalyst. In order to further study this reaction system, the XRD and FT-IR of SO_4^{2-}/Ti_3AlC_2 was detected and analyzed. All results indicate that SO_4^{2-}/Ti_3AlC_2 can serve as an acid catalyst.

Keywords: Esterification; Ti_3AlC_2; SO_4^{2-}/Ti_3AlC_2; Ethyl benzoate

1. Introduction

The use of ceramics as heterogeneous catalysts represents an extension of "non-traditional" ceramic applications that is now a burgeoning topic of research because of its high resistance to wear, corrosion, and temperature [1]. Ceramic catalysts have been applied widely in the automotive [2,3] and petroleum industries [4–7]. Oxides ceramics, such as ZrO_2, CeO_2, and Al_2O_3, have been used to make automotive catalytic converters [8–11]. These ceramics are also very fascinating catalysts used for refining, hydrogenation, isomerization, and so on in the petroleum industry [8–11]. However, the application of ceramic catalysts in organic synthesis, especially nonoxide ceramics, is limited [12–14]. Among such catalysts, Ti_3AlC_2 and Ti_2AlC are the most light-weight and oxidation-resistant ternary carbides belonging to the MAX phases ($M_{n+1}AX_n$ phases) [15]. Ti–Al–C materials display superior properties such as fracture toughness, electrical and thermal conductivities, and oxidation resistance over their binary counterpart [16–18]. Although Ti–Al–C ceramics have been widely used in industry, there is no report about applying these types of ceramics in the organic synthesis or the petroleum industry.

Esters are widespread in nature and are important chemical compounds for various pharmaceutical and agricultural applications [19–20]. Thus, chemists are looking for a new method for synthesizing esters in order to minimize the environmental pollution caused by traditional methods [21–24]. The focus is on the synthesis of benzoic esters as important drug substances [25–27]. In this communication, our group reports for the first time the esterification of benzoic acid to ethyl benzoate using Ti_3AlC_2 and SO_4^{2-}/Ti_3AlC_2 as catalysts (Scheme 1).

2. Experimental

A Ti–Al–C ceramic catalyst was prepared according to our previously reported procedure [28,29]. A SO_4^{2-}/Ti_3AlC_2 catalyst was prepared from Ti_3AlC_2 and 3 mol/L H_2SO_4 (1 g Ti_3AlC_2 in 10 mL H_2SO_4) by a simple impregnation protocol involving calcination for 2 h at 673 K in N_2. All the catalytic esterification experiments were processed at atmospheric pressure in a 250 mL

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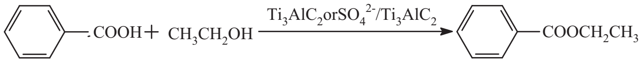
three-neck flask equipped with a reflux condenser, magnetic stirrer, super constant temperature oil bath, and thermometer. In a typical experiment, benzoic acid (1 mmol), Ti_3AlC_2 (0.1 mmol), and ethanol (150 mL) were charged to the reactor and the contents were refluxed for 12 h at 110 °C. The reaction process was monitored by the HPLC method using a C-18 column.

High-performance liquid chromatography (HPLC) analyses were recorded with a Purkinje General HPLC liquid chromatograph (LC-600) equipped with a UV detector and a C-18 column (250 mm × 4.6 mm × 10 μm). Methanol and 0.1% phosphoric acid (7:3, v/v) was used as the eluent. The other parameters were a flow rate of 1.0 mL/min, UV detector 239 nm, column temperature 25 °C, stop time 15 min, and sample size 20 μL.

3. Results and discussion

To determine the catalytic activity of Ti_3AlC_2 alone, we investigated the influence of the temperature and reaction time in this system. Little ethyl benzoate was obtained when the reaction temperature was less than 90 °C; however, about 5% benzoic acid was fully converted into ethyl benzoate at 95 °C. Higher temperatures would help to convert benzoic acid and ethanol to ethyl benzoate. In contrast to H_2SO_4 (Table 1, entries 6–7) as the catalyst, the single Ti_3AlC_2 catalyst was unsatisfactory (Table 1, entries 2–5). Moreover, to improve the amount of ethyl benzoate obtained, a 4 Å molecular sieve as a dehydrant was used in the H_2SO_4 (Table 1, entry 7) and Ti_3AlC_2 (Table 1, entry 2) systems. 4 Å molecular sieve as a catalyst was also tested (Table 1, entry 8). Benzoic acid was hardly converted into ethyl benzoate in this catalytic system. In the H_2SO_4 catalytic system, the amount of ethyl benzoate obtained increased remarkably. However, the expected product was not improved in the Ti_3AlC_2 catalytic system. From Table 1, it was also found that the selectivity of ethyl benzoate was almost 100% both in the two catalytic systems. No by-products was found when Ti_3AlC_2 was used as the catalyst, but some by-products (ether and ethylene) were detected in the H_2SO_4 system.



Scheme 1.

According to Rad's report [30], a base could accelerate the reaction between benzoic acid and alcohol. Simultaneously, alkali-catalyzed transesterification has been widely used in the production of biodiesel [31–33]. Therefore, we studied several bases that could affect the synthesis of benzoate in order to improve the amount of ester obtained. However, the bases used in our study (Table 2, entries 1–8, 10–11) not only failed to improve the results but also decreased the conversion of

Table 2
The effect of base using Ti_3AlC_2 as the catalyst.

Entry	**Time (h)**	**Base**[a]	**Conversion of benzoic acid (mol%)**	**Selectivity of ethyl benzoate (mol%)**
1	2.0	NaOH (1:0.2)	<0.1	> 99
2	8.0	NaOH (1:0.2)	<0.1	> 99
3	2.0	NaOH (1:0.6)	0.1	> 99
4	6.0	NaOH (1:0.6)	0.1	> 99
5	2.0	Na_2CO_3 (1:0.2)	<0.1	> 99
6	8.0	Na_2CO_3 (1:0.2)	≈0	> 99
7	2.0	Na_2CO_3 (1:0.6)	0.4	> 99
8	8.0	Na_2CO_3 (1:0.6)	0.1	> 99
9	2.0	Na_2SO_4 (1:0.6)	<0.1	> 99
10	8.0	Na_2SO_4 (1:0.6)	≈0.1	> 99
11	2.0	$NaHCO_3$ (1:0.2)	0.3	> 99
12	8.0	$NaHCO_3$ (1:0.2)	0.2	> 99
13	2.0	SiO_2 (1:0.2)	2.0	> 99
14	8.0	SiO_2 (1:0.2)	2.2	> 99

Reaction conditions: Ti_3AlC_2, 0.195 g; benzoic acid, 1.220 g; ethanol, 150 mL and temperature, 110 °C.

[a] Benzoic acid: base.

Table 1
Esterification of benzoic acid over single Ti_3AlC_2.

Entry	**Catalyst (mg)**	**Time (h)**	**Temperature (°C)**	**Conversion of benzoic acid (mol%)**	**Selectivity of ethyl benzoate (mol%)**
1	Ti_3AlC_2 (195)	6.0	95	5	> 99
2[a]	Ti_3AlC_2 (195)	8.0	95	5	> 99
3	Ti_3AlC_2 (195)	6.0	110	7	> 99
4	Ti_3AlC_2 (195)	6.0	120	9	> 99
5	Ti_3AlC_2 (195)	6.0	130	11	> 99
6[b]	H_2SO_4 (9.8)	2.0	95	50	> 99
7[c]	H_2SO_4 (9.8)	2.0	95	60	> 99
8[d]	4 Å molecular sieve	12	110	Trace (< 0.01)	–

Reaction conditions: benzoic acid, 1.220 g and ethanol, 150 mL.

[a] Dehydrant: 4 Å molecular sieve.

[b] Catalyst: 98% H_2SO_4, 0.005 mL (about 9.8 mg).

[c] Catalyst: 98% H_2SO_4, 0.005 mL (about 9.8 mg); dehydrant: 4 Å molecular sieve.

[d] Catalyst: 4 Å molecular sieve, 10.0 g.

benzoic acid and the production of ethyl benzoate. We found that when the base had a higher strength, the conversion of benzoic acid was lower. We also found that the longer the reaction time was, the lower the production of ester was. The possible reasons were as follows: In the initial stage of the reaction, benzoic acid as the acid could also catalyze its own react with ethanol to produce ethyl benzoate. Meanwhile, benzoic acid reacted with NaOH and Na_2CO_3 to generate sodium benzoate. The solubility of generated sodium benzoate in ethanol was significantly greater than NaOH and Na_2CO_3, and it would lead ethyl benzoate to hydrolyze benzoic acid and ethanol. It therefore seems possible that a base could accelerate the hydrolysis of ester. Na_2SO_4 (Table 2, entries 9–10), as a representative of a neutral salt, was investigated. The results revealed that a neutral salt was more helpful in converting benzoic acid to ethyl benzoate, although it was unsatisfactory too. Furthermore, considering the cooperative effect of bases and acids, we experimented with amphoteric SiO_2 as co-catalyst (Table 2, entries 13–14). Obviously, the amount of ester obtained using amphoteric SiO_2 was higher than that obtained using other co-catalysts. Also, the conversion of benzoic acid and the productivity increased with the reaction time. These results indicated that a base would reduce the catalytic activity of Ti_3AlC_2 and that an acid would enhance its catalytic activity.

To corroborate the assisting action of acid, SO_4^{2-}/Ti_3AlC_2 was prepared and investigated in the synthesis of ethyl benzoate. Fig. 1 shows the XRD patterns of the SO_4^{2-}/Ti_3AlC_2 catalyst prepared in this work, and it can be seen that the XRD peaks displayed a structure similar to that of single Ti_3AlC_2. Furthermore, the weak peaks of $TiO(SO_4)$ and $AlO(SO_4)$ in the SO_4^{2-}/Ti_3AlC_2 XRD pattern implied that the Ti and Al in the surface of Ti_3AlC_2 were joined with SO_4^{2-} by the –O– bridge [34,35]. To verify SO_4^{2-} to be grafted on Ti_3AlC_2, the FT-IR spectrum of SO_4^{2-}/Ti_3AlC_2 (Fig. 2) was detected and analyzed. SO_4^{2-}/Ti_3AlC_2 showed infrared absorption bands at 1400, 1170, 1000, 690 and 600 cm^{-1}. The peak centered at 1400 cm^{-1} was assigned to the characteristic $–O–SO_2–O–$ stretching vibration. The absorption band at 1170 cm^{-1} was caused by the bending vibration of S=O. The band at 1000 cm^{-1} could be assigned to the stretching vibration of the S–O band [36]. The peaks located 690 and 600 cm^{-1} were likely due to the vibration of the Ti–O or Al–O bonds in the surface of Ti_3AlC_2 ceramic [37,38].

Fig. 3 shows the conversion of benzoic acid obtained using different reaction times and temperatures under the $>99\%$ selectivity of ethyl benzoate. After 12 h, the reaction temperature significantly affected the percent of ethyl benzoate

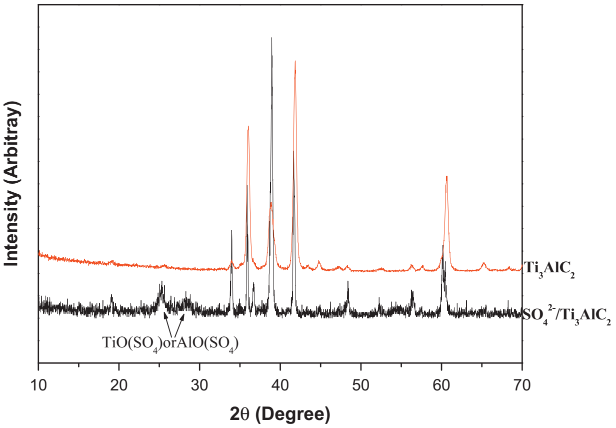


Fig. 1. XRD patterns of SO_4^{2-}/Ti_3AlC_2 and Ti_3AlC_2 catalysts.

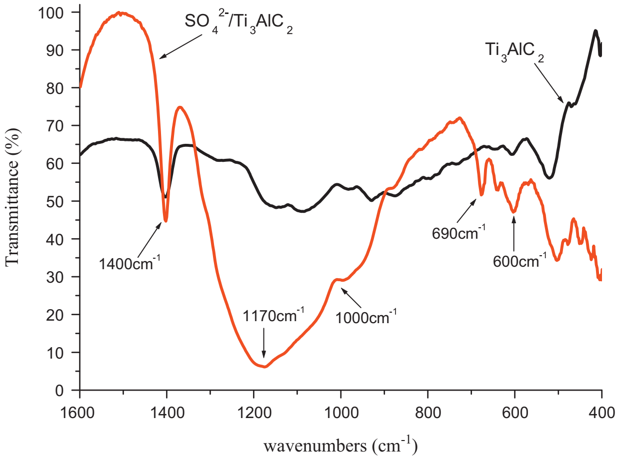


Fig. 2. The FT-IR spectrum of SO_4^{2-}/Ti_3AlC_2.

Table 3
The kinetic data of catalytic reaction and activation energy.

Entry	T	k (× 10^{-3})[a]	R^2	$\ln(k_2/k_1)$[b]	$\ln(k_2/k_1)$[c]	$\ln(k_2/k_1)$[d]	$\ln(k_2/k_1)$[e]	E_a[b]	E_a[c]	E_a[d]	E_a[e]	$\overline{E}_a$
1	323	2.4	0.953	–	–	–	–	–	–	–	–	42.65
2	343	5.4	0.986	0.811	–	–	–	37.35	–	–	–	(42.10)
3	363	17.3	0.993	1.975	1.164	–	–	48.14	60.26	–	–	
4	373	16.2	0.997	1.910	1.100	–	–	38.25	38.95	–	–	
5	393	36.6	0.997	2.708	1.897	0.733	0.799	40.83	42.52	28.97	48.66	

$\overline{E}_a = \Sigma E_a/9 = 42.65$ ($\overline{E}_a = \Sigma E_a/7 = 42.10$, removal 60.26 and 28.97).

[a] $\ln(C/C_0) = -kt \rightarrow k = -(1/t)\ln(C/C_0)$.

[b] $k_1 = 2.4 \times 10^{-3}$, $k_2 = 5.4 \times 10^{-3}$, 17.3×10^{-3}, 16.2×10^{-3}, and 36.6×10^{-3}, $\ln(k_2/k_1) = (E_a/R)[(T_2-T_1)/T_1T_2]$.

[c] $k_1 = 5.4 \times 10^{-3}$, $k_2 = 17.3 \times 10^{-3}$, 16.2×10^{-3}, and 36.6×10^{-3}, $\ln(k_2/k_1) = (E_a/R)[(T_2-T_1)/T_1T_2]$.

[d] $k_1 = 17.3 \times 10^{-3}$, $k_2 = 36.6 \times 10^{-3}$, $\ln(k_2/k_1) = (E_a/R)[(T_2-T_1)/T_1T_2]$.

[e] $k_1 = 16.2 \times 10^{-3}$, $k_2 = 36.6 \times 10^{-3}$, $\ln(k_2/k_1) = (E_a/R)[(T_2-T_1)/T_1T_2]$.

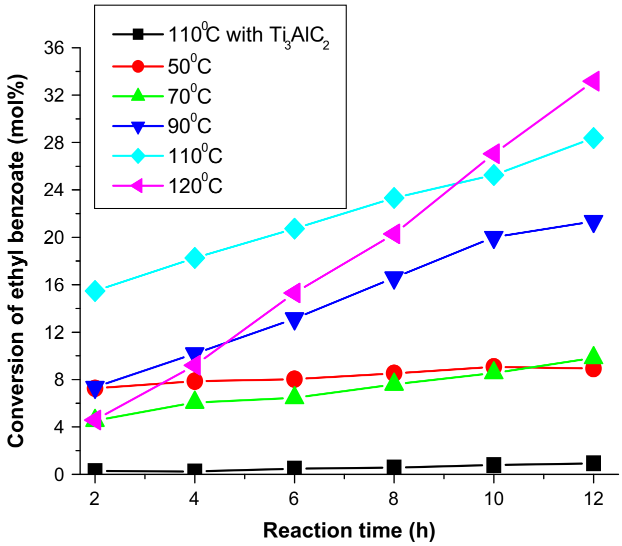


Fig. 3. Effect of reaction time on benzoic acid esterification over SO_4^{2-}/Ti_3AlC_2.

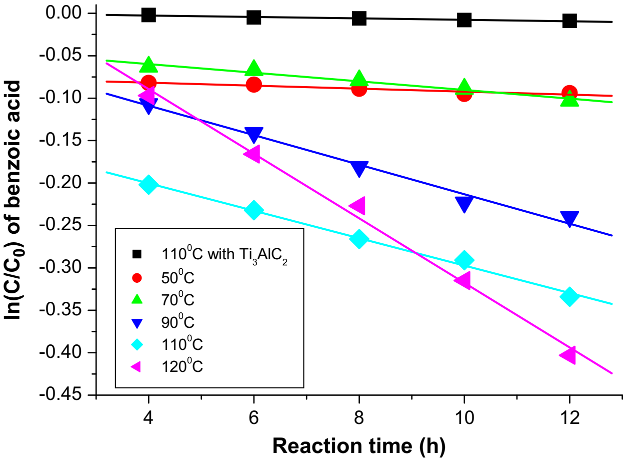


Fig. 4. Reaction rate of SO_4^{2-}/Ti_3AlC_2.

obtained. Below 70 °C, the conversion of benzoic acid and the selectivity of ethyl benzoate did not evidently increase. When the temperature was higher than 90 °C (Fig. 3, 90 °C, 110 °C, and 120 °C), the conversion of benzoic acid rapidly improved and the selectivity of ethyl benzoate achieved almost 100% (detected by HPLC). Most of the benzoic acid crystallized in the reaction vessel wall because of sublimation at 120 °C, which led to less ethyl benzoate produced than at 110 °C over 8 h; however, these results reversed after 10 h due to the sublimated substrate dissolving again. Moreover, the catalytic activity of Ti_3AlC_2 was examined under 110 °C, only 1% of benzoic acid was converted into ethyl benzoate after 12 h. Simultaneously, it was found that the conversion of benzoic acid reached into 28% using SO_4^{2-}/Ti_3AlC_2 under the same conditions. These results indicated that the catalytic activity of SO_4^{2-}/Ti_3AlC_2 was superior to single Ti_3AlC_2.

To further reveal the reaction activation of SO_4^{2-}/Ti_3AlC_2, the chemical reaction rate laws and the Arrehenius parameters of SO_4^{2-}/Ti_3AlC_2 and Ti_3AlC_2 were calculated and compared. Because reaction rate laws have differential equations (including first-order, second-order, third-order, etc.), we investigated the linear correlation of SO_4^{2-}/Ti_3AlC_2 and Ti_3AlC_2 according to the formula of various integrated rate laws. An assumption of first-order kinetics was made and plots of the ln(C/C_0) versus time are shown at different temperatures (Fig. 4). Good linear correlation ($R^2=0.953$–0.998, Table 3. entries 1–5) was observed, suggesting that all reactions were first-order with respect to the esterification of benzoic acid. These data were also fitted to second- and third-order kinetics, which resulted in poorer correlation. We also found that the linearity ($R^2=0.998$, Table 3, entry 4) of SO_4^{2-}/Ti_3AlC_2 catalyst was better than that ($R^2=0.998$, Table 3, entry 1) of single Ti_3AlC_2 catalyst at the same reaction conditions. Furthermore, as the temperature increased the reaction rate constant (k) increased using the SO_4^{2-}/Ti_3AlC_2 as the catalyst. This suggested that an increase in the reaction temperature would accelerate the synthesis of ethyl benzoate. On the other hand, the k value ($k=16.2\times10^{-3}$) of SO_4^{2-}/Ti_3AlC_2 was much high than that ($k=2.4\times10^{-3}$) of single Ti_3AlC_2 at 110 °C. The rate constants further revealed the catalytic activity of SO_4^{2-}/Ti_3AlC_2 was superior to that of single Ti_3AlC_2. The activation energy (E_a) was also calculated according to the Arrhenius equation (Table 3). The average E_a of the esterification of benzoic acid is 42.65 kJ mol^{-1}. The value was significantly lower than the results of H_2SO_4 ($E_a=80.5$ kJ mol^{-1}) [39], Amberlyst-15 ($E_a=69.1$ kJ mol^{-1}) [39], and Amberlyst-39 ($E_a=79.99$ kJ mol^{-1}) [40]. All E_a data of the synthesis of ethyl benzoate indicated that the SO_4^{2-}/Ti_3AlC_2 was an excellent catalyst.

Table 4
Recycling of SO_4^{2-}/Ti_3Al_2C.

Entry	Run	Conversion of benzoic acid (mol%)	Selectivity of ethyl benzoate (mol%)
1	Fresh	80.4	> 99
2	1	80.1	> 99
3	2	80.4	> 99
4	3	80.1	> 99

Reaction conditions: SO_4^{2-}/Ti_3AlC_2, 0.195 g, benzoic acid, 1.220 g, ethanol, 150 mL; reaction temperature, 120 °C and reaction time, 34 h.

To achieve a satisfactory productivity rate, we extended the reaction time to attain higher productivity of ethyl benzoate (Fig. 5). The expected result was successfully achieved with a 80.4% conversion of benzoic acid and a > 99% selectivity of ethyl benzoate. The optimized reaction conditions were as follows: SO_4^{2-}/Ti_3AlC_2, 0.195 g, benzoic acid, 1.220 g, ethanol, 150 mL; reaction temperature, 120 °C; reaction time, 34 h. To check the activity and stability of the SO_4^{2-}/Ti_3AlC_2 sample, the catalyst was used three times in the esterification of benzoic acid. After reaction of each cycle, the catalyst was filtered off, washed with ethanol, and dried at 125 °C in the presence of air 2 h to drastically eliminate the effects of residual benzoic acid and ethyl benzoate. The reaction was then carried out on the activated recycled catalyst at 120 °C under the optimum condition. Table 4 lists the results of these experiments. It is noteworthy that the catalytic activity

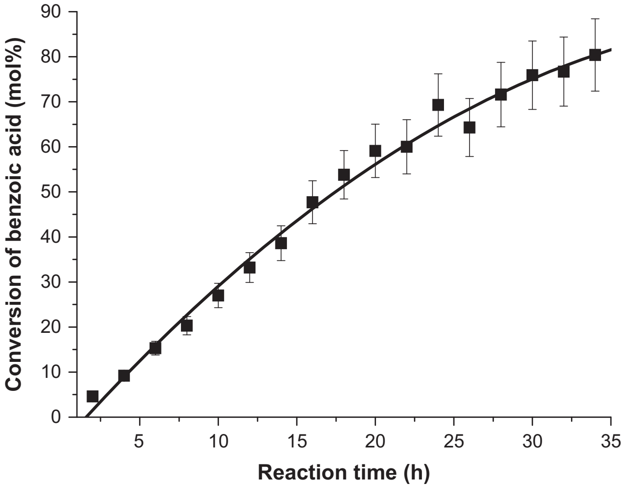


Fig. 5. Effect of reaction time at 120 °C.

remained nearly the same even after the third run. In order to check the structure of the SO_4^{2-}/Ti_3AlC_2 after each reaction, The XRD patterns were recorded and indicated the catalyst retains the same structure. The results obtained in the experiment suggest that SO_4^{2-}/Ti_3AlC_2 act as a heterogenous catalyst in the reaction.

4. Conclusions

In conclusion, we demonstrated for the first time that SO_4^{2-}/Ti_3AlC_2 is an excellent catalyst for the esterification of benzoic acid with ethanol. Moreover, the results imply the SO_4^{2-}/Ti_3AlC_2 is an acid catalyst. Its applications as an acid catalyst in the organic synthesis are in progress.

Acknowledgments

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