



AN OVERVIEW ON SYNTHETIC METHODS OF ISOPROPYL CHLOROACETATE

Liu Shu^{[a]*} and You Hongjun^[b]

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Nowadays a lot of synthetic methods of isopropyl chloroacetate using different catalysts such as sulfonic acids (p-toluene-sulfonic acid and amino-sulfonic acid), inorganic metal salts of organic sulfonates ($\text{Ce}(\text{CH}_3\text{SO}_3)_3 \cdot \text{H}_2\text{O}$, $\text{Ca}(\text{CH}_3\text{SO}_3)_2 \cdot 2\text{H}_2\text{O}$, $\text{Al}(\text{CH}_3\text{SO}_3)_3 \cdot 4\text{H}_2\text{O}$, $\text{Zn}(\text{CH}_3\text{SO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{La}(\text{CH}_3\text{SO}_3)_3 \cdot 4\text{H}_2\text{O}$, $\text{Cu}(\text{CH}_3\text{SO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Zn}(\text{p-CH}_3\text{C}_6\text{H}_4\text{SO}_3)_2 \cdot 5\text{H}_2\text{O}$, $\text{Zn}(\text{C}_6\text{H}_5\text{SO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{CH}_3(\text{CH}_2)_{11}\text{SO}_3\text{Na}$ and $(\text{CH}_3(\text{CH}_2)_{11}\text{SO}_3)_3\text{Fe}$), ionic liquids ($[(\text{CH}_2)_4\text{SO}_3\text{HPy}]\text{HSO}_4$ and $[\text{C}_{10}\text{imCH}_2\text{COOH}]\text{HSO}_4$), inorganic salts ($\text{Ce}(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$, NaHSO_4 , KHSO_4 , $[\text{Fe}_2(\text{OH})_n(\text{SO}_4)_{3-n/2}]_m$, CPVC-FeCl_3 , $\text{NH}_4\text{Fe}(\text{SO}_4) \cdot 12\text{H}_2\text{O}$, PVC-FeCl_3 , $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and SnCl_4), PCl_3 , heteropolyacids (H_3PO_4 , $\text{W}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$ and $\text{TiSiW}_{12}\text{O}_{40}/\text{TiO}_2$), solid superacids ($\text{SO}_4^{2-} \cdot \text{Fe}_2\text{O}_3$, $\text{SO}_4^{2-}/\text{TiO}_2 \cdot \text{La}^{3+}$, $\text{SO}_4^{2-}/\text{TiO}_2$, $\text{SO}_4^{2-}/\text{TiO}_2 \cdot \text{Sm}^{3+}$, $\text{SO}_4^{2-} \cdot \text{NiO}$, $\text{SO}_4^{2-}/\text{TiO}_2 \cdot \text{Nd}^{3+}$, $\text{SO}_4^{2-} \cdot \text{Al}_2\text{O}_3$, $\text{SO}_4^{2-}/\text{TiO}_2 \cdot \text{Gd}^{3+}$ and $\text{SO}_4^{2-}/\text{TiO}_2 \cdot \text{Ce}^{3+}$) and inorganic salts of organic acids ($\text{Nd}(\text{CF}_3\text{COO})_3$) have been reviewed in the present paper. The yields of isopropyl chloroacetate are improved by the addition of above catalysts. These methods are having the advantages of simple process and low investment costs.

* Corresponding Author

Fax: 86-24-56860869

E-Mail: youhongjun@hotmail.com

[a] Liaoning Shihua University, Fushun, Liaoning, P.R. China.

[b] SAIT Polytechnic, Calgary AB, Canada.

Introduction

Isopropyl chloroacetate is one of the important organic chemical materials, intermediates and a colourless liquids. It is used as an organic solvent or as a synthetic medicine. Its molecular formula, boiling point, relative density (25 °C), refractive index n_D^{20} and flash point are $\text{C}_5\text{H}_9\text{O}_2\text{Cl}$, 149.5 °C, 1.0812, 1.0423 and 56 °C,¹ respectively. The demands for isopropyl chloroacetate have gradually increased in the country like *China*. It is used mainly in pharmaceutical industries to synthesize non-steroid anti-inflammatory drug such as naproxen and ketoprofen, etc. It is beneficial for industrial processes to use isopropyl chloroacetate instead of ethyl chloroacetate.² Concentrated sulphuric acid is one of the main catalysts, but apart from several advantages, such as more secondary reaction taking place, low yield and purity of isopropyl chloroacetate, it has a lot of disadvantages also. Lot of waste water is discharged during the process causing severe environmental pollution problem and at the same time equipments are corroded.³

In the present paper, different catalysts such as sulfonic acids (p-toluene-sulfonic acid and amino-sulfonic acid), inorganic metal salts of organic sulfonates ($\text{Ce}(\text{CH}_3\text{SO}_3)_3 \cdot \text{H}_2\text{O}$, $\text{Ca}(\text{CH}_3\text{SO}_3)_2 \cdot 2\text{H}_2\text{O}$, $\text{Al}(\text{CH}_3\text{SO}_3)_3 \cdot 4\text{H}_2\text{O}$, $\text{Zn}(\text{CH}_3\text{SO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{La}(\text{CH}_3\text{SO}_3)_3 \cdot 4\text{H}_2\text{O}$, $\text{Cu}(\text{CH}_3\text{SO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Zn}(\text{p-CH}_3\text{C}_6\text{H}_4\text{SO}_3)_2 \cdot 5\text{H}_2\text{O}$, $\text{Zn}(\text{C}_6\text{H}_5\text{SO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{CH}_3(\text{CH}_2)_{11}\text{SO}_3\text{Na}$ and $(\text{CH}_3(\text{CH}_2)_{11}\text{SO}_3)_3\text{Fe}$), ionic liquids ($[(\text{CH}_2)_4\text{SO}_3\text{HPy}]\text{HSO}_4$ and $[\text{C}_{10}\text{imCH}_2\text{COOH}]\text{HSO}_4$), inorganic salts ($\text{Ce}(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$, NaHSO_4 , KHSO_4 , $[\text{Fe}_2(\text{OH})_n(\text{SO}_4)_{3-n/2}]_m$, CPVC-FeCl_3 , $\text{NH}_4\text{Fe}(\text{SO}_4) \cdot 12\text{H}_2\text{O}$, PVC-FeCl_3 , $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, SnCl_4), PCl_3 , heteropolyacids (H_3PO_4 , $\text{W}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$ and $\text{TiSiW}_{12}\text{O}_{40}/\text{TiO}_2$), solid superacids ($\text{SO}_4^{2-} \cdot \text{Fe}_2\text{O}_3$, $\text{SO}_4^{2-}/\text{TiO}_2 \cdot \text{La}^{3+}$, $\text{SO}_4^{2-}/\text{TiO}_2$, $\text{SO}_4^{2-}/\text{TiO}_2 \cdot \text{Sm}^{3+}$, $\text{SO}_4^{2-} \cdot \text{NiO}$, $\text{SO}_4^{2-}/\text{TiO}_2 \cdot \text{Nd}^{3+}$, $\text{SO}_4^{2-} \cdot \text{Al}_2\text{O}_3$, $\text{SO}_4^{2-}/\text{TiO}_2 \cdot \text{Gd}^{3+}$ and $\text{SO}_4^{2-}/\text{TiO}_2 \cdot \text{Ce}^{3+}$) and inorganic salts of organic acids ($\text{Nd}(\text{CF}_3\text{COO})_3$) have been discussed.

DISCUSSION

Sulfonic acids as catalysts to produce isopropyl chloroacetate

Shi Lei⁴ introduced the preparation of isopropyl chloroacetate and the effect of the reaction conditions on its yield. In microwave conditions, using p-toluene-sulfonic acid as a catalyst and chloroacetic acid and isopropanol as feedstocks, isopropyl chloroacetate was produced. The optimum conditions were the reaction time (0.75 hours) and the weight ratio of p-toluene-sulfonic acid to chloroacetic acid (11.11%). The maximum yield and purity of isopropyl chloroacetate were 78.3% and 99.8%, respectively. The experimental results indicated that out of a few catalysts tested the performance of p-toluene-sulfonic acid was good enough. The secondary reaction almost did not take place at all. It was also observed that equipment corrosion and environmental pollution by p-toluene-sulfonic acid was less than that of concentrated sulphuric acid. Therefore, p-toluene-sulfonic acid was one of the good catalysts and replaced the concentrated sulphuric acid.

Jing Boyi⁵ described the synthetic method of isopropyl chloroacetate and studied that the different conditions had also an effect on its yield. Using amino-sulfonic acid as a catalyst and chloroacetic acid and isopropanol as feedstocks synthesised isopropyl chloroacetate. The experimental results indicated that the best conditions were that the reaction time, the molar ratio of chloroacetic acid to isopropanol and the amount of amino-sulfonic acid were 2.5 hours, 1.0:1.3 and 2.65% of chloroacetic acid weight, respectively. The maximum yield of isopropyl chloroacetate was 85.0%. Amino-sulfonic acid showed a good catalytic performance in the process, further it has an advantage to be controlled easily in the reaction process and proved to be a good, stable and solid catalyst.

Inorganic metal salts of organic sulfonates as catalysts to generate isopropyl chloroacetate

Table 1 showed that different inorganic metal salts of organic sulfonates, such as $\text{Ce}(\text{CH}_3\text{SO}_3)_3 \cdot \text{H}_2\text{O}$, $\text{Ca}(\text{CH}_3\text{SO}_3)_2 \cdot 2\text{H}_2\text{O}$, $\text{Al}(\text{CH}_3\text{SO}_3)_3 \cdot 4\text{H}_2\text{O}$, $\text{Zn}(\text{CH}_3\text{SO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{La}(\text{CH}_3\text{SO}_3)_3 \cdot 4\text{H}_2\text{O}$,

Cu(CH₃SO₃)₂·4H₂O, Zn(p-CH₃C₆H₄SO₃)₂·5H₂O, Zn(C₆H₅SO₃)₂·6H₂O, CH₃(CH₂)₁₁SO₃Na and (CH₃(CH₂)₁₁SO₃)₃Fe, had an effect on the yield of isopropyl chloroacetate. Methanesulfonate included Ce(CH₃SO₃)₃·H₂O, Ca(CH₃SO₃)₂·2H₂O, Al(CH₃SO₃)₃·4H₂O, Zn(CH₃SO₃)₂·4H₂O, La(CH₃SO₃)₃·4H₂O, Cu(CH₃SO₃)₂·4H₂O. They almost had the same construction, but only had the different metal element. The experimental results showed that the yield of isopropyl chloroacetate had big difference. This maybe related with their metal performance such as metal activity. The higher the metal activity is in the reactivity series, the higher the yield of

isopropyl chloroacetate became. Organic sulfonic acid zinc consisted of Zn(p-CH₃C₆H₄SO₃)₂·5H₂O, and Zn(C₆H₅SO₃)₂·6H₂O. Their catalytic performance was very poor because the yield of isopropyl chloroacetate was very low. Sodium dodecyl sulfate and iron dodecyl sulphate had the same results like methanesulfonate. Sodium activity was more than that of iron so the yield of isopropyl chloroacetate with additional use of sodium dodecyl sulphate was more than that of iron dodecyl sulphate. Ce(CH₃SO₃)₃·H₂O was one of the best catalysts in inorganic metal salts of organic sulfonates based on the above review.

Table 1. The effect of different inorganic metal salts of organic sulfonates on the yields of isopropyl chloroacetate

Catalyst	Chloroacetic acid/ isopropanol ratio	Weight ratio of catalyst to chloro- acetic acid (%)	Reaction time (hours)	Yield of isopropyl chloro- acetate	Reference
Ce(CH ₃ SO ₃) ₃ ·H ₂ O	1:1.1	1.0	2.5	98.6	6
Ca(CH ₃ SO ₃) ₂ ·2H ₂ O	1:1.2	1.0	2.5	98.1	7
Al(CH ₃ SO ₃) ₃ ·4H ₂ O	1:1.2	1.0	2.5	96.8	8
Zn(CH ₃ SO ₃) ₂ ·4H ₂ O	1:1.2	1.0	2.5	92.7	9
La(CH ₃ SO ₃) ₃ ·4H ₂ O	1:1.2	1.0	2.5	88.7	10
Cu(CH ₃ SO ₃) ₂ ·4H ₂ O	1:1.2	1.0	2.5	75.3	10
Zn(p-H ₃ C ₆ H ₄ SO ₃) ₂ ·5H ₂ O	1:1.2	1.0	2.5	74.9	9
Zn(C ₆ H ₅ SO ₃) ₂ ·6H ₂ O	1:1.2	1.0	2.5	73.2	9
CH ₃ (CH ₂) ₁₁ SO ₃ Na	1:1.2	1.0	2.5	97.2	11
(CH ₃ (CH ₂) ₁₁ SO ₃) ₃ Fe	1:1.3	2.0	1.0	86.7	12

Table 2. The effect of different inorganic salts on the yield of isopropyl chloroacetate

Catalyst	chloroacetic acid/ isopropanol ratio	Weight ratio of catalyst to chloroacetic acid (%)	Reaction time (Hours)	Yield of isopropyl chloroacetate	Reference
Ce(SO ₄) ₃ ·4H ₂ O	1.0:1.3	3.5	3.0	97.5	15
NaHSO ₄	1.0:1.2	1.0	3.0	97.1	16
KHSO ₄	1.0:1.3	17.6	2.5	87.4	17
[Fe ₂ (OH) _n (SO ₄) _{3-n/2}] _m	1.0:2.0	3.8	6.0	84.9	18
CPVC-FeCl ₃	1.0:2.0	21.2	2.5	81.8	19
NH ₄ Fe(SO ₄)·12H ₂ O	1.0:1.3	10.6	4.0	81.4	20
PVC-FeCl ₃	1.0:2.0	10.5	2.5	80.3	21
FeCl ₃ ·6H ₂ O	1.0:2.0	5.3	2.5	80.0	22
SnCl ₄	1.0:1.6	4.6	4.0	77.0	23

Ionic liquids as catalysts to produce isopropyl chloroacetate

Zhu Xiangqin¹³ described the synthetic method of isopropyl chloroacetate by using [(CH₂)₄SO₃HPy]HSO₄ as a catalyst. The effect of the reaction conditions such as the reaction time, temperature, molar ratio of ionic liquid to chloroacetic acid and isopropanol, the amount of ionic liquid and the number of reusable catalyst had been discussed. The best conditions were that the reaction time, the reaction temperature, the molar ratio of ionic liquid to chloroacetic acid to isopropanol and the number of reusable catalyst were 4 hours, 60 °C, 1.0:5.0:5.0 and 5 times respectively. The maximum yield of isopropyl chloroacetate was 91.0%. After recovery and reuse of [(CH₂)₄SO₃HPy]HSO₄ as a catalyst, it was noticed that its catalytic performance was very good. For example, when [(CH₂)₄SO₃HPy]HSO₄ was reused 5 times, the yield of isopropyl chloroacetate still reached 89.0%.

Wang Chan¹⁴ explained why [C₁imCH₂COOH]HSO₄ as a catalyst replaced concentrated sulfuric acid to synthesise isopropyl chloroacetate. The effect of the reaction conditions such as the reaction time, the reaction temperature, the molar ratio of ionic liquid to chloroacetic acid to isopropanol and the number of reusable catalyst had been discussed. The experimental results indicated that the best conditions were that the reaction time, the reaction temperature, the molar ratio of ionic liquid to chloroacetic acid to isopropanol and the number of reusable catalyst were 3 hours, 60 °C, 1.0:5.0:5.0 and 5 times, respectively.

The maximum yield of isopropyl chloroacetate was 90.6%. When [C₁imCH₂COOH]HSO₄ as a catalyst was recovered and reused, their catalytic performance was found to be very good. For example, when [C₁imCH₂COOH]HSO₄ was reused 5 times, the yield of isopropyl chloroacetate still reached 89.1%.

Inorganic salts as catalysts to generate isopropyl chloroacetate

Table 2 presented the effect of different inorganic salts on the yield of isopropyl chloroacetate such as $\text{Ce}(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$, NaHSO_4 , KHSO_4 , $[\text{Fe}_2(\text{OH})_n(\text{SO}_4)_{3-n/2}]_m$, CPVC-FeCl_3 , $\text{NH}_4\text{Fe}(\text{SO}_4) \cdot 12\text{H}_2\text{O}$, PVC-FeCl_3 , $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and SnCl_4 . Different inorganic salt had different catalytic performance. This did not follow any rules. $\text{Ce}(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$ and NaHSO_4 were two of the best catalysts in inorganic salt used so far. Furthermore, their yields reached more than 97.0%. On the other hand, SnCl_4 was found to be one of the worst catalysts in inorganic salts. Its yield only arrived at 77.0%. PCl_3 as a catalyst to produce isopropyl chloroacetate

Liang Chungen²⁴ described the synthetic method of isopropyl chloroacetate by using PCl_3 as a catalyst. The effect of the reaction conditions such as the amount of n-butanol, the molar ratio of chloroacetic acid to isopropanol and the amount of catalyst had been discussed. The best conditions were that the amount of isopropanol, the molar ratio of chloroacetic acid to isopropanol and the amount of PCl_3 were 0.35 mol, 1.0:1.4 and 6.65% of chloroacetic acid weight, respectively. The maximum yield of isopropyl chloroacetate was 89.5%.

Heteropolyacids as catalysts to generate isopropyl chloroacetate

Liu Xinhe²⁵ studied the preparation of heteropolyacids ($\text{H}_3\text{PO}_4\text{W}_{12}\text{xH}_2\text{O}$) and the effect of the reaction conditions such as the molar ratio of chloroacetic acid to isopropanol and the amount of catalyst on the yield of isopropyl chloroacetate. The best conditions were that the molar ratio of chloroacetic acid to isopropanol and the amount of $\text{H}_3\text{PO}_4\text{W}_{12}\text{xH}_2\text{O}$ were 1 hour, 1.0:1.4 and 2.12% of chloroacetic acid weight,

Table 3. effect of different t solid super acid on the yield of isopropyl chloroacetate

Catalyst	Chloroacetic acid/ isopropanol ratio	Weight ratio of catalyst to chloroacetic acid (%)	Reaction time (hours)	Yield of isopropyl chloroacetate	Reference
$\text{SO}_4^{2-} - \text{Fe}_2\text{O}_3$	1.0:3.0	4.0	4.0	91.6	27
$\text{SO}_4^{2-} - \text{NiO}$	1.0:3.0	3.8	5.0	84.8	28
$\text{SO}_4^{2-} - \text{Al}_2\text{O}_3$	1.0:3.0	3.4	4.0	81.8	29
$\text{SO}_4^{2-}/\text{TiO}_2 - \text{La}^{3+}$	1.0:3.0	4.5	4.0	90.7	30
$\text{SO}_4^{2-}/\text{TiO}_2 - \text{Sm}^{3+}$	1.0:3.0	4.5	4.0	86.6	30
$\text{SO}_4^{2-}/\text{TiO}_2 - \text{Nd}^{3+}$	1.0:3.0	4.5	4.0	84.5	30
$\text{SO}_4^{2-}/\text{TiO}_2 - \text{Gd}^{3+}$	1.0:3.0	4.5	4.0	81.3	30
$\text{SO}_4^{2-}/\text{TiO}_2 - \text{Ce}^{3+}$	1.0:3.0	4.5	4.0	74.3	30

Organic salts as catalysts to generate isopropyl chloroacetate

Lai Junling² used $\text{Nd}(\text{CF}_3\text{COO})_3$ as a catalyst to generate isopropyl chloroacetate. The effect of the reaction conditions such as the reaction time, the molar ratio of chloroacetic acid to isopropanol and the amount of catalyst had been discussed. The best conditions were that the reaction time, the molar ratio of chloroacetic acid to isopropanol and the amount of $\text{Nd}(\text{CF}_3\text{COO})_3$ were 0.75 hours, 1.0:1.2 and 3.17% of chloroacetic acid weight, respectively. The maximum yield of isopropyl chloroacetate was 91.2%.

respectively. The maximum yield of isopropyl chloroacetate was 87.2%.

Yang Shuijin²⁶ used $\text{TiSiW}_{12}\text{O}_{40}/\text{TiO}_2$ as a catalyst to produce isopropyl chloroacetate. The effect of the reaction conditions such as the reaction time, the molar ratio of chloroacetic acid to isopropanol and the amount of catalyst had been discussed. The best conditions were the reaction time, the molar ratio of chloroacetic acid to isopropanol and the amount of $\text{TiSiW}_{12}\text{O}_{40}/\text{TiO}_2$ were 2.0 hours, 1.0:1.3 and 1.5% of total reactant weight, respectively. The maximum yield of isopropyl chloroacetate was 73.3%.

Solid superacids as catalysts to produce isopropyl chloroacetate

Table 3 showed that different solid superacids had an effect on the yield of isopropyl chloroacetate such as $\text{SO}_4^{2-} - \text{Fe}_2\text{O}_3$, $\text{SO}_4^{2-}/\text{TiO}_2 - \text{La}^{3+}$, $\text{SO}_4^{2-}/\text{TiO}_2$, $\text{SO}_4^{2-}/\text{TiO}_2 - \text{Sm}^{3+}$, $\text{SO}_4^{2-} - \text{NiO}$, $\text{SO}_4^{2-}/\text{TiO}_2 - \text{Nd}^{3+}$, $\text{SO}_4^{2-} - \text{Al}_2\text{O}_3$, $\text{SO}_4^{2-}/\text{TiO}_2 - \text{Gd}^{3+}$ and $\text{SO}_4^{2-}/\text{TiO}_2 - \text{Ce}^{3+}$. The catalysts had the same acid active centre, but it had the different load such as $\text{SO}_4^{2-} - \text{Fe}_2\text{O}_3$, $\text{SO}_4^{2-} - \text{NiO}$ and $\text{SO}_4^{2-} - \text{Al}_2\text{O}_3$.

The experimental results showed that Fe_2O_3 was one of the best loads because acid was evenly distributed on its surface, so the yield of isopropyl chloroacetate was very high. On the other hand, the catalyst had the same acid active centre, however it had the different metals such as $\text{SO}_4^{2-}/\text{TiO}_2 - \text{La}^{3+}$, $\text{SO}_4^{2-}/\text{TiO}_2$, $\text{SO}_4^{2-}/\text{TiO}_2 - \text{Sm}^{3+}$, $\text{SO}_4^{2-}/\text{TiO}_2 - \text{Nd}^{3+}$, $\text{SO}_4^{2-}/\text{TiO}_2 - \text{Gd}^{3+}$ and $\text{SO}_4^{2-}/\text{TiO}_2 - \text{Ce}^{3+}$. This phenomenon maybe related with their metal acidity. Higher the metal acidity, higher the yield of isopropyl chloroacetate observed.

CONCLUSION

Based on the above discussion and review, $\text{Ce}(\text{CH}_3\text{SO}_3)_3 \cdot \text{H}_2\text{O}$ is found to be one of the best catalysts. It is used to produce the highest isopropyl chloroacetate yields (98.6%). However, due to costly chemical, $\text{Ce}(\text{CH}_3\text{SO}_3)_3 \cdot \text{H}_2\text{O}$ as a catalyst, it was not included as a good choice. Due to the economic viability NaHSO_4 is used as a good catalyst, though its yield of isopropyl chloroacetate (97.1%) is less than that of $\text{Ce}(\text{CH}_3\text{SO}_3)_3 \cdot \text{H}_2\text{O}$. NaHSO_4 is still popular because it is very cheap, stable and insoluble in organic acids and organic alcohol. After the reaction is over, NaHSO_4 becomes insoluble material and is

easily separated from the reaction system. It has high catalytic and selectivity performance. On the other hand, $\text{TiSiW}_{12}\text{O}_{40}/\text{TiO}_2$ is found to be one of the worst catalysts and its maximum yield of isopropyl chloroacetate only reaches 73.3%.

REFERENCES

- ¹You, H. J. *J Liaoning Univ. Petrol. Chem. Technol.*, **2004**, 24(3), 35.
- ²Lai, J. L., Cheng, Y. L., Liu, C. S. and Luo, G. X. *Chem. Agents*, **2009**, 31(3), 197.
- ³Gao, X. H., Gao, J., Zhang, H. F. and Lin, L. *Chem. Ind. Eng.*, **2011**, 28(6), 6.
- ⁴Shi, L., Wu, D. H., Su, G. J. and Wu, D. H. *Fine Chemical Intermediates*, **2003**, 33(3), 37.
- ⁵Jing, B. Y. *Journal of Hetao University*, **2007**, 4(2), 33.
- ⁶Wang, M., Jiang, H., Gong, H. and Su, T. T. *Fine Chemical Intermediates*, **2004**, 34(4), 36.
- ⁷Wang, M., Jiang, H., Gong, H., Su, T. T. and Liu, L. J. *Chemical Agents*, **2004**, 26(4), 201.
- ⁸Wang, M., Jiang, H., Gong, H., Wang, R. and Liu, L. J. *Science & Technology in Chemical Industry*, **2003**, 11(5), 40.
- ⁹Ma, J. Wang, X. K., Jiang, H., Gong, H. and Wang, R. *Science & Technology in Chemical Industry*, **2005**, 13(1), 49.
- ¹⁰Wang, M., Tian, J. J., Liu, L., J. Jiang, H., Gong, H. and Su, T. T. *Chinese Journal of Inorganic Chemistry*, **2003**, 19(7), 731.
- ¹¹Xu, J. S., Wang, M. Jiang, H., Gong, H. and Wang, R. *Journal of Fudan University*, **2003**, 42(3), 329.
- ¹²Li, X. O., Liu, C. S. Huang, Z. K. and Luo, G. X. *Journal of Liaoning Shihua University*, **2004**, 24(1), 26.
- ¹³Zhu, X. Q., Gui, J. Z., Liu, D., Zhang, X. T., Song, L. J. and Sun, Z. L. *Industrial Catalysts*, 2006, 14(11), 33.
- ¹⁴Wang, C. and Yan, Y. L. *Science & Technology in Chemical Industry*, **2010**, 18(2), 38.
- ¹⁵Yang, L. Z., Chu, L. F., Li, F. and Zhang, D. H. *Speciality Petrochemicals*, **2000**, 3, 27.
- ¹⁶Zhang, J. Xu, J. S. and Qian, J. H. *Science Technology and Engineering*, **2011**, 11(11), 2519.
- ¹⁷Liu, G. H., Zhu, X. R., Chu, K. H. and Qian, Y. *Chemical World*, **2002**, 3, 153.
- ¹⁸Du, Q. Y., Shen, Y. Y. and Guo, X. M. *Speciality Petrochemicals*, **2000**, 2, 17.
- ¹⁹Wang, C. R., Yu, S. X. and Zeng, Y. *Journal of Gansu Education College*, **2000**, 14(1), 34.
- ²⁰Li, Y. Q. *Chemical World*, **1998**, 9, 482.
- ²¹Ping, W. J. and Yu, S. X. *Journal of Hunan Light Industry College*, **1999**, 1(2), 7.
- ²²Yu, S. X., Zhao, Z. B. and Peng, X. Z. *Journal of Hunan Normal University*, **1995**, 18(4), 31.
- ²³Wu, D. H., Luo, J. and Yang, X. J. *Synthetic Chemistry*, **2001**, 9(4), 347.
- ²⁴Liang, C. G., Lin, Y. B. and Shen, D. S. *Natural Science Journal of Xiantan Univeristy*, **1997**, 19(2), 49.
- ²⁵Liu, X. H. *Journal of Shenyang Institute of Chemical Technology*, **2000**, 14(4), 313.
- ²⁶Yang, S. J., Yu, X. Q. and Liang, Y. G. *Advances in Fine Petrochemicals*, **2000**, 12(1), 1.
- ²⁷Jiang, S. B., Liao, G. Y., Qu, X. L. and She, W. N. *Chemical Engineering*, **2001**, 5, 6.
- ²⁸Jiang, S. B., Liao, G. Y., She, W. N. and Qu, X. L. *Petrochemical Technology & Application*, **2001**, 19(4), 238.
- ²⁹Jiang, S. B., Liao, G. Y., Qu, X. L. and She, W. N. *Chemical World*, **2001**, 42(1), 368.
- ³⁰Li, D. J. and Fu, H. Q. *Science & Technology in Chemical Industry*, **2005**, 13(3), 20.

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