Article ID: 1001-3555(2007)02-0139-05

Catalytic Acylation of Anisole over Co-catalysts

ZHAO Zhen-hua

(*Department of Bioengineering and Environmental Science, Changsha University, Changsha* 410003, *Hunan, China*)

Abstract: The co-catalysts was first used to catalyse the acylation reaction of anisole with an acylating agent, acetyl chloride. It was found that the single use of various zeolites gave only a very low yield of 4-methoxyacetophenone, but that the co-catalysts consisting of HY (SiO_2/Al_2O_3 molar ratio = 40) or USY zeolite and SnO possessed much higher activity than the use of zeolite only. Increasing the amount of SnO present in the co-catalysts consisting of USY zeolite and various amounts of SnO led to a rise in the yield of 4-methoxyacetophenone. The activity of the co-catalysts consisting of H form zeolites (HY, H-β and HZSM-5) and SnO in the reaction of anisole with acetyl chloride mainly depended upon the SiO_2/Al_2O_3 molar ratio of the zeolite used.

Key words: Catalytic acylation; Anisole; Acetyl chloride; 4-Methoxyacetophenone; Aromatic ketone; Co-catalysts

CLC number: O643.32 **Document code**: A

It is well known that Friedel-Crafts acylation is one of the most important methods for the synthesis of aromatic ketones[1]. Lewis acids or some other catalysts are applied in order to allow the reaction of anisole to proceed at a convenient rate. But, the use of some conventional catalysts, such as aluminium chloride, polyphosphoric acid, etc. results in a lot of problems such as corrosion, pollution and waste, and loss of the catalysts. On the other hand, the use of environmentally friendly catalysts such as solid catalysts can overcome many of those problems[2]. 4-Methoxyacetophenone (4-MAP) is one of important aromatic ketones and very important perfumes. It has widely been applied in the perfume etc. industries. 4-Methoxyacetophenon can be prepared by the acylation reaction of anisole with an acylating agent in the presence of a catalyst. It is very interesting to see whether recoverable solid catalysts could be used to catalyse the reaction of anisole with an acylating agent. The acylation of anisole by acyl chlorides or carboxylic acids over 1 g of zeolite per mmol substrate in 50 mL of solvent gives modest yields of the acylated product[3]. The acylation of anisole with carboxylic acids over HZSM-5 zeolite at reflux for 48 h was reported to give two products, p-$RCOC_6H_4OMe$ and RCO_2Ph[4]. Wang et al.[5] reported zeolite-catalyzed Friedel-Crafts reaction of anisole with carboxylic acids. The zeolites used by them included HY zeolites with two different framework Si/Al ratios, 5.0 and 9.1, respectively, and HZSM-5 with a framework Si/Al ratio of 30. Another literature also reported the use of zeolites as catalysts in the acylation of anisole[6]. The liquid phase acetylation of anisole with acetic anhydride over a HBEA zeolite was described[7], and the aim of this paper[7] was to understand the origin of the deactivation of the HBEA zeolite (Si/Al = 10) during the acylation. Yin et al.[8,9] reported the regioselectivity and catalytic activity of Friedel-Crafts acylation of anisole using microwave modified $ZnCl_2$/HY zeolite catalysts.

Clearly, there is still considerable scope for development of superior methods which could be applicable on a commercial scale. The co-catalysts was first used

Received date: 2006-02-09; **Revised date**: 2006-06-12.

Biography: Zhao Zhen-hua, male, born in 1943, Ph. D. (obtained in the UK), and Professor.
E-mail: zhaozh@hunnu.edu.cn. Tel.: 0731-8871591.

to catalyse the acylation reaction of anisole with acetyl chloride. In this paper, we would like to report our results obtained from the acylation reaction of anisole by acetyl chloride in the presence of co-catalysts.

1 Experimental

1.1 Main chemicals

Anisole (99%, Lancaster) and acetyl chloride (98%, Aldrich) were used.

1.2 Catalyst

All heterogeneous catalysts used in this work were activated in an air atmosphere at 400 ℃ or higher temperatures for 2-3 h prior to use.

1.3 General procedure for catalytic acylation reaction of anisole

The co-catalysts was added to a solution consisting of anisole, and a fixed amount of acetyl chloride (4 mmol). The mixture was stirred at 25 ℃ or under heating for a given time. The reaction products were filtered after a certain reaction time, and the co-catalysts was washed 4 times with diethyl ether. The filtrate and washings were combined and evaporated on a rotary evaporator. The obtained residue was analysed by GC, or purified further by distillation under reduced pressure.

The yield of 4-methoxyacetophenone was determined by GC. The GC conditions used were as follows: Apiezon for stationary phase, column length 2 m, column temperature 175 ℃, and carrier gas (N_2) flow rate 35 mL/min.

1.4 Characterization and analysis of the acylated product

The ^1H NMR spectra were recorded in $CDCl_3$ solution at 400 MHz using a Bruker AC-400 instrument. ^{13}C NMR spectra were taken on a Bruker AC-400 spectrometer at 100 MHz. J values were given in Hz. IR spectra were recorded on a Perkin-Elmer 1 725 X FT-IR Spectrometer. The mass spectra were obtained at the EPSRC Mass Spectrometry Centre, University of Wales Swansea, UK, by means of electron impact (EI) and ammonia chemical ionization (CI) techniques. The melting point was determined on a Griffin melting point apparatus, and was uncorrected.

2 Results and Discussion

2.1 Comparison of the activities for different catalysts

To compare the activities of various catalysts, keeping anisole/acetyl chloride molar ratio = 1/1, a series of catalysts was used for the reaction of anisole with acetyl chloride. Table 1 summarizes the results obtained.

Table 1 Comparison of catalytic activities for different catalysts[a]

Catalyst	G or mmol catalyst (mmol anisole)	Reaction temp. (℃)	Reaction time (h)	Yield of 4-MAP (%)	Conversion of anisole (%)	Selectivity for 4-MAP (%)
HY	0.100 g	75	1	4.7	4.8	98
USY	0.050 g	25	2	1.2	1.22	98
P_2O_5	0.500 mmol	25	1	2.9	3.3	88
$ZnCl_2$	0.500 mmol	25	1	15.1	16.4	92
$SnCl_2 \cdot 2H_2O$	0.500 mmol	25	1	7.9	8.6	92
H_3PO_4	0.500 mmol	25	1	2.5	2.8	89
PPA[b]	0.500 mmol	25	1	2.1	2.4	88

[a]The zeolites were calcined at 400 ℃ for 2.5 h prior to use.

[b]Polyphosphoric acid

The results listed in Table 1 indicate that only $ZnCl_2$ possessed higher catalytic activity, while all the zeolites gave only very low yields of 4-methoxyacetophenone even in the case of heating. This could be due to formation of HCl during the reaction, which inhibits the reaction to proceed further. But zeolites showed the highest selectivity for 4-methoxyacetophenone within all the catalysts studied. The zeolites were therefore studied further by modifying.

2.2 Co-catalysts consisting of zeolite and oxide

To improve the catalytic activities of the zeolites, the zeolite was first mixed with an oxide, and then cal-

cined at a certain temperature for a given time, preparing a co-catalysts. The co-catalysts consisting of HY zeolite and various oxides were applied to catalyse the reaction of anisole with acetyl chloride. Tables 2 and 3 list the results achieved, respectively..

The results given in Table 2 show that the use of single HY zeolite in the reaction of anisole with acetyl chloride gave only a very low yield of 4-methoxyacetophenone, the co-catalysts consisting of HY zeolite and SnO exhibited much higher activity than HY zeolite only, the co-catalysts consisting of HY zeolite and ZnO gave better yield of 4-methoxyacetophenone than HY only, but the co-catalysts consisting of HY zeolite and MgO gave a poor yield of 4-methoxyacetophenone.

Table 2 Reaction of anisole with acetyl chloride over co-catalysts[a,b]

Catalyst	Yield of 4-MAP (%)
HY only	6.9
HY + SnO	45.8
HY + MgO	4.4
HY + ZnO	20.1

[a] HY zeolite (SiO_2/Al_2O_3 = 40) and oxide were first mixed, and then calcined at 400 ℃ for 3 h prior to use.

[b] All reactions were carried out using (0.400 g HY zeolite + 4 mmol oxide), acetyl chloride (4 mmol), anisole (48 mmol), i.e. (0.100 g HY zeolite + 1 mmol oxide)/1 mmol acetyl chloride/12 mmol anisole at 25 ℃ for 3 h.

Table 3 Reaction of anisole with acetyl chloride over co-catalysts[a,b]

Catalyst	Yield of 4-MAP (%)
USY + SnO	42.0
USY + Al_2O_3	2.8
USY + ZnO	21.0
USY + MgO	3.4
USY + Synclyst 13[c]	3.0

[a] All reactions were carried out using (0.100 g USY zeolite + 1 mmol oxide)/1 mmol acetyl chloride/12 mmol anisole at 25 ℃ for 5 h.

[a] USY zeolite was first mixed with oxide, and then calcined at 400 ℃ for 3 h prior to use.

[c] An amorphous solid compound containing Si, Al and O etc. elements

The results listed in Table 3 show that the co-catalysts consisting of USY zeolite and SnO possessed the highest activity, while the co-catalysts consisting of USY zeolite and other oxides besides ZnO gave only very low yields of 4-methoxyacetophenone.

Therefore, SnO was selected for further studying co-catalysts.

2.3 Comparison of the catalytic activities for various co-catalysts consisting of different zeolites and SnO

The co-catalysts consisting of SnO and various zeolites were used for the reaction of anisole with acetyl chloride at the same ratios of co-catalysts/anisole/acetyl chloride in order to compare their activities. Table 4 summarizes the results obtained.

Table 4 Comparison of the catalytic activities for various co-catalysts consisting of different zeolites and SnO[a,b]

Zeolite in co-catalysts	SiO_2/Al_2O_3 (mol. ratio)	Yield of 4-MAP (%)
USY	Unknown	42.1
H-β	25	40.0
HY	5.0	16.0
HY	5.2	16.3
HY	12	29.2
HY	40	43.1
HY	53	49.0
HY	80	49.4
H-ZSM-5	80	44.0

[a] Zeolite was first mixed with SnO, and then calcined at 400 ℃ for 3 h prior to use.

[b] All reactions were carried out using (0.100 g zeolite + 1 mmol SnO)/12 mmol anisole/1 mmol acetyl chloride at 25 ℃ for 5 h.

The results listed in Table 4 suggest that the yields of 4-methoxyacetophenone obtained mainly depended upon the SiO_2/Al_2O_3 ratio of the zeolite in the co-catalysts, i.e. in general, the yield of 4-methoxyacetophenone increased with a rise in the SiO_2/Al_2O_3 ratio of the zeolite. It is well known that an increase in the SiO_2/Al_2O_3 ratio of the zeolite generally leads to a rise in the strength of its acid sites. Therefore, we conclude that the acylation reaction of anisole with acetyl chloride could mainly be catalysed by the strong acid sites. While the structure of the zeolite produced only a little

effect on the reaction.

2.4 Effect of the amount of SnO present in the co-catalysts

To investigate the effect of the amount of SnO present in the co-catalysts consisting of SnO and USY zeolite on the reaction, a series of tests was performed by varying the amount of SnO but keeping the amount of USY zeolite and the ratio of anisole/acetyl chloride constant. The results obtained are given in Table 5.

It is clear from Table 5 that the yield of 4-methoxyacetophenone increased with a rise in the amount of SnO present in the co-catalysts.

Table 5 Effect of the amount of SnO present in co-catalysts[a,b]

Run	Amount of SnO (mmol/mmol acetyl chloride)	Yield of 4-MAP (%)
1	0.1	19.0
2	0.2	22.1
3	0.3	24.3
4	0.4	28.0
5	0.5	34.1
6	0.6	38.1
7	0.8	39.2
8	0.9	42.1
9	1.0	43.2

[a] USY zeolite was mixed with SnO, and then calcined at 400 ℃ for 3 h prior to use.

[b] All reactions were carried out using (0.100 g USY zeolite + various amounts of SnO)/12 mmol anisole/1 mmol acetyl chloride at 25 ℃ for 3 h.

2.5 Effect of the amount of anisole

In addition, the effect of the amount of anisole on the reaction in the presence of the co-catalysts consisting of HY zeolite (SiO_2/Al_2O_3 = 40) and SnO has been examined. Table 6 shows the results obtained.

Table 6 Effect of the amount of anisole[a,b]

Anisole/acetyl chloride (mol. ratio)	Yield of 4-MAP (%)
4/1	30.1
6/1	33.1
12/1	43.2

[a] HY zeolite was first mixed with SnO, and then calcined at 400 ℃ for 3 h prior to use.

[b] All reactions were carried out using (0.100 g HY zeolite + 1 mmol oxide)/1 mmol acetyl chloride at 25 ℃ for 5 h.

It is clear from Table 6 that when the molar ratio of anisole/acetyl chloride = 12/1, the reaction gave the highest yield of 4-methoxyacetophenone.

3 Conclusions

The co-catalysts consisting of HY (SiO_2/Al_2O_3 molar ratio = 40) or USY zeolite and SnO exhibited much higher activity than the use of zeolite only. A rise in the amount of SnO present in the co-catalysts consisting of USY zeolite and various amounts of SnO resulted in an increase in the yield of 4-methoxyacetophenone. The activity of the co-catalysts consisting of H form zeolites (HY, H-β and H-ZSM-5) and SnO in the reaction of anisole with acetyl chloride mainly depended upon the SiO_2/Al_2O_3 molar ratio of the zeolite used.

Acknowledgements

The author would like to thank Professor K. Smith of Chemistry Department at University of Wales Swansea for his supervision and guidance, Dr. Philip K. G. Hodgson at BP Company for his useful discussion, the British Government for an ORS Award, BP for financial support, the EPSRC Mass Spectrometry Centre at Swansea for mass spectra, and the EPSRC and the University of Wales for grants which enabled the purchase of the NMR equipment used in the course of this work.

References:

[1] Olah G A, Friedel-Crafts Chemistry [M], Wiley-Interscience, New York, 1973

[2] Clark J H, Cullen S R, Barlow S J, Bastock T W. *J.*

Chem. Soc., *Perkin Trans.* 2 [J], 1994,1 117
[3] Corma A, Climent M J, Garcia H, Primo J. *Appl. Catal.* A [J], 1989, **49**: 109
[4] Wang Q L, Ma Y D, Ji X D, *et al. J. Chem. Soc.*, *Chem. Commun.* [J], 1995, 2 307
[5] Wang Q L, Ma Y D, Zuo B J. *Chin. J. Catal.* [J], 1996, **17**(5): 425
[6] Ma Y D, Wang Q L, Jiang W, Zuo B J. *Appl. Catal.* A [J], 1997, **165**: 199
[7] Rohan D, Canaff C, Fromentin E, Guisnet M. *J. Catal.* [J], 1998, **177**: 296
[8] Yin D H, Yin D L, Fu Z H. *J. Mol. Catal.* (China) [J], 1998, **12**(6): 401
[9] Yin D H, Yin D L, Fu Z H, Li Q H. *Chin. J. Catal.* [J], 2002, **23**(6): 567

苯甲醚在复合催化剂上的催化酰化

赵振华
（长沙大学　生物工程与环境科学系，湖南 长沙 410003）

摘　要：复合催化剂首次用于催化苯甲醚与酰化剂乙酰氯的酰化反应. 发现不同沸石的单独使用仅给出很低产率的对-甲氧基苯乙酮. 但是由 HY 沸石（硅铝比 = 40）或 USY（超稳 Y 沸石）和 SnO 组成的复合催化剂的催化活性比单独使用沸石时高得多. 增加由 USY 沸石和不同量的 SnO 组成的复合催化剂中的 SnO 的量，导致对-甲氧基苯乙酮产率的提高. 由 H 型沸石（HY 和 H-ZSM-5 沸石）和 SnO 组成的复合催化剂在苯甲醚与乙酰氯的酰化反应中的催化活性主要取决于所用沸石的硅铝比.

关　键　词：催化酰化；苯甲醚；乙酰氯；对-甲氧基苯乙酮；芳香酮；复合催化剂