CHEMCOMM
Communication
www.rsc.org/chemcomm

Calcium oxide and strontium oxide as environmentally benign and highly efficient heterogeneous catalysts for the Tishchenko reaction of furfural

Tsunetake Seki, Kazumasa Akutsu and Hideshi Hattori*

Center for Advanced Research of Energy Technology, Hokkaido University, Kita-13, Nishi-8, Kita-ku, Sapporo 060-8628, Japan. E-mail: hattori@carbon.caret.hokudai.ac.jp

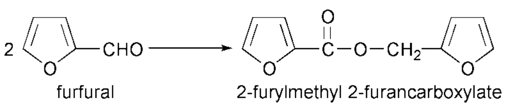
Received (in Cambridge, UK) 13th March 2001, Accepted 24th April 2001
First published as an Advance Article on the web 15th May 2001

CaO and SrO exhibit high activities for the challenging Tishchenko reaction of furfural.

The Tishchenko reaction is dimerization of aldehydes to yield the corresponding esters by the action of aluminium alkoxides.[1–5] For about a century, a number of catalysts for the Tishchenko reaction of various types of aldehydes have been developed to obtain the product esters in high yields. While many aldehydes have been converted to the Tishchenko dimers in good yields, few studies have been successfully carried out on the Tishchenko reaction of furfural. This reaction has been reported to be difficult when carried out using traditional aluminium alkoxides, boric acid or tetracarbonylferrate(−II) as catalysts.[2,6,7] Recently, some homogeneous catalysts such as $(C_5Me_5)_2LaCH(SiMe_3)_2$ and $La[N(SiMe_3)_2]_3$ have been reported to be effective for the Tishchenko reaction of furfural, though these catalysts require a long reaction time to give the product ester in a synthetically satisfactory level of yield.[8,9] In addition, removal of those homogeneous catalysts from the resulting solution causes loss of catalyst and reduction of the product yields. Moreover, in view of environmental concerns, avoidance of use of toxic transition metal catalysts in industrial processes is encouraged. Herein, we report environmentally benign, highly effective heterogeneous catalysts for the Tishchenko reaction of furfural. The general reaction equation is shown in Scheme 1.

Alkaline earth oxides, MgO, CaO, SrO and BaO, were prepared from $Mg(OH)_2$, $Ca(OH)_2$, $SrCO_3$ and $BaCO_3$, respectively, by thermal decomposition at elevated temperatures *in vacuo*. Lanthanum oxide was prepared from $La(OH)_3$ by the same procedure as the alkaline earth oxides, the $La(OH)_3$ being obtained from an aqueous solution of $La(NO_3)_3$ upon hydrolysis with aqueous ammonia, followed by washing with distilled water and drying at 373 K. ZrO_2 and ZnO were prepared from $Zr(OH)_4$ and $Zn(OH)_2$, respectively, by thermal decomposition at elevated temperatures *in vacuo*. γ-Alumina used as a catalyst and as a KOH/alumina-supported catalyst was supplied from the Catalysis Society of Japan (JRC-ALO4). Hydrotalcite (Mg/Al = 2) was synthesized as reported.[10] Alumina-supported KF (KF/alumina) was purchased from Fluka, and its KF content was determined as 8.2 mmol g^{-1} by XRF. Alumina-supported KOH catalyst (KOH/alumina) was prepared by impregnation of γ-alumina (JRC-ALO4) with an aqueous solution of KOH, followed by drying at 373 K in air; the KOH content was 1.2 mmol g^{-1}. The pretreatment temperatures and surface areas of the catalysts examined are listed in Table 1.

Furfural was purchased from Aldrich, and was purified by distillation under a reduced pressure.



Scheme 1 Tishchenko reaction of furfural.

The reaction was carried out in an H-shaped glass batch reactor. The two branches of the reactor were separated by a breakable seal. A sample of the catalyst precursor was placed in one branch, outgassed at an elevated temperature for 2 h, and sealed. The reactant was stored in the other branch until it was introduced through the breakable seal by distillation into the branch containing the catalyst thermostated at liquid nitrogen temperature. Reaction was initiated by melting the reactant at a reaction temperature followed by stirring. The product was identified by ^1H NMR and GC–MS analysis. GC analyses to determine yields of the product ester were carried out using a column of DB-1 (total length: 60 m; diameter: 0.25 mm).

Table 1 shows the activities of solid base catalysts for the Tishchenko reaction of furfural when the reaction was carried out with 100 mg of catalyst using 10 mmol of furfural as reactant. Among the solid base catalysts examined, only CaO and SrO gave the product ester in high yields. When the reaction was carried out at 353 K for 6 h in the presence of 100 mg of SrO, the product ester was obtained in almost quantitative yield. To our knowledge, there have been no reports of catalysts giving the Tishchenko dimer in > 77% yield.[8] Even at a lower reaction temperature of 323 K, the product ester was obtained in a yield of 70% over SrO. In addition to the high activities, the catalytic selectivities of CaO and SrO to 2-furylmethyl 2-furancarboxylate were almost 100%. This clearly emphasizes that CaO and SrO are highly efficient for the Tishchenko reaction of furfural. Although MgO and BaO were reported to

Table 1 Activities of solid base catalysts for the Tishchenko reaction of furfural[a]

Catalyst	Pretreatment temperature/K	Surface area/ $m^2\ g^{-1}$	Yield[b] (%)
MgO	873	267	< 1
CaO	873	48	61
CaO	873	48	78[c]
SrO	1273	12	83
SrO	1273	12	95[c]
SrO	1273	12	70[d]
BaO	1273	2	0
La_2O_3	873	33	0
ZrO_2	873	42	0
ZnO	873	2	0
γ-Alumina	773	173	0
Hydrotalcite (Mg/Al = 2)	673	118	0
Fluka-KF/alumina	673	40	0
1.2 mmol g^{-1}-KOH/alumina	873	160	0

[a] Catalyst weight, 100 mg; furfural, 10 mmol; reaction temp., 353 K; reaction time, 4 h. [b] Yield was determined by the GC analysis of the resulting solution and was calculated by the equation: yield (%) = $\{[2 \times (\text{mol\% of 2-furylmethyl 2-furancarboxylate})]/[(\text{mol\% of furfural}) + 2 \times (\text{mol\% of 2-furylmethyl 2-furancarboxylate})]\} \times 100$. [c] Reaction time, 6 h. [d] Reaction temp., 323 K; reaction time, 12 h.

DOI: 10.1039/b102389f

be active for the Tishchenko reaction of other aldehydes such as benzaldehyde and pivalaldehyde,[11,12] they were inactive for the present reaction. Based on a previous study,[11] it is conjectured that both basic (O^{2-}) and acidic (metal cation) sites on alkaline earth oxides participate in the Tishchenko reaction of furfural. The strength of basic sites lies in the order MgO < CaO < SrO < BaO, while that of acidic sites is in the opposite order. Thus, it appears that CaO and SrO having moderate acidic and basic sites in comparison with MgO and BaO are appropriate for the dimerization of furfural.

Other solid base catalysts such as La_2O_3, ZrO_2, ZnO, γ-alumina, hydrotalcite, KF/alumina and KOH/alumina were all inactive for the Tishchenko reaction of furfural. Although KF/alumina has been reported to show high activities for the Tishchenko reaction of benzaldehyde and pivalaldehyde,[12,13] it was not active at all for the Tishchenko reaction of furfural.

This work is supported by a Grant-in aid for Scientific Research of Ministry of Education, Science, Sports, and Culture, Japan.

Notes and references

1 W. Tischtschenko, *Chem. Zentralbl.*, 1906, **77**, **I**, 1309.

2 W. C. Child and H. Adkins, *J. Am. Chem. Soc.*, 1925, **47**, 798.

3 F. J. Villani and F. F. Nord, *J. Am. Chem. Soc.*, 1947, **69**, 2605.

4 L. Lin and A. R. Day, *J. Am. Chem. Soc.*, 1952, **74**, 5133.

5 T. Saegusa and T. Ueshima, *J. Org. Chem.*, 1968, **33**, 3310.

6 P. R. Stapp, *J. Org. Chem.*, 1973, **38**, 1433.

7 M. Yamashita, Y. Watanabe, T-a. Mitsudo and Y. Takegami, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 3597.

8 S. Onozawa, T. Sakakura, M. Tanaka and M. Shiro, *Tetrahedron*, 1996, **52**, 4291.

9 H. Berberich and P. W. Roesky, *Angew. Chem., Int. Ed.*, 1998, **37**, 1569.

10 S. Miyata, T. Kumura, H. Hattori and K. Tanabe, *Nippon Kagaku Zasshi*, 1971, **92**, 514.

11 K. Tanabe and K. Saito, *J. Catal.*, 1974, **35**, 247.

12 H. Kabashima, H. Tsuji, S. Nakata, Y. Tanaka and H. Hattori, *Appl. Catal., A*, 2000, **194–195**, 227.

13 H. Handa, T. Baba, H. Sugisawa and Y. Ono, *J. Mol. Catal.*, 1998, **134**, 171.