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Effective Aerobic Oxidation of Alcohols over Chromium Containing Mesoporous Molecular Sieve Catalyst with Supercritical Carbon Dioxide and Polyethylene Glycol Biphasic Reaction System

Sudhir E. Dapurkar,* Hajime Kawanami,* Toshishige M. Suzuki, Toshirou Yokoyama, and Yutaka Ikushima
Research Center for Compact Chemical Process, National Institute of Advanced Industrial Science and Technology (AIST),
4-2-1 Nigatake, Miyagino-ku, Sendai 983-8551

(Received November 7, 2007; CL-071231; E-mail: s-dapurkar@aist.go.jp; h-kawanami@aist.go.jp)

Aldehyde and ketone were selectively obtained by aerobic oxidation of alcohols over mesoporous CrMCM-41 catalyst with supercritical carbon dioxide and polyethylene glycol ($scCO_2$/PEG) as a biphasic reaction system.

Oxidation of alcohols to the corresponding oxo-compounds are of primary industrial importance.[1] Traditionally, these transformations are carried out in organic solvents using stoichiometric amounts of toxic chromium(VI) reagents.[2] Even though these reagents show good oxidative performance, problems related to corrosion, handling, recovery, and reuse of the reagent set up limitations of their use at industrial scale. Therefore, the introduction of heterogeneous catalytic processes with alternative solvents is one of the main objectives of current industrial and academic research. In this context, using supercritical carbon dioxide as reaction medium to perform the oxidation of alcohols by O_2 with many heterogeneous catalysts, based on noble and rare metals have been reported.[3] However, these catalysts are expensive and some of them are deactivated easily. Recently, supported chromium trioxide (Cr/SiO_2) has been used for the catalytic oxidation of alcohols using $scCO_2$.[4] In this case, chromic oxide is used as an oxidizing agent but the handling of the catalyst could be a problem and also Cr-species can detach from the support. In view of the concerns related to the toxicity of Cr^{VI} compounds, Cr-based (heterogeneous) molecular sieve catalysts, such as CrSilicalite-1,[5] CrAPO-5,[6] CrBeta,[7] CrHMS,[8] CrMCM-41,[9,10a] CrMCM-48,[10b] etc., can be some of the alternative catalysts. Among the various chromium catalysts mentioned above, it was found that the mesoporous molecular sieve can stabilize the active chromium species and thus facilitate the catalyst reusability/separation from the product.[10]

In this investigation, we studied the oxidation of alcohols by molecular oxygen over mesoporous CrMCM-41 catalyst with $scCO_2$/PEG biphasic reaction system. CrMCM-41 catalyst having 2.5 wt % chromium was prepared as described previously with slight modification in molar gel composition.[10a] Oxidation of alcohols were carried out in a stainless steel high pressure reactor equipped with a Teflon insert. In a typical experiment, 1-mmol alcohol, 0.1-g CrMCM-41, and 0.5-mL PEG-400 were placed inside the reactor vessel. To start the reaction, the reactor was charged with 0.5-MPa O_2 and CO_2 upto 16 MPa (The detail catalyst synthesis and reaction procedure is given in Supporting Information).[11]

Powder XRD patterns of catalyst CrMCM-41 shows four well-resolved reflections, (100), (110), (200), and (210), characteristics of hexagonal MCM-41 structure (Figure S1 in Supporting Information).[11] The specific surface area, pore volume, and pore diameter were determined from N_2 adsorption isotherm for CrMCM-41 which was found to be $1250\,m^2\cdot g^{-1}$, 1.06 $cm^3\cdot g^{-1}$, and 2.4 nm, respectively. Other characterizations of the catalyst are discussed in detail in previous work.[10] Figure 1 shows the results of benzyl alcohol oxidation over CrMCM-41 with various reaction systems. It can be seen from the figure that the catalyst shows poor activity in $scCO_2$ (at 16 MPa total pressure), further over wide range of CO_2 pressure from 10 to 18 MPa, the conversion remains less than 10%. The addition of co-solvent (0.5 mL of acetone) does not improve the catalytic performance. Recently, $scCO_2$/PEG biphasic system has been proved to be effective for oxidation reactions.[3d,12] So we tested this biphasic system for alcohol oxidation. The addition of PEG dramatically promotes the reaction and gives 91% conversion with 84% benzaldehyde yield. The reaction was also performed using only PEG as well as acetonitrile (3-mL ACN) as a solvent. However, the conversion was low compared to the reaction carried out in $scCO_2$/PEG.

To determine the optimum reaction conditions, we studied the effect of reaction time, temperature, and oxygen concentration on conversion of benzyl alcohol. Figure 2 shows the effect of reaction temperature on conversion of benzyl alcohol. As expected, with increasing temperature from 333 to 373 K, the conversion increases but the selectivity of benzaldehyde decreases. This is due to the further auto-oxidation of benzaldehyde into benzoic acid. This was also confirmed by increasing the O_2 pressure from 0.5 to 2 MPa at 353 K, where remarkable decrease from 92 to 75% in benzaldehyde selectivity was noticed. Similar observation was also made in earlier study.[3a]

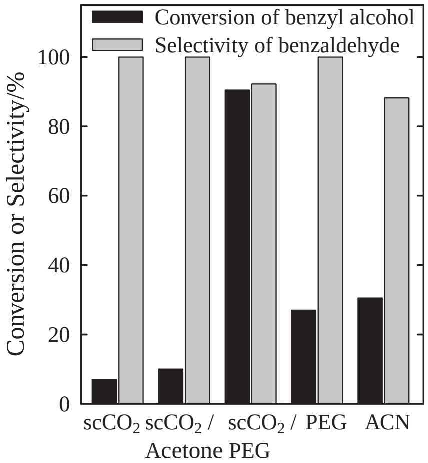

Figure 1. Oxidation of benzyl alcohol by molecular oxygen over CrMCM-41 with various solvent system (1-mmol benzyl alcohol; 0.1-g CrMCM-41; $T = 353\,K$; $t = 14\,h$).

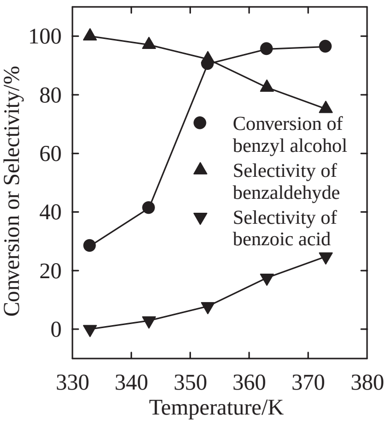

Figure 2. Effect of reaction temperature on benzyl alcohol oxidation over CrMCM-41 using $scCO_2$/PEG ($t = 14$ h).

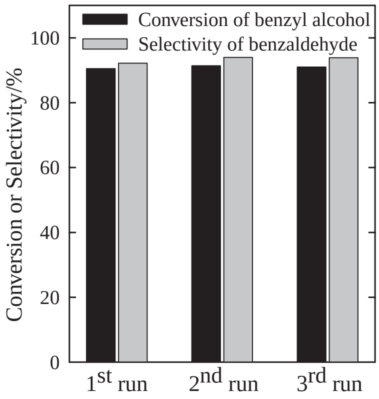

Figure 3. Recycling study of CrMCM-41 for benzyl alcohol oxidation using $scCO_2$/PEG ($T = 353$ K; $t = 14$ h).

Similarly, with increasing reaction duration from 4 to 24 h, conversion reaches maximum in 14 h with no further improvement in conversion with slight decrease in benzaldehyde selectivity. Following are the optimized reaction conditions: reaction temperature, 353 K; reaction time, 14 h; oxygen pressure, 0.5 MPa.

To check the reusability of the CrMCM-41 catalyst, recycling experiment was carried out for the oxidation of benzyl alcohol using $scCO_2$/PEG under optimized reaction conditions and results are shown in Figure 3. It is noteworthy here that the catalytic activity remains nearly the same even after the third run.

Furthermore, the structure of CrMCM-41 remains intact after the reaction which is confirmed by XRD. (Figure SI Supporting Information).[11] In the case of using 2.5 wt % Cr/SiO_2,[4] the catalyst activity was decreased upon recycling from 90 to 60%, owing to the leaching of chromium. Therefore, the CrMCM-41 catalyst in this reaction system can be used for the effective oxidation with molecular oxygen.

Table 1. Oxidation of benzylic and aliphatic secondary alcohol over CrMCM-41 using $scCO_2$/PEG[a]

Substrate	Product	Conv. /%	Sel. /%
1-Indanol	1-Indanone	>99	>99
1-Tetralol	1-Tetralone	>97	>99
Cyclooctanol	Cyclooctanone	40	>99
Cyclododecanol	Cyclododecanone	46	>99

[a] 1-mmol alcohol; 0.1-g CrMCM-41; 0.5-mL PEG; 0.5-MPa O_2; 16 MPa total pressure; $T = 353$ K; $t = 14$ h.

We also tested few benzylic and aliphatic secondary alcohol oxidations over CrMCM-41 using $scCO_2$/PEG under optimized reaction conditions. Table 1 summarizes the results of benzylic and aliphatic secondary alcohol oxidation over CrMCM-41 with molecular oxygen. It can be seen from this table that benzylic alcohol, viz. 1-indanol and 1-tetralol are oxidized almost completely and gave >99% ketone selectivity. In the case of aliphatic secondary alcohol, viz. cyclooctanol and cyclododecanol, the conversion of ketones was obtained as 40 and 46%, respectively. However, without PEG these secondary alcohols were almost unreactive.

In summary, we demonstrated that mesoporous CrMCM-41 catalyst with $scCO_2$/PEG biphasic reaction system is efficient and reusable for the aerobic oxidation of benzylic alcohols.

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