Alkane Oxidation Catalysis by Homogeneous and Heterogeneous Catalysts

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Abstract

Cobalt-based complexes are widely used in industry and organic synthesis as catalysts for the oxidation of hydrocarbons. The Co/Mn/Br (known as "CAB system") catalyst system is effective for the oxidation of toluene. The Co/Mn/Br/Zr catalyst system is powerful for the oxidation of *p*-xylene, but not for the oxidation of toluene. $[Co_3O(OAc)_5(OH)(py)_3][PF_6]$ (Co^{3+} trimer 5) is more effective than $[Co_3O(OAc)_6(py)_3][PF_6]$ (Co^{3+} trimer 6) as a catalyst in the CAB catalyst system. Higher temperatures favour the oxidation of toluene. Zr^{4+} does not enhance the oxidation of toluene. Zr^{4+} could inhibit the oxidation of toluene in the combination of Co/Br/Zr, Co/Mn/Zr or Co/Zr. NHPI enhances the formation of benzyl alcohol, but the formation of other by-products is a problem for industrial processes. Complex(es) between cobalt, manganese and zirconium might be formed during the catalytic reaction. However, attempts at the preparation of complexes consisting of Co/Zr or Mn/Zr or Co_3ZrP or Co_8Zr_4 clusters failed.

The oxidation of cyclohexane to cyclohexanone and cyclohexanol is of great industrial significance. For the homogeneous catalysis at 50 ^oC and 3 bar N_2 pressure, the activity order is: $Mn(OAc)_3 \bullet 2H_2O$ > $Mn_{12}O_{12}$ cluster > Co^{3+} trimer 6 > $[Co_3O(OAc)_3(OH)_2(py)_5][PF_6]_2$ (Co^{3+} trimer 3) > Co^{3+} trimer 5 > $Co(OAc)_2 \bullet 4H_2O$ > $[Co_2(OAc)_3(OH)_2(py)_4][PF_6]_{-asym}$ (Co $dimer_{asym}$) > $[Co_2(OAc)_3(OH)_2(py)_4][PF_6]_{-sym}$ (Co $dimer_{sym}$); whereas $[Mn_2CoO(OAc)_6(py)_3] \bullet HOAc$ (Mn_2Co complex) and zirconium(IV) acetate hydroxide showed almost no activity under these conditions. But at 120 ^oC and 3 bar N_2 pressure, the activity order is changed to: Co $dimer_{asym}$ > $Co(OAc)_2 \bullet 4H_2O$ > Co trimer 3 and $Mn(OAc)_3 \bullet 2H_2O$ > Co^{3+} trimer 6 > Mn_2Co complex > Co^{3+} trimer 5 > Co $dimer_{sym}$ > $Mn_{12}O_{12}$ cluster. The molar ratio of the products was close to cyclohexanol/cyclohexanone=2/1. Mn(II) acetate and zirconium(IV) acetate hydroxide showed almost no activity under these conditions. Among those cobalt dimers and trimers, only the cobalt $dimer_{asym}$ survived after the stability tests, this means that $[Co_2(OAc)_3(OH)_2(py)_4][PF_6]_{-asym}$ might be the active form for cobalt(II) acetate in the CAB system.

Metal-substituted (silico)aluminophosphate-5 molecular sieves (MeAPO-5 and MeSAPO-5) are important heterogeneous catalysts for the oxidation of cyclohexane. The preparation of MeAPO-5 and MeSAPO-5 and their catalytic activities were studied. Pure MeAPO-5 and MeSAPO-5 are obtained and characterised. Four new pairs of bimetal-substituted MeAPO-5 and MeSAPO-5(CoZr, MnZr, CrZr and MnCo) were prepared successfully. Two novel trimetal-subtituted MeAPO-5 and MeSAPO-5 (MnCoZr) are reported here. Improved methods for the preparation of four monometal-substituted MeAPO-5 (Cr, Co, Mn and Zr) and for CoCe(S)APO-5 and CrCe(S)APO-5 are reported. Novel combinational mixing conditions for the formation of gel mixtures for Me(S)APO-5 syntheses have been developed.

For the oxidation of cyclohexane by TBHP catalysed by MeAPO-5 and MeSAPO-5 materials, CrZrSAPO-5 is the only active MeSAPO-5 catalyst among those materials tested under conditions of refluxing in cyclohexane. Of the MeAPO-5 materials tested, whereas CrCeSAPO-5 has very little activity, CrZrAPO-5 and CrCeAPO-5 are very active catalysts under conditions of refluxing in cyclohexane. MnCoAPO-5, MnZrAPO-5 and CrAPO-5 are also active. When Cr is in the catalyst system, the product distribution is always cyclohexanone/cyclohexanol=(2-3)/1, compared with 1/2 for other catalysts. For MeAPO-5, the activity at 150 ^{o}C and 10 bar N_2 pressure is: CrZrAPO-5 > CrCeAPO-5 > CoZrAPO-5. For MeAPO-5 and MeSAPO-5, at 150 ^{o}C and 13 bar N_2 pressure, the selectivity towards cyclohexanone is: CrZrAPO-5 > CrZrSAPO-5 > CrCeAPO-5 > CrAPO-5 > MnCoAPO-5 > MnZrAPO-5; and the selectivity towards cyclohexanol is: MnZrAPO-5 > CrZrAPO-5 > MnCoAPO-5 > CrZrSAPO-5 > CrCeAPO-5 > CrAPO-5. Overall the selectivity towards the oxidation of cyclohexane is: CrZrAPO-5 > CrZrSAPO-5 > CrCeAPO-5 > CrAPO-5 > MnCoAPO-5 > MnZrAPO-5. The amount of water in the system can affect the performance of CrCeAPO-5, but has almost no effect on CrZrAPO-5. Metal leaching is another concern in potential industrial applications of MeAPO-5 and MeSAPO-5 catalysts. The heterogeneous catalysts prepared in the present work showed very little metal leaching. This feature, coupled with the good selectivities and effectivities, makes them potentially very useful.

Abbreviations

AAS	atomic absorption spectra
Ac_2O	acetic anhydride
AIBN	2,2´-azobis(2-methylpropionitrile)
$AlPO_4$	aluminophosphate molecular sieves
APO-5	aluminophosphate-5 molecular sieves
APO-36	aluminophosphate-36 molecular sieves
APO-n	aluminophosphate-based molecular sieves
[asym][PF_6]	[$Co_2(\mu\text{-}OH)_2(\mu\text{-}OAc)(OAc)_2(py)_4$][$PF_6$] $_{\text{-asym}}$ (Co $\text{dimer}_{\text{asmy}}$)
atm	atmosphere
CAB system	Co/Mn/Br catalyst system
Catapal A	a *pseudo*-boehmite phase comprising 72 wt.% Al_2O_3
4-CBA	4-carboxybenzaldehyde
CTAB	cetyltrimethylammonium bromide
CoAPOs	cobalt-substituted aluminophosphate molecular sieves
CoAPO-5	cobalt-substituted aluminophosphate-5 molecular sieves
CoAPO-11	cobalt-substituted aluminophosphate-11 molecular sieves
CoAPO-16	cobalt-substituted aluminophosphate-16 molecular sieves
CoAPO-18	cobalt-substituted aluminophosphate-18 molecular sieves
Co^{3+} trimer 3	[$Co_3O(OAc)_3(OH)_2(py)_5$][PF_6]$_2$
Co^{3+} trimer 5	[$Co_3O(OAc)_5(OH)(py)_3$][PF_6]
Co^{3+} trimer 6	[$Co_3O(OAc)_6(py)_3$][PF_6]
CoCeAPO-5	cobalt and cerium-substituted aluminophosphate-5 molecular sieves
CoCeSAPO-5	cobalt and cerium-substituted silicoaluminophosphate-5 molecular sieves
CoZrAPO-5	cobalt and zirconium-substituted aluminophosphate-5 molecular sieves
CoZrSAPO-5	cobalt and zirconium-substituted silicoaluminophosphate-5 molecular sieves
CrAPO-5	chromium-substituted aluminophosphate-5 molecular sieves
CrCeAPO-5	chromium and cerium-substituted aluminophosphate-5 molecular sieves

CrCeSAPO-5	chromium and cerium-substituted silicoaluminophosphate-5 molecular sieves
CrZrAPO-5	chromium and zirconium-substituted aluminophosphate-5 molecular sieves
CrZrSAPO-5	chromium and zirconium-substituted silicoaluminophosphate-5 molecular sieves
CyOOH	cyclohexyl hydroperoxide
1-D	one dimension
3-D	three dimension
DAE	2-diethylaminoethanol
DEA	diethanolamine
EDAX	energy dispersive X-ray fluorescence and electron backscattered diffraction
FAB	fast atom bombardment
g	gram
GC	gas chromatography
h	hour
HOAc	acetic acid
HPLC	high performance liquid chromatography
ICP	inductively coupled plasma analysis
Ionol®	2,6-di-*tert*-butyl-4-methylphenol
I.R.	infrared
K	Kelvin
L	liter
M	mol L^{-1}
mCPBA	*m*-chloroperbenzoic acid
MeAPO-n	metal-substituted aluminophosphate-n molecular sieves
MeAPO-5	metal-substituted aluminophosphate-5 molecular sieves
MeSAPO-5	metal-substituted silicoaluminophosphate-5 molecular sieves
min	minutes
mL	milliliter
MnAPO-5	manganese-substituted aluminophosphate-5 molecular sieves
Mn_2Co complex	$[Mn_2CoO(OAc)_6(py)_3]\bullet HOAc$

Mn_{12} cluster	$[Mn_{12}O_{12}(OAc)_{16}(H_2O)_4]\bullet 2HOAc\bullet 4H_2O$
MnCoAPO-5	manganese and cobalt-substituted aluminophosphate-5 molecular sieves
MnCoSAPO-5	manganese and cobalt-substituted silicoaluminophosphate-5 molecular sieves
MnCoZrAPO-5	manganese and cobalt and zirconium-substituted aluminophosphate-5 molecular sieves
MnCoZrSAPO-5	manganese and cobalt and zirconium-substituted silicoalumino phosphate-5 molecular sieves
MnZrAPO-5	manganese and zirconium-substituted aluminophosphate-5 molecular sieves
MnZrSAPO-5	manganese and zirconium-substituted silicoaluminophosphate-5 molecular sieves
NHPI	*N*-hydroxyphthalimide
NMR	nuclear magnetic resonance
OAc	acetate (CH_3COO^-)
PBS-1	sodium perborate monohydrate
PhCHO	benzaldehyde
PhCOOH	benzoic acid
^{i}Pr	isopropyl
1,2,4-pseudocumene	1,2,4-trimethylbenzene
Pseudo-boehmite	a hydrated aluminium oxide comprising 70 wt.% Al_2O_3
Pural SB	a *pseudo*-boehmite phase comprising 75.1 wt.% Al_2O_3
PX	*para*-xylene
py	pyridine
pyromellitic acid	1,2,4,5-benzenetetracarboxylic acid
QN	quinuclidine
S	total spin
SAPO-5	silicoaluminophosphate-5 molecular sieves
SEM	scanning electronic microscopy
[sym][PF_6]	$[Co_2(\mu\text{-}OH)_2(\mu\text{-}OAc)(OAc)_2(py)_4][PF_6]_{\text{-sym}}$ (Co $dimer_{sym}$)
TA	terephthalic acid
TBHP	*tert*-butyl hydroperoxide

TEA	triethylamine
TEAOH	tetraethylammonium hydroxide
TFA	trifluoroacetic acid
TMAOH	tetramethylammonium hydroxide
TS-1	titanium silicalite
TPA	tripropylamine
TPAOH	tetrapropylammonium hydroxide
μL	microliter
UV	ultraviolet
UV/Vis	ultraviolet /visable light
XRD	X-Ray powder diffraction
ZrAPO-5	zirconium-substituted aluminophosphate-5 molecular sieves

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