

Xia Changjiu

Chinese State Key Laboratory of Catalytic Material and Reaction Engineering, Research Institute of Petroleum Processing, SINOPEC, at Beijing

Industrial Catalysis, Master

China

A4.2

In the case of (a) H_2 as reducing agent; $T=600^\circ C$; Max. Pressure 200 bars. About this topic many researchers [1,2] have reviewed ketones are converted directly to the corresponding hydrocarbons in the presence of hydrogen at normal pressures and Ni based Al_2O_3 catalyst in a simple gas-phase reactor. It could be applied H_2 -TPR, XPS and in situ FT-IR to character the catalysts before and after oxidation. And in situ FT-IR may study the catalyst at its working place under real reaction conditions.

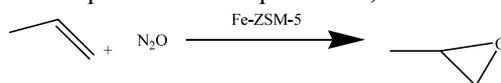
In the case of (b) $NaHCO_2$ as reducing agent; $T=30^\circ C$; $PH=10.5$; Max. Pressure 1.1 bars. Although I do not retrieve some articles in the aspects of reducing cyclohexanone and cyclohexanols back to Cyclohexane, in accordance with the backgrounds of catalytic reduction, I suggest that the supported novel metal (palladium) based catalysts is one of the best choices. E. Guibal et al [3] have applied Chitosan-supported palladium as catalyst to degrade nitrophenol in dilute solutions in the presence of sodium formate as reductant, the reaction temperature is mild and close to room temperature. In 1990 Shimizu et al [4] showed that native cyclodextrins functioned as inverse phase transfer catalysts for the reduction of aryl bromides with sodium formate in the presence of a charcoal-supported palladium catalyst. And here we suggest using H_2 -TPR, XPS and XRD to character the catalysts before and after oxidation.

In the case of (3) $CH_3CH(OH)CH_3$ as reducing agent; $T=80^\circ C$, max. Pressure 3 bars. It has been reported by Jacek Kijeński et al [5] that the direct synthesis of alkenylaromatics during catalytic transfer reduction (CTR) of alkyl ketones with isopropyl alcohol over MgO of enhanced acidity. They studied ketones, acetophenone, 4-isopropylacetophenone, propiophenone, and 5-nonanone, were quantitatively transformed to alkenes under the adopted conditions. Here XRD and the Hammett acidity function H_0 were introduced to character the catalyst before and after reaction.

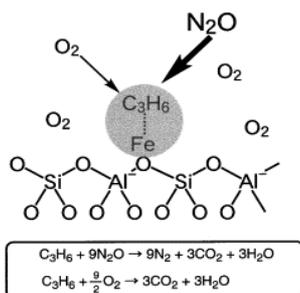
A4.3

(a) I suggest the best choice for this process is iron containing MFI zeolite (Fe-ZSM-5).

(b) The stoichiometric reaction equation for this process is,



Kenji Yamada et al [6] implied that C_3H_6 is a suitable reductant for the selective reduction of N_2O over Fe-ZSM-5, whereas Cu-ZSM-5 has a tendency to promote the combustion of C_3H_6 . They also proposed the possible mechanism of selective catalytic reduction of N_2O can be illustrated as follows. In the initial step of the reaction, C_3H_6 adsorbs and is activated in the Lewis active sites of the Fe-ZSM-5. Second, N_2O reacts with the adsorbed C_3H_6 species, the oxidation of C_3H_6 occurs and CO_2 is mainly generated. Fe-ZSM-5 reveals the highest catalytic activity for the selective catalytic reduction of N_2O in the presence of C_3H_6 .



And In my opinion, the adsorptions and activations of C_3H_6 in the Fe-ZSM-5 is the determining step. Kenji Yamada et al[7] also found that the adsorptions and activations of C_3H_6 are related to the numbers of Lewis acid sites, which means those active sites could make more reactants activated. However, in the experiments of Time-dependent product concentrations of N_2 detected over various Fe-containing Fe-ZSM-5 catalysts, the lower exchange levels showed almost the same behavior, it could be concluded that the numbers of Lewis acid sites is of less impact on the processing of N_2O reacts with the absorbed C_3H_6 species. So we could indicate that the adsorptions and activations of C_3H_6 and formation of the absorbed C_3H_6 species is the rate-determining step in this processing.

(c) It was acknowledged that $\text{N}_2\text{O}/\text{Fe-ZSM-5}$ system is very effective for gas/liquid oxidation to produce phenol from benzene [8,9]. In the Fe-ZSM-5 catalyst, N_2O can oxidize Fe active species and generate ‘ α -oxygen’, which can transfer benzene to phenol. G.I. Panov et al [10] have found that oxidation of benzene to phenol by nitrous oxide over Fe-ZSM-5 zeolites provided 20–25% benzene conversion with 100% phenol selectivity.

References

- 1 Etienne Laurent and Bernard Delmon.(1994) Study of the hydrodeoxygenation of carbonyl, carboxylic and guaiacyl groups over sulfated $\text{CoMo}/\gamma\text{-Al}_2\text{O}_3$ and $\text{NiMo}/\gamma\text{-Al}_2\text{O}_3$ catalysts: I. Catalytic reaction schemes. *Applied Catalysis A: General*, 109, 1, 77-96
- 2 W. F. Maier, K. Bergmann, W. Bleicher and P. v. R. Schleyer. (1981) Heterogeneous deoxygenation of ketones. *Tetrahedron Letters*, 22, 42, 1981, 4227-4230.
- 3 E. Guibal. (2005) Heterogeneous catalysis on Chitosan-based materials: a review. *Progress in Polymer Science*, 30, 1, 71-109.
- 4 Shimizu, S.; Sasaki, Y.; Hirai, C. (1990) Inverse phase transfer catalysis by cyclodextrins. Palladium Catalyzed reduction of bromoanisoles with sodium formate. *Bull. Chem. Soc. Jpn.*, 63, 176- 178.
- 5 Jacek Kijeski, Marek Gliski and C. W. Aquilar Quiroz. (1997) The direct synthesis of alkenylaromatics during catalytic transfer reduction (CTR) of aralkyl ketones with isopropyl alcohol over MgO of enhanced acidity. *Applied Catalysis A: General*, 150, 1, 77-84
- 6 Kenji Yamada, Christian Pophal and Kohichi Segawa. (1998) Selective catalytic reduction of N_2O by C_3H_6 over Fe-ZSM-5. *Microporous and Mesoporous Materials*, 21, 4-6, 549-555.
- 7 Kenji Yamada, Satoshi Kondo and Kohichi Segawa. (2000) Selective catalytic reduction of nitrous oxide over Fe-ZSM-5: the effect of ion-exchange level. *Microporous and Mesoporous Materials*, 35-36, 227-234.
- 8 R. Leanza, I. Rossetta, I. Mazzolab and L. Forn. (2001) Study of Fe-silicalite catalyst for the N_2O oxidation of benzene to phenol. *Applied Catalysis A: General*, 205, 1-2, 93-99.
- 9 A. S. Kharitonov, G. A. Sheveleva, G. I. Panov, V. I. Sobolev, Ye. A. Paukshtis and V. N. Romannikov. (1993) Ferrisilicate analogs of ZSM-5 zeolite as catalysts for one- step oxidation of benzene to phenol. *Applied Catalysis A: General*, 98, 1, 33-43.
- 10 G.I. Panov, G.A. Sheveleva, A.S. Kharitonov, V.N. Romannikov and L.A. Vostrikova.(1992) Oxidation of benzene to phenol by nitrous oxide over Fe-ZSM-5 zeolites. *Applied Catalysis A: General*, 1, 82, 31-36.