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題目(和文)	高難度選択酸化反応用Fe含有ゼオライト触媒に関する研究
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（博士課程）

論文審査の要旨及び審査員

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論文審査の要旨（2000 字程度）

This thesis is entitled “Study on Fe-containing zeolite catalysts for extremely difficult selective oxidation reactions” and the approaches to obtain highly active Fe-containing zeolites catalysts for extremely difficult selective oxidation reactions, including direct conversion of methane to methanol (MTM) and benzene to phenol (BTP) with H_2O_2 are addressed.

In Chapter 1, which was named the “Introduction”, the research background was described to demonstrate the importance of the thesis.

Chapter 2 entitled “Direct synthesis of phenol by hydroxylation of benzene with hydrogen peroxide over Fe-containing MFI zeolite catalysts” explored the role of different Fe species on Fe-containing MFI zeolites by different methods. Directly synthesized Fe-silicalite-1 achieved better catalytic performance than the post synthesis ones in BTP reaction. The formation of isolated and oligomeric extra framework Fe species played a key role for achieving high yield of phenol. Moreover, post-alkaline treatment was advantageous to the formation of mesopores and oligomeric Fe species on the extra framework, thus the highest phenol yield of 7.6% was achieved.

Chapter 3 entitled “Dramatic impacts of the distribution of Fe species in Fe-silicalite-1 zeolites and solvent on liquid-phase methane conversion to methanol with H_2O_2” investigated Fe distribution in Fe-silicalite-1 zeolites using TPAOH as OSDA with or without Na cations. Fe-sillicalite-1 zeolites synthesized without Na cations showed more uniform Fe distribution than those synthesized with Na cations. Sulfolane was useful to improve the production of methanol and its stability during MTM reaction. The use of sulfolane in water with an appropriate proportion led to an extremely high methanol production with a high selectivity. Fe-silicalite-1 zeolites synthesized using TPAOH as OSDA without Na cations showed better catalytic performance than those with Na cations possibly due to the position of Fe species.

Chapter 4 entitled “The influence of iron and aluminum location in MFI zeolites on the catalytic performance in hydroxylation of benzene to phenol and methane to methanol with H_2O_2” discussed Fe distribution in Fe-ZSM-5 zeolites using TPAOH as OSDA with and without Na cations. Fe-ZSM-5 zeolites synthesized without Na cations (FZ(T)*x*) displayed more uniform Fe distribution than those synthesized with Na cations (FZ(TN)*y*). In general, FZ(T)*x* zeolites showed better catalytic performance than FZ(TN)*y* in both BTP and MTM reactions. The introduction of Al in FZ(T)*x* zeolites improved the catalytic performance in BTP and MTM reactions, but in FZ(TN)*y* zeolites, the catalytic performance was not obviously increased possibly due to the location of iron and aluminum.

In Chapter 5 entitled “Alkaline treatment on as-synthesized and calcined Fe-silicalite-1 and Fe-ZSM-5 zeolites for hydroxylation of benzene to phenol with H_2O_2” the influence of desilication on Fe-ZSM-5 and Fe-silicalite-1 zeolites was researched. Both template and aluminum can prevent desilication and protect the crystal structure. Alkaline treatment was an effective post modification method to affect both the porosity of the zeolite and the nature of Fe species. The increased porosity improved the transport properties, reduced diffusion resistance and increased the active Fe species.

In Chapter 6 entitled “Direct synthesis of Fe-containing MWW zeolite for direct hydroxylation of benzene to phenol and methane to methanol with H_2O_2” the effects of calcination temperature on the catalytic performance of Fe-MWW and Fe, Al-MWW were discovered. High temperature calcination to remove OSDA was beneficial to produce more isolated and oligomeric Fe species on the extra framework for Fe-MWW, thus activate the catalytic performance. But the presence of Al in Fe, Al-MWW dispersed Fe and high temperature calcination produced the FeAlOx species, which may be not beneficial to the catalytic performance. In addition, increasing the calcination temperature to prepare H-type zeolite made more seriously Fe aggregation for both Fe-MWW and Fe, Al-MWW, thus decrease the catalytic performance.

Chapter 7 entitled “Iron- and copper-exchanged Beta zeolite catalysts for hydroxylation of benzene to phenol and methane to methanol with H_2O_2” included Fe and/ or Cu exchanged Beta catalysts with varied metal contents. Fe-Cu/Beta catalysts showed dramatically high catalytic activity due to the synergetic effect. 6Fe-6Cu/Beta achieved the highest phenol yield of 10.5 % in BTP reaction and MeOH yield of 720 μmol in MTM reaction. The catalytic stability in the BTP reaction was investigated. The synergetic effect was influenced by the metallic states instead of the content.

Chapter 8 entitled “Summary” gave a summary based on the whole thesis.

On a whole, this thesis satisfies the academic level of doctor of engineering.

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