Multi-scale phenomena in heterogeneous catalytic processes—impact of chemical phenomena under the micro-scale level on catalyst development and design

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Received 29 August 2003; received in revised form 9 January 2004; accepted 31 January 2004

Abstract

Catalyst design requires consideration of all the different dimensional scales involved in heterogeneous catalysis. Identifying phenomena at every scale and defining all the dominant mechanisms are of significance to the multi-scale analysis. Rather than systematically summarizing all the principles of catalyst design encountered at every dimensional scale, the impact of chemical phenomena under the levels of nano-scale and subnano-scale (micro-scale) on catalyst design is illustrated in this paper with two examples in detail. The demonstrations are based on the recent advances of the surface structure and reaction performance of a commercially important Pt–Sn/Al₂O₃ catalyst for reforming and dehydrogenation of hydrocarbons, and the dehydro-aromatization of methane in the absence of oxygen over a recently explored Mo/HZSM-5 catalyst. The studies of these two cases include the interaction among active components and the synergy between active sites on the catalyst surface. Emphasis is given to the realization and understanding of solid catalyst structure and catalytic performance under the micro-scale level through the use of advanced analytical techniques.

Keywords: Multi-scale approach; Heterogeneous catalysis; Bimetallic catalyst; Bifunctional catalyst

1. Introduction

Heterogeneous catalysis reactions involve processes with the catalyst and the reactants in different phases. The presence of several phases requires mass transfer through the inter-phase between reactant and catalyst in order to allow reaction to take place. The heterogeneous catalysis reaction occurs in a typical multi-scale system. Several different physical and chemical phenomena can be distinguished on various characteristic dimensional scales during the reaction. At a reactor scale (macro-scale level), the hydrodynamics and external mass transfer play an important role. At the catalyst particle scale (meso-scale level), mass transfer phenomena on the surface or inside the catalyst particle are significant. As for the chemical events, i.e. adsorption, desorption and surface reaction, the controlling step is restricted within the micro-scale level (nano-scale level and subnano-scale).

The multi-scale nature of heterogeneous catalysis presents a challenge in the process and catalyst designs. To confront the multiple disciplines people proposed integrated or sequential approaches to the process and catalyst designs for integrating chemical and physical phenomena at various scales into systematic models (mathematical or otherwise) of catalyst performance. Catalytic reaction engineering relies on the interaction of disciplines at various scale levels. The choice of reactor and catalyst with optimized performance is determined by combining intrinsic kinetics, transport phenomena and hydrodynamics. The catalyst should be optimized with respect to structure and composition of surface (micro-scale active site and surface state), topology (nano-scale pore structure and activity distribution in a particle) and morphology (size and shape of the catalyst in meso-scale). A number of scientific publications have covered the field of catalyst design on microscale level (e.g.
Barteau et al., 2003; Davis, 2000; Neurock, 2003; Tada and Iwasawa, 2003), on meso-scale and macro-scale level (e.g. Dudukovic, 1999; Hegedus and Pereira, 1990; Krishna and Sie, 1994). Considerable efforts have also been made to explore the multi-scale nature of heterogeneous catalysis and to establish an integrated approach to catalyst design (Centi and Perathoner, 2003a,b; Lerou and Ng, 1996; Smit and Krishna, 2003).

The multi-scale methodology provides an integrated approach to deal with the complex nature of heterogeneous catalysis, which combines multiple disciplines at various dimensional scales, embracing three kinds of methodology, descriptive, correlative and variational (Li and Kwauk, 2003). Among them, the most popular is the descriptive multi-scale methodology, which is used for describing the appearance of structure at various scales. Clearly, to establish the multi-scale approach depends on distinguishing the phenomenological difference of structures at various scales in detail. Nevertheless, catalytic reaction engineering has made significant contributions above the meso-scale level, especially when the catalytic rate phenomena can be mathematically modeled in term of the process and catalyst design variables. However, the chemical phenomena on the catalyst surface at the micro-scale level and beyond (nano-scale, even molecular scale) have not yet been well quantified, due to their complex nature. A phenomenological description of the chemical events on the catalyst surface is still necessary. An accumulation of knowledge at the micro-scale level of catalyst would contribute to the development of the integrated approach involving process and catalyst design.

The purpose of this paper is to illustrate some important chemical phenomena on the catalyst surface based on recent advances in methane dehydro-aromatization in the absence of oxygen over a Mo/HZSM-5 catalyst and in surface structure and reaction performance of a Pt–Sn/Al2O3 catalyst for reforming and dehydrogenation of hydrocarbons. The above two catalysts have been extensively investigated in the Dalian Institute of Chemical Physics. It was found that the micro-scale structures on the catalyst surface appear to markedly influence the catalytic properties. In each case, it will be shown that advanced analytical techniques have contributed to a full realization and thorough understanding of micro-scale structures and chemical phenomena on the catalyst surface. Where appropriate, it will also be shown to what extent can this understanding be used to guide the development and design of catalysts.

Most supported catalysts contain more than one active component, e.g., metallic cluster and oxide promoters on a supported metallic catalyst, metallic sites and acidic sites on a bifunctional catalyst. The performance of catalysts can depend on the synergy and interaction between these active components or sites during catalytic reaction. Through the use of advanced characterization techniques, a wealth of information has been gained regarding the interaction of different components and the synergy between active sites.

2. Interaction among active components

Highly dispersed platinum and platinum-containing bimetallic catalysts have been widely used for reforming and dehydrogenation of hydrocarbon feed stocks. The addition of a second metallic component can remarkably enhance the selectivity and stability of the platinum catalyst. Therefore, the studies of the interaction between the metallic components and the support are crucial on the research of bimetallic catalysts. However, the actual nature of the interaction and the manner in which it modifies catalyst performance are still not very clear.

In early studies, due to the strong influence of catalytic theory of alloys and the limitations of characterization techniques, the states of the two highly dispersed catalytic components in the bimetallic catalyst were usually considered to exist as an alloy or bimetallic clusters (Sinfelt, 1983). Recently, with the development of highly sensitive and in situ physical techniques for the characterization of catalysts, it has been reported that, for alumina-supported bimetallic catalysts, due to the strong interaction between the catalytic components and the support, only the noble metal is in the metallic state, while the second component still remains in the oxidized states even after reduction.

In the earlier study of Lin et al. (1984), two types of Pt active sites have been identified on the Pt–Sn/Al2O3 catalysts by a modified C2H4–H2 titration method. The active sites on which the chemisorbed H2 can react with ethylene to form ethane are designated as M1, while those active sites on which no reaction takes place between chemisorbed H2 and ethylene are designated as M2. M1 sites are more favorable for “demanding” reactions that require sites of multi-platinum ensembles, e.g., hydrogenolysis and carbon deposition, while for “facile” reactions that can be performed on single metal sites (such as dehydrogenation, isomerization, etc.), M2 sites are more adequate. The hydrogen adsorption properties of Pt–Sn/Al2O3 catalyst were also compared with the Pt/Al2O3 catalyst (Zhang et al., 1991). In the Pt/Al2O3 catalyst, there exist only M1 sites, which adsorb more H2 at low temperature (0°C) and less H2 at high temperature (330°C and 450°C), while for M2 sites on Pt–Sn/Al2O3 catalyst, the active energy for H2 adsorption is higher than that of M1, and the adsorption of H2 takes place at high temperature. The M1 sites or the mono-metallic Pt sites are easily covered by carbon deposits under severe reaction conditions, whereas M2 sites can, to a large extent, resist carbon deposition under the same reaction conditions.

By studying the influence of preparation on the performance of Pt–Sn/Al2O3 catalyst, it was found (Lin et al., 1984, 1990) that complex methods, in which PtSn complexes were used as precursor compounds, are suitable for the formation of M2 sites on the catalyst surface. When the catalysts were prepared by complex incorporation, the concentration of the M2 sites was proportional to the content of the Sn component, although no such correlation existed for the conventionally impregnated catalysts (Fig. 1). This
indicates that the complex method is more favorable for the interaction between Pt and Sn, and the M2 sites are associated with Pt–Sn assemblies.

It was found that significantly enhanced selectivity and operation stability of the catalysts prepared by the complex methods were closely related to the role of the M2 sites due to certain interaction between the Pt and Sn components (Lin et al., 1990; Zhang et al., 1991). The carbonaceous materials that originate from the metal surface during reaction may be converted carbon through successive dehydrogenation on Pt metal sites, or they may continuously migrate to the support with irreversible coke formation through condensation or hydrogen transfer reaction. The results of chemisorption and thermal desorption of ethylene on Pt and PtSn catalysts showed that the incorporation of Sn reduced the strength of chemisorption of hydrocarbons on the Pt surface, so that the carbon precursors could migrate towards the support more easily. The proportion of carbon deposited on the support of the Pt–Sn/Al2O3 catalyst was greater than that of the Pt/Al2O3 catalyst. The results of H2 chemisorption showed that with the same level of carbon deposition the metal surface on the Pt–Sn/Al2O3 catalyst covered by carbonaceous materials was less than that of the Pt/Al2O3 catalyst. The high stability of the Pt–Sn/Al2O3 catalyst is closely related to the large bare Pt metal surface under high temperature conditions.

Further studies indicated that the M2 sites on the Pt–Sn/Al2O3 catalyst could be considered to be platinum particles that strongly interact with SnO and γ-Al2O3 (Yang et al., 1992). The states of Pt and Sn in a working Pt–Sn/Al2O3 catalyst were extensively investigated by means of high resolution electron-microscopy (Lin et al., 1984), 119Sn in situ Mössbauer spectroscopy (Fan et al., 1991; Yang et al., 1992), XPS (Jia et al., 1997) and Pt L-edge EXAFS (Lin et al., 1999a). High resolution electron-micrograph showed very clear surface crystalline rows of Pt metal particles, and that the measured lattice distance was 0.23 Å corresponding to the lattice parameter of the Pt(1 1 1) plane. On the other hand, no alloy lattice was observed. It was found from Mössbauer spectroscopy that Sn exists as Sn4+ before reduction while it is partially reduced to Sn2+ after being reduced at 480°C, and that no Sn0 appeared on the reduced samples. These results, which coincide with the results of XPS characterization and Pt L-edge EXAFS, reveal that after reduction the surface species of Sn on the Pt–Sn/Al2O3 catalyst remains in the oxidized state due to metal oxide-support interaction, while Pt is highly dispersed on the Al2O3 surface as metallic particles, without forming any Pt–Sn alloy.

Xie and Tang (1990) have pointed out that the metal oxide tends to form a mono-layer distribution on the Al2O3 surface. In fact, the content of Sn oxide in Pt–Sn/Al2O3 catalyst was less than 1 wt%, and its coverage on the Al2O3 surface was less than 10% of a mono-layer dispersion. Thus, a “sandwich” model (Fig. 2) of interaction among Pt, metal oxide and Al2O3 in which Pt is considered to be anchored to the Al2O3 support via the promoter metal oxide (e.g. SnO) has been proposed (Lin et al., 1999a,b). According to this “sandwich” model, it seems that with the addition of Sn to the Pt/Al2O3 catalyst, Pt–SnO–Al2O3 “sandwich” geometric structures (M2 sites) are formed, thus the selectivity and stability of catalyst are enhanced. And only with the complex method, could the Pt crystallites be guaranteed to be located on top of the promoter oxide surface and sandwich structures can be formed.

A study of influence of the coking-regeneration cycles (CRC) on the structure and surface properties of Pt–Sn/Al2O3 catalyst provided more evidence for this proposal (Fan et al., 1991). The results of Mössbauer spectroscopy, which showed that Sn2+ decreases and Sn4+ as well as Sn0
increases with the increasing CRC, indicates the M2 sites “sandwich” structure are continuously destroyed and the PtSn alloy forms concurrently during CRC. The activity and stability of the Pt–SnO–Al2O3 “sandwich” structures are higher than that of mono-metallic Pt particles on Al2O3 surface. The carbon precursors produced on the metal surface of the Pt–SnO catalyst migrate to the alumina support more easily than those on the platinum catalyst. The formation of PtSn alloy results in the permanent deactivation of Pt–Sn/Al2O3 catalyst.

The “sandwich” geometric structures on the supported bimetallic catalysts are short-range-ordered amorphous phase comprising Pt, SnO and Al2O3 support. This is the first model proposed for the design of a highly dispersed bi-metallic catalyst base on the surface structures of the amorphous features of the catalyst. The Pt–Sn/Al2O3 catalyst prepared by complex impregnation has been successfully employed in China for the dehydrogenation of long chain paraffin to produce olefin (Lin et al., 2001). In contrast to crystallography, however, XAFS, which is a very sensitive probe of such short-range-ordered systems, provides only limited information about radial structure. The site-symmetries, coordination numbers and inter-atomic distances obtained are averaged over all the different types of coordination. Thus, when a structural model is considered, these XAFS-derived parameters are often found to be consistent with more than one possible structure. This phenomenon is usually considered to be a technical limitation of XAFS but is seldom recognized as a limitation caused by the amorphous system itself. Thus, the lack of a fundamental approach, other than the limitation of the technique, usually makes understanding difficult and conclusions are often thought to be speculative. Lin et al. (2001) presented an amorphous approach to understanding the structure of a working Pt–Fe/Al2O3 catalyst by using XAFS at both the Pt LIII- and the Fe K-edges. The “sandwich” model of Pt–Fe/Al2O3 catalyst has also been induced, in which iron oxide with a formula of Fe12O19 is present as an interface between Pt and Al2O3 while Pt atoms are randomly distributed on the iron oxide surface as a mixture of monomers, dimers and trimers well separated from each other.

The presence of “sandwich” structure of Pt–SnO(FeO)–Al2O3 could improve the dispersion of the Pt atoms significantly. The Pt–SnO(FeO) interaction may have an important influence on resisting carbon deposition and maintaining the metallic state of the Pt sites, and all these seem to be the reason of high activity and stability for dehydrogenation reaction over the Pt–Sn(Fe)/Al2O3 catalyst. Comparing the results of CO adsorption microcalorimetry with the performance of dehydrogenating C4 alkanes over Pt–Fe/Al2O3 and Pt–Sn/Al2O3 catalyst according to the “sandwich” model, it seems that with the addition of Sn to the Pt/Al2O3 catalyst, more Pt–SnO–Al2O3 “sandwich” structures are formed than in the case where Fe is added to the Pt/Al2O3 catalyst. Thus, the dehydrogenation performance of Pt–Sn/Al2O3 catalyst is superior to that of Pt–Fe/Al2O3 catalyst (Jia et al., 1998, 1999).

Following the above idea, we may hope to improve the catalyst more rationally according to the practical requirements of different reactions (such as reforming, dehydrogenation, hydrogenation), by selecting a suitable metal oxide interface and suitable preparation techniques, e.g., the complex method. In fact, a commercial Pt–Sn/γ-Al2O3 catalyst prepared by the complex method, brand named as DF-2, brought about industrialization for long-chain normal paraffin dehydrogenation since the early 1980s in PetroChina (Lin et al., 1999b).

3. Synergy between active sites

Methane can be converted into benzene and other aromatics under nonoxidative conditions over Mo/HZSM-5 catalyst (Wang et al., 1993; Xu et al., 2003). A bifunctional pathway for dehydroaromatization of CH4 (MDA) over Mo/HZSM-5 has been generally accepted, which involves molybdenum carbide species (e.g. MoC and/or Mo4C3) and Brønsted acid sites as active sites. However, the bifunctionality of Mo/HZSM-5 catalyst and the role of the active sites during the reaction are not quite clear.

So far, the kinetic coupling and synergy between the bifunctional active sites have been a main concern of researchers. Iglesia et al. (1997) pointed out that the behavior of synergy between the active sites on heterogeneous catalysts could be analogous to concerted and sequential bifunctional pathways in homogeneous and enzymatic catalysis. However, in heterogeneous catalysis concerted interaction may be prevented by the fixed and inappropriate location of the sites. In such case, sequential bifunctional pathways play a role via migration of gas-phase or surface intermediates between distant sites.

Due to the similarities between the catalysis for MDA and dehydroaromatization of light alkanes (LHDA), the general description of the bifunctional pathway of MDA reaction on Mo/HZSM-5 catalysts, as well as its dispute, has followed those of LHDA. Some researchers describe bifunctional pathways of MDA reaction over Mo/HZSM-5 as follows: methane is first activated and dehydrogenated into CHx, which will oligomerize into C2-species on Mo2C and/or MoOxCx species on the external surface and/or in the zeolite channels, and then it oligomerizes further and cyclizes into aromatics on the Brønsted acid sites (Fig. 3).

Solyomosi et al. (1997) investigated the interaction of methane with unsupported and supported molybdenum compounds (Mo, MoO2, MoO3, Mo2C, and MoC1−x) at 973 K. They found that only when these compounds were contacted with ZSM-5, the formation of ethane, ethylene, and benzene came into prominence during the steady state, and XPS analysis of Mo-containing catalysts demonstrated the formation of Mo carbides during the catalytic reaction. They suggested that Mo2C is the active surface species in the
Mo-containing catalysts, which converts methane into ethylene, the primary compound for the production of benzene on the zeolite surface. These authors (Solymosi et al., 1999a,b) also generated adsorbed CH₃, CH₂ and C₂H₅ species on a Mo₂C/Mo(111) surface by the dissociation of the corresponding iodo-compound, and studied the reaction pathways of adsorbed species by means of TPD, XPS and HREELS. They found that the main products of the reaction of adsorbed CH₃ on Mo₂C were H₂, CH₄ and C₂H₄, while the coupling of CH₃ to C₂H₆ was not observed. Meanwhile, the CH₂ species was easily self-hydrogenated to CH₄ and dimerized into C₂H₄. The reaction of C₂H₅ on Mo₂C/Mo(111) surface yielded C₂H₆ and C₂H₄. Neither the cleavage of the C–C bond nor the coupling of C2 compounds occurred to any detectable extent under the reaction conditions. Therefore, it was suggested that Mo₂C is the active component for methane activation and the coupling of CH₂ to C₂H₄, and the subsequent reactions of ethylene (oligomerization and aromatization) take place on the surface of HZSM-5, catalyzed by Bronsted acid sites. In addition, Derouane-Abd Hamid et al. (2000) and Bouchy et al. (2000) found that a face-centered cubic structured α-MoC₁₋ₓ species was more effective than a hexagonally close-pack structured β-Mo₂C species for MDA reaction, demonstrating higher activity, selectivity, and stability.

By comparing the performances of integrated Mo/HZSM-5 catalyst and hybrid catalysts of Mo₂C + HZSM-5 and 3 wt% Mo/SiO₂ + HZSM-5, Liu et al. (1999) observed a significant conversion of CH₄ and formation of aromatics on physically mixed catalysts. Considering the poor mobility of Mo₂C, they concluded that C₂-species formed on Mo₂C particles at the vicinity of the external surface of HZSM-5 could diffuse and migrate to the interface of HZSM-5 and then be converted into benzene and aromatic products.

However, as the viewpoint of Iglesia et al. (1997) on LHDA reaction, another description of the bifunctional pathways of MDA reaction over Mo/HZSM-5 (Fig. 4), which involves dehydrogenation of methane and chain-growth steps on Bronsted acid sites aided by hydrogen desorption on MoCₓ species, could not be easily excluded (Borry III et al., 1999). Ma et al. (2000a) investigated the induction period of MDA reaction over Mo/HZSM-5, Mo/MCM-22 and Mo/TiO₂ by a temperature-programmed surface reaction of methane, and observed no aromatics formation in catalytic evaluation over Mo/TiO₂ at all. They attributed these to the fact that the Mo/TiO₂ catalyst lacks any strong acidity that is responsible for intermediate aromatization. However, it is worth to note that no apparent formation of C₂-species (i.e. ethene and ethane) over Mo/TiO₂ is observed after Mo₂C is formed. This is accordant with the results of Solymosi et al. (1997), that the dominant process on unsupported Mo carbides was the decomposition of methane to hydrogen and carbon. These features indicate that the formation of C₂ intermediates has to be assisted by Bronsted sites, i.e., a kind of acid-assisted formation. Chen et al. (1995, 1996a) carried out a comparative FT-IR study on the interaction of CH₄ with silica, alumina, HZSM-5 and Mo/HZSM-5. The band shift of the surface OH groups and adsorbed methane gave evidence of interaction between adsorbed methane and the surface hydroxyl group of HZSM-5. They observed that the strength of the interaction between the OH groups and CH₄ decreased in accordance with the order of their acidities (Si–OH > Al–OH > Si–OH), and that the infrared inactive v1 mode (2917 cm⁻¹) of free methane became active and shifted to lower frequencies. The results demonstrated that OH groups of zeolite played a very important role in CH₄ activation. The authors considered that the weakening of the C–H bond of methane caused by distortion of the methane molecule resulted from its interaction with
Bromsted acid site of zeolite, and might be the first step in methane activation. The introduction of Mo species into HZSM-5 considerably attenuates the adsorption of methane, due to the abatement of Brønsted acid sites caused by Mo species exchange.

The interaction between the Mo species and HZSM-5 is of special significance for the understanding of MDA reaction over Mo/HZSM-5 catalysts. Liu et al. (1999) found that a close relationship exists between the activity of C₂H₆ formation in MDA and the Brønsted acidity on their 3% Mo/HZSM-5 catalysts. The HZSM-5 supports with SiO₂/Al₂O₃ ratios around 40 demonstrated the maximum activity for MDA. Meanwhile, FT-IR measurements of pyridine adsorption revealed that the Brønsted acidity of HZSM-5 showed a sharp maximum for the HZSM-5 having the SiO₂/Al₂O₃ ratio of 40 among the catalysts with SiO₂/Al₂O₃ ratios of 20–1900, which is identical to that of benzene formation rates. Su et al. (2002) also found a maximum activity for MDA on their 6% Mo/HZSM-5 catalysts with an optimum SiO₂/Al₂O₃ ratio of 55 among the catalysts with SiO₂/Al₂O₃ ratios of 24–250. However, further investigation has revealed that the performance of Mo/HZSM-5 catalysts substantially depended on the Mo/[H⁺] ratio per unit cell. The optimum Mo/[H⁺] ratio per unit cell of the active precursors in Mo/HZSM-5 catalysts for MDA, measured by ¹H MAS NMR and XRF, was found to be about 1 when the Mo/[H⁺] ratio per unit cell was adjusted by altering either the SiO₂/Al₂O₃ ratios or the Mo loading. And also, these authors found that the exchange between the Mo species and the Brønsted acid sites in Mo/HZSM-5 catalysts, as well as the number of Brønsted acid sites per unit cell, decreased with the increase in their SiO₂/Al₂O₃ ratios. This indicated that the driving force behind the migration of the Mo species into the zeolite channels strongly depends on the Brønsted acid sites.

The Mo/HZSM-5 catalyst was usually prepared by the impregnation method with (NH₄)₆Mo₇O₂₄ as the starting material of the Mo component. Thus, the Mo species in the form of MoO₂₄ would locate themselves on the zeolite surface during the impregnation stage. When calcined at 773 K, the Mo-containing ions decompose into MoO₃ crystallites, some of which migrate into the zeolite channels and interact with the Brønsted acid sites. NH₃-TPD, ¹H MAS NMR spectra of Mo/HZSM-5 with various Mo loadings, and ESR studies confirmed that the Mo species do migrate into the zeolite channels and interact with and replace the Brønsted acid sites, as both the peak area of the high-temperature peak in the NH₃-TPD profiles and the intensity of the chemical shift at ca. 3.9 ppm of the ¹HMAS NMR spectra decrease with increasing Mo loading (Ma et al., 2000b).

Borry III
et al. (1999) studied the mechanistic details of the synthesis of Mo/H-ZSM5 from mixtures of MoO3 and HZSM-5 powders. They found that MoO3 species migrate onto the external ZSM-5 surface at about 623 K. Between 773 and 973 K, MoO3 species migrate inside zeolite channels via surface and gas phase transport, exchange at acid sites, and react to form H2O. The amount of H2O evolved during exchange and the amount of residual OH groups detected by isotopic equilibrium with D2 showed that each Mo atom replaces one H+ during exchange. This stoichiometry and the requirement for charge compensation suggest that exchanged species consist of (Mo2O5)2+ ditetrahedral structures interacting with two cation exchange sites.

An induction period has been found before aromatization occurs, which has been attributed to the conversion of MoO3 into Mo2C under the action of the methane reactant. Ding et al. (2001) investigated the structure and density of Mo species in Mo/HZSM-5 during catalytic CH4 reactions using in situ X-ray absorption spectroscopy (XAS), and the isotopic exchange of D2 with OH groups in HZSM-5 before and after CH4 reactions. They found that the (Mo2O5)2+ species would be reduced by CH4 in the initial stage of the reaction and be carbonized to form small MoC1 clusters, with the concurrent regeneration of the bridging OH groups that were initially replaced by Mo oxo dimmers during the exchange. They estimated that MoC1 clusters are ca. 0.6 nm in diameter and contain ca. 10 Mo atoms. MoC1 clusters of this size are likely to reside in the zeolite channels.

Although the Bronsted acid sites are necessary for MDA reaction (Ma et al., 2000c), excess Bronsted acid sites are detrimental for the reaction, since severe coke formation will occur on them. For example, Bronsted acid sites on external zeolite surfaces have been implicated in many nonselective catalytic reactions. Such sites are easily accessed by reactants and are not protected against undesired side reactions by the shape-selective environment within zeolite channels. Selective silanation of external acid sites on HZSM-5 by using large organosilane molecules could decrease the content of acid sites and greatly depress the rate of coke formation. After treatment with CH3OH, the number of acid sites on Mo/HZSM-5 catalysts (Lu et al., 1999; Ding et al., 2002). Recently, Lu et al. (Lu et al., 2001; Ma et al., 2002) significantly improved the selectivity and durability of Mo/HZSM-5 catalysts in MDA reaction by steam pretreatment of parent zeolite supports. The C6H6 yield increased by 32% while the selectivity to coke dramatically dropped, from 20% to 8%, when compared with the Mo/unpretreated HZSM-5 catalysts. In their study, multi-nuclear solid state NMR, TPD, TPO, and UV-Raman methods are applied to characterize and rationalize the structure property relationship of the improved catalytic performance of the modified catalysts. They inferred that only a small fraction of tetrahedral framework aluminum, which corresponds to the Bronsted acid sites, is sufficient to accomplish the aromatization of the intermediates in methane aromatization reaction, while the superfluous strong Bronsted acid sites, which can be removed upon steaming treatment, are shown to be related with the aromatic carbonaceous deposits on the catalysts.

Up to now, considerable effort has been devoted to developing active and selective catalysts and understanding the bifunctionality of Mo/HZSM-5 catalysts. The activity and the stability of the Mo/HZSM-5 catalysts could be significantly improved by adjusting the interaction of Mo species and the Bronsted acid sites, e.g., adjusting the Bronsted acid sites and their distribution, the distribution of Mo species on/in the zeolite and their particle size. Considering that Mo/HZSM-5 catalysts have achieved near equilibrium methane conversions with high selectivity to benzene in most studies, more attentions should be paid to the catalyst deactivation due to coke formation on the catalyst. In general, coke formation might change the density of acid sites, the distribution of acid site strength, and the pore structure in zeolite catalysts.

Weckhuysen et al. (1998) identified three different types of surface carbon species on a used Mo/HZSM-5 catalyst by using angle-resolved XPS. Species A, characterized by a C 1s binding energy (BE) of 284.6 eV, can be attributed to adventitious or graphitic-like carbon which is mainly present in the zeolite channels. Species B, with a C 1s BE of 282.7 eV, is due to carbodic-like carbon in Mo2C and is predominantly located on the external surface of the zeolite. Species C, with a C 1s BE of 283.2 eV, is a hydrogen-poor sp-type or pregraphitic-type of carbon. Species C is also mainly present on the external surface of the zeolite, and its amount increases with increasing time on stream. The sp-type carbon gradually covers both the zeolite surface and the Mo2C phase during MDA and is responsible for the deactivation of the Mo/HZSM-5 catalyst.

To increase the stability of the Mo/HZSM-5 catalysts, more information on the nature of the MDA reaction and its mechanisms at the molecular level is still needed. Is the coke formed on the same active sites for aromatics formation? Is the coke formed in parallel or consecutive reactions of aromatics? Can the coke formation be suppressed by fine adjusting of the interaction of Mo species and Bronsted acid sites? Can the coke be removed by in situ hydrogenation during MDA reaction as an early attempt as was done by Chen et al. (1996b)? An ultimate improvement of the stability of Mo/HZSM-5 catalysts may rely on the solution to these problems.

4. Concluding remarks

This paper has illustrated the extent to which progress in catalyst science has contributed to the realization and understanding chemical phenomena on the catalyst surface. It is evident that through the use of advanced analytical techniques, it is becoming possible to understand catalysis and catalyzed reactions at the micro-scale level and beyond. The information gained from these levels has already been used to guide the development of catalysts. For the moment, however, catalysts are still developed in practice mainly by
separating the stages of active phase discovery and optimization from those of catalyst and reaction engineering, i.e. a sequential approach.

The sequential approach is not only time consuming and costly in the process and catalyst design, but also sometimes may lead to incorrect results due to the restriction of one level on another level. The development of more efficient catalysts is an ever-increasing goal in catalysis research; this need for better catalysts leads to the need of developing faster and more efficient ways to develop the catalysts themselves. The multi-scale approach is a methodology of developing catalysts focused on considering the catalyst in its multi-scale components at the same time, which include active sites, solid architecture and texture, nano- and macro-structure. The application of the multi-scale approach in catalyst design presents a challenge to researchers. First of all, we should know how to identify phenomena at every scale and how to define all the dominant mechanisms. Then, we could understand the multi-scale nature in the heterogeneous catalysis.

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