

Direct conversion of methane under nonoxidative conditions

Yide Xu,* Xinhe Bao, and Liwu Lin

State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, PO Box 110,
Dalian 116023, China

Received 9 July 2002; revised 3 September 2002; accepted 11 September 2002

Abstract

Direct conversion of methane into hydrogen and valuable chemicals under nonoxidative conditions is a process severely limited thermodynamically. However, the movement from the present era of fossil fuels into the coming hydrogen energy age makes it an interesting and important approach compared with the direct conversion of methane under the aid of oxidants. This paper gives a brief overview of the direct conversion of CH₄ under nonoxidative conditions. At the same time, our understanding of methane dehydroaromatization over Mo/HZSM-5 catalysts for the simultaneous formation of hydrogen and light aromatics is discussed in general, while the bifunctionality of Mo/HZSM-5 catalysts and the role of carbonaceous deposits formed during the reaction are reviewed in more detail. A perspective of the topic from both academic points of view and potential industrial applications is also presented.

© 2003 Elsevier Science (USA). All rights reserved.

Keywords: Direct conversion of methane; Nonoxidative condition; Dehydroaromatization; Mo/HZSM-5; Bifunctionality; Carbonaceous deposits

1. Introduction

Methane is the main component of gaseous/solid fossil fuel resources, such as natural gas, coal-bed gas, and methane hydrates deposited in the earth, and constitutes one of the largest organic carbon reserves. Methane is the simplest and smallest hydrocarbon molecule, and an important task confronting catalytic chemists is how to realize direct conversion of methane to versatile fuels and valuable chemicals by building up the desired C–C (or C–O) bond. This presents an entirely different difficulty from what we have become familiar with in petroleum processing, in which the main problem is how to effectively and selectively break the C–C bond. Thermodynamic constraints on the reactions in which all four C–H bonds of CH₄ are totally destroyed, such as CH₄ reforming into synthesis gas or CH₄ decomposition into carbon and hydrogen, are much easier to overcome than the reactions in which only one or two of the C–H bonds are broken under either oxidative or nonoxidative conditions. For this reason, only indirect conversions of CH₄ via synthesis gas into higher hydrocarbons or chemicals are currently available for commercialization. As for the direct conversion of

CH₄ into higher hydrocarbons and/or valuable chemicals, despite enormous efforts conducted via various approaches, such as thermal, homogeneous or heterogeneous catalysis, photocatalysis, and electrocatalysis, profitable and practical applications have not yet been developed.

Direct conversion of CH₄ with the assistance of oxidants is thermodynamically more favorable than that under nonoxidative conditions. Therefore, the direct conversion of CH₄ under the aid of oxidants has received much more attention than that under nonoxidative conditions, especially when considering the production of fuels and valuable chemicals from CH₄ in order to solve the “oil crisis.” The study of the oxidative coupling of methane (OCM) was a well-known example that started in the early 1980s and quickly bloomed from the mid-1980s to the mid-1990s [1]. However, no catalysts could reach a C₂₊ yield higher than 25% and selectivity to C₂₊ higher than 80%, which are the main criteria for industrial application of the OCM, and the research passion on the topic was gradually weakened. On the other hand, despite the easy activation and conversion of CH₄ into CH₃OH by enzymes such as monooxygenases under ambient temperature and/or mild conditions in biological domains, the direct oxidation of CH₄ into CH₃OH is perhaps a toughest project in heterogeneous catalysis, and a comprehensive review of it was recently published [2].

* Corresponding author.

E-mail address: xuyd@ms.dicp.ac.cn (Y. Xu).

With the urge to quest for renewable energy and cleaner fuels, it is recognized that we are now moving from a fossil energy age into a hydrogen energy age, and hydrogen energy will inevitably replace fossil fuel energy in the near future due to the fact that the burning of hydrogen is pollution free. The ability to produce H_2 will be a major determining factor in realizing this goal. The cleanest way to produce H_2 is undoubtedly from H_2O by using sunlight in combination with a photovoltaic cell via water electrolysis. However, attaining this ultimate goal will be difficult, and we need a practical way to produce H_2 from fossil fuel sources for the time being. One of the best ways to bridge the fossil energy age and hydrogen energy age will be the production of H_2 from CH_4 , due to its high H/C atomic ratio and great abundance in reserves. Therefore, the direct conversion of CH_4 under nonoxidative conditions into H_2 and/or H_2 accompanied with basic chemicals is closely related to the effective utilization of CH_4 -containing resources and thus to sustainable progress and development of the living conditions of mankind. It will certainly receive much greater attention in the 21st century than ever before.

2. Direct conversion of CH_4 under nonoxidative conditions: a brief overview

The direct conversion of CH_4 under nonoxidative conditions is thermodynamically unfavorable. Nevertheless, as an alternative approach, it has still attracted the attention of many researchers. In homogeneous catalysis, it was reported as early as the 1970s that CH_4 could be converted into higher hydrocarbons via the homologation reaction in a superacid medium [3]. Up to now, extensive research in this area has been undertaken in this direction [4]. In heterogeneous catalysis, various metals have been discovered that can chemisorb CH_4 at moderate temperatures and that can decompose CH_4 to C and H_2 at higher temperatures. Amariglio and co-workers [5] and van Santen and co-workers [6] independently and almost simultaneously reported a “two-step” process.

Amariglio and co-workers studied the “two-step” process on Pt (including EUROPT-1), Ru, and Co in isothermal experiments. In a series of publications, the authors suggested that C–C bonding could take place between H-deficient CH_x formed during the first step of methane chemisorption, while H_2 saturated the alkane precursors in the second step and removed them from the surface [7–11]. In view of the fact that hydrogenation at a temperature lower than that of CH_4 chemisorption is favorable for lessening hydrogenolysis, Amariglio et al. recently reported a nonoxidative conversion of methane to higher hydrocarbons through a dual-temperature two-step reaction on Pt/SiO₂ (EUROPT-1) and Ru/SiO₂ catalysts [12]. Indeed, when chemisorption of methane was set at a fixed temperature (usually lower than 593 K), the selectivity to heavier alkanes increased with the lowering of hydrogenation temperature on both cata-

lysts. On the other hand, when the hydrogenation temperature was less than 393 K, hydrogenolysis was negligible, and thus the variations of the products can only be attributed to the changes affected by the adlayer formed during the chemisorption of methane at a certain temperature. It was discovered that the products of C_{2+} hydrocarbons at every hydrogenation temperature displayed a maximum versus the methane chemisorption temperature on both catalysts.

Van Santen and co-workers suggested that CH_4 first dissociated on a precious metal to form carbide and H_2 . Then, the carbide was hydrogenated by H_2 to produce higher hydrocarbons. C–C bonds were supposed to be created during the hydrogenation step. Since the reactivity of the CH_x surface intermediates formed from CO and CH_4 was quite similar, the authors suggested that the chain-growth probability would depend on the metal–carbon bond strength and that the mechanism of C–C bond formation in the two-step route should be related to that occurring in the Fisher–Tropsch reaction [13,14]. Van Santen and co-workers also demonstrated that the homologation of olefins (C_2H_4 , C_3H_6 , C_2H_2 , etc.) with methane could occur over Ru/SiO₂ and Co/SiO₂ catalysts [15].

The two-step route is also feasible over a number of oxide- or zeolite-supported transition metal and bimetal catalysts [16–19]. Solymosi and Cserenyi illustrated that over a Cu-promoted Rh/SiO₂ catalyst, the enhanced formation of C_2H_6 and higher hydrocarbons could be observed in the two-step process [17]. Guzzi et al. reported that the chemisorption of CH_4 at 523 K and the subsequent hydrogenation of the CH_x species at 523 K over Co–Pt/NaY and Co–Pt/Al₂O₃ performed the best of all the catalysts tested [19]. The chemisorbed CH_x species had the highest concentration, and all CH_x species were hydrogenated in the second step, giving a selectivity of C_{2+} close to 84%.

Generally, three forms of carbon, referred to as C_α , C_β , and C_γ , are formed in the first step, which were distinguishable by the temperature at which they react with H_2 [13]. The maximum yield of C_{2+} products on a Ru/SiO₂ catalyst was reported to be in coincidence with a maximum surface coverage by C_β [20]. On the other hand, three distinct forms of carbon (methyldiyne CH, vinylidene CCH₂, and graphitic carbon) were identified by HREELS after CH_4 was adsorbed and activated on Ru(0001) and Ru(1120) surfaces [21]. The nature of carbonaceous species formed by CH_4 adsorption on Pt/SiO₂ (EUROPT-1) was carefully studied after hydrogenation steps of various durations by using a temperature-programmed oxidation (TPO) technique [22]. Two groups of surface carbonaceous species were characterized by their different reactivities toward O_2 , but their responsiveness to H_2 at 573 K was similar. CH_4 was the main product of hydrogenation, but one-half of the reactive carbonaceous species deposited on the catalyst surface formed other alkanes. In the case of the Pt/SiO₂ catalyst, mainly C_2H_6 and $n-C_5H_{12}$ were produced during the first minute of the reaction. This illustrates that C–C bonds could form during CH_4 adsorption, and the

authors assumed a surface intermediate of C_5 precursor bonded on dispersed and coordinately unsaturated Pt atoms.

Guczzi et al. found that there was a correlation between the hydrogen content of the surface CH_x species (the optimum value of x being around 2) and the chain length of the hydrocarbons produced in the hydrogenation step in their mechanistic study of the two-step process [18]. Recently, they reported that the two-step process could be simplified into a one-step process with a C_{2+} hydrocarbons production higher than that obtained in the two-step process over Pt–Co/NaY bimetallic catalyst. These results could be obtained if the CH_4 was pulsed with H_2/He mixture at 523 K [23,24].

Bradford reported the results of the isothermal, nonoxidative, two-step conversion of CH_4 to C_{2+} hydrocarbons over supported and unsupported Pt and Ru catalysts at moderate temperatures and elevated pressures [25]. It was shown that an increase in reaction pressure increased the branching and molecular weight distribution of the product.

Despite all substantial research efforts into nonoxidative two-step or one-step CH_4 homologation, its low efficiency is the main problem to further developing it as a commercial process. However, these studies enhanced our knowledge in methane catalytic chemistry and stimulated catalytic chemists to explore new methane conversion processes.

Several researchers suggested the preparation of a multifunctional catalyst on the basis of multicomponent catalysis, so as to avoid the use of a two-step process. A patent filed by Mitchell and Wanyhorne [26] indicated that if CH_4 was passed over $M/M'O_n/M''O$ (M is a precious metal, M' is a VIB element, and M'' is an IIA element) multicomponent catalysts at 977 K for 30 min, C_6H_6 could be detected in the product. Furthermore, it was recently reported that dehydrogenative coupling of CH_4 without any oxidant could be carried out over Pt– SO_4/ZrO_2 catalysts [27]. A steady conversion of 0.2% (the equilibrium conversion of CH_4 into C_2H_6 and H_2 is estimated to be 0.6%) was observed after the catalyst was reduced in H_2 at 773 K, and could be maintained for over 360 min.

In order to overcome the thermodynamic limit and to enhance the reactivity for obtaining high yields in direct conversion of CH_4 under nonoxidative conditions, plasma excitation has also been attempted. The product distribution is dependent on the method by which plasma excitation is produced. For example, in pulsed corona discharges at atmospheric pressure, C_2 hydrocarbons (mainly C_2H_2) were obtained with a high selectivity of around 70 to 90%, while high selectivity toward C_2H_6 was attained in a dielectric barrier discharge reactor. In microwave plasmas, the product distribution shifted from C_2H_6 to C_2H_4 and finally to C_2H_2 with an increase in power density [28–31]. By introducing a proper catalyst into the microwave plasma reactor, CH_4 could be converted to higher hydrocarbons at atmospheric pressure. In addition, with a CH_4 and H_2 mixture as the feed gas, the selectivity to C_2H_2 was 88% and that to C_2H_4 was 6% at a CH_4 conversion of 76% [32]. Here, again, the

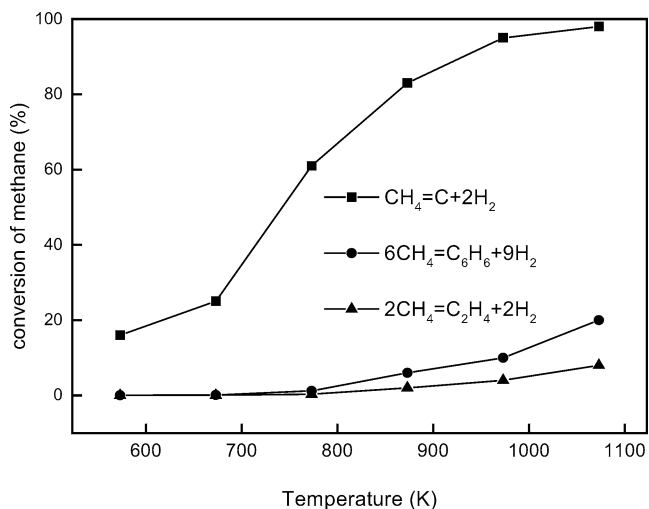


Fig. 1. Thermodynamics of direct conversion of CH_4 under nonoxidative conditions.

main drawback is the low energy efficiency to drive this thermodynamically unfavorable reaction.

Thermodynamically, the transformation of CH_4 under nonoxidative conditions is more favorable to aromatics than to olefins, as shown in Fig. 1. The direct conversion of CH_4 to aromatics was tested on several catalysts in either a pulse or a flow reactor [33,34]. In 1993, Wang et al. reported on the dehydroaromatization of methane (MDA) for the formation of aromatics (mainly C_6H_6) and H_2 under a nonoxidizing condition in a continuous flow reactor on Mo/HZSM-5 catalysts [35]. More-detailed studies on the reaction revealed that the channel structure and acidity of the HZSM-5 zeolite, as well as the valence and location of the Mo species, are crucial factors for the catalytic performance of the Mo/HZSM-5 catalysts.

Since then, many research groups, particularly the groups of Solymosi, Lunsford, Ichikawa, and Iglesia, have been interested in this reaction and have made encouraging progress. The most important features and findings of the reaction are as follows:

- Mo/HZSM-5 is a bifunctional catalyst;
- There is an induction period in the early stage of the reaction in which the MoO_x species are reduced by CH_4 into Mo_2C and/or MoO_xC_y species;
- Heavy carbonaceous deposits are formed during the reaction and lead to severe deactivation of the Mo/HZSM-5 catalysts;
- Many interactions, such as the interaction between the Mo species and the framework Al, and that between the Mo species and the acid sites of the zeolite, can be involved and would impose crucial influence on the catalytic performances;
- The molecular shape selectivity posed by the zeolite channels will remarkably affect the product distribution of the reaction.

Silica–alumina-type zeolites with a two-dimensional structure and a pore size near the dynamic diameter of benzene (0.59 nm) are good supports of the Mo-based catalysts for MDA. In addition to Mo, W, and Re are also reported to be active elements for MDA. Two review articles were published on this reaction, in 1999 and 2001 [36,37]. Readers who are interested in this subject may refer to these two papers and the references cited. In this paper, we will focus our attention on two fundamental and pivotal aspects of MDA over the Mo-modified HZSM-5 catalysts, namely, bifunctionality and the role of carbonaceous deposits. The active sites and reaction mechanism of MDA will be discussed in each of the relevant sections. In addition, some possible approaches for further improvement of the activity, selectivity, and stability of the Mo/HZSM-5 catalysts will also be considered.

3. The bifunctionality of the Mo/HZSM-5 catalysts

In the early studies of MDA, it was noticed that both the Mo species and the Brønsted acid sites are essential ingredients of an active catalyst, since neither HZSM-5 nor Mo/NaZSM-5 is active for MDA. Ichikawa and co-workers found that the formation rates of C₆H₆ on their 3% Mo/HZSM-5 catalysts substantially depended on the SiO₂/Al₂O₃ ratios of the HZSM-5 [38]. 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 3% Mo/HZSM-5 catalysts having the optimum SiO₂/Al₂O₃ ratio of around 40 showed maximum Brønsted acidity. A close relationship, however, only exists between the activity of C₂H₆ formation in MDA and the Brønsted acidity of Mo/HZSM-5, and no such relationship exists for the Lewis acidity.

Most researchers prepared the Mo/HZSM-5 catalysts by the impregnation method, with (NH₄)₆Mo₇O₂₄ as the starting material of the Mo component. Thus, the Mo species in the form of Mo₇O₂₄⁶⁻ would locate themselves on the external zeolite surface during the impregnation stage. When calcining at 773 K, the Mo-containing ions decompose into MoO₃ crystallites, and some of them migrate into the zeolite channels and interact with the Brønsted acid sites. Depending on the zeolite used and the preparation methods, the optimum Mo loading for MDA ranges from 2 to 6%. 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 ¹H MAS NMR spectra decrease with increasing Mo loading [39].

Solyosi and co-workers [40–42] and Lunsford and co-workers [43,44] characterized the Mo/HZSM-5 catalyst by means of XPS and found that during the initial induction pe-

riod, the original Mo⁶⁺ ions in the zeolite were reduced by CH₄ to Mo₂C, accompanied by the depositing of carbonaceous cokes. They suggested that Mo₂C provides active sites for C₂H₄ formation from CH₄, while the acidic sites catalyze the subsequent conversion to C₆H₆. The Mo₂C species are probably highly dispersed on the outer surface, and some of them reside in the channels of the zeolite. To characterize the active structure of the Mo/HZSM-5 catalysts, Ichikawa's group carried out Mo K-edge XAFS studies of a calcined Mo/HZSM-5 sample, and the results suggested that the Mo oxide species are highly dispersed in the internal channels of the HZSM-5 [38]. Meanwhile, the spectra of Mo/HZSM-5 samples reacted with CH₄ at 973 K for 1 and 24 h were basically identical to the Mo₂C reference spectrum, except for a partial contribution from the Mo oxide, given rise by MoO_xC_y. These authors claimed that the Mo oxide species dispersed in the HZSM-5 framework may migrate onto the external surface of the HZSM-5, be converted by CH₄ to Mo₂C, and disperse on the support surface.

Bao and co-workers, using TPSR of CH₄, clearly demonstrated that there is an induction period for the Mo-based catalysts in an early stage of MDA [45]. In their study of in situ ¹H MAS NMR spectroscopy of proton species over Mo/HZSM-5 catalysts during the reactions of CH₄, they reported that when the temperature was at or below 873 K, only a small decrease in the Brønsted acidity could be observed due to the temperature effect [46]. After increasing the temperature to 973 K for 10 min, the color of the catalyst changed from blue-white to black, indicating a transformation of the Mo component into molybdenum carbide. In conjunction with this observation, the intensity of the signal of Brønsted acid sites at ca. 4.0 ppm dramatically decreased instead of increasing. This is evidence proving that the Mo species keep in contact with the framework Al through two oxygen bridges. It seems that only the oxo bonds of the Mo species will be reduced and transformed into an oxycarbide form.

The ratio of the Mo species located on the external surface to those in the channels is difficult to determine definitely when the catalysts are prepared by impregnation. Iglesia and co-workers prepared the Mo/HZSM-5 catalysts using solid-state reaction method and studied the location and change of the Mo species during the preparation process in greater detail [47]. They found that the MoO_x species migrated onto the external surface first at ca. 623 K. Then, at temperatures between 773 and 973 K, the MoO_x species migrated into the zeolite channels via surface movement and gas-phase transport, exchanged at the acid sites, and reacted to form H₂O. In order to avoid obvious sublimation, these authors developed a procedure with which the sublimation of MoO_x species was found to be negligible [48]. Based on the amount of H₂O evolved during the exchange process and the number of residual OH groups detected by isotopic equilibration with D₂ and subsequently with H₂, they inferred that each Mo atom replaced one H⁺ during the exchange. With this stoichiometric measurement, in combination with

the requirement for charge compensation, Iglesia and co-workers suggested that the exchanged species consist of a ditetrahdral structure of $(\text{Mo}_2\text{O}_5)^{2+}$, which interacts with two cationic exchangeable sites. The $(\text{Mo}_2\text{O}_5)^{2+}$ species would be reduced by CH_4 in the initial stage of the reaction and be carbonized to form small MoC_x clusters, with the concurrent regeneration of the bridging OH groups that were initially replaced by Mo oxo dimmers during the exchange. The reduction and carbonization of the $(\text{Mo}_2\text{O}_5)^{2+}$ and the regeneration of the Brønsted acid sites were confirmed by monitoring the formation of H_2O and the isotopic exchange of D_2 with OH groups in HZSM-5 before and after the reaction with CH_4 at different intervals of time. In this way, the catalytically inactive Mo oxo species are activated during their contact with CH_4 . Thus, two sites required for the conversion of CH_4 to aromatics are formed: MoC_x for C–H bond activation and initial C–C bond formation, and acid sites for oligomerization and cyclization of C_{2+} hydrocarbons to form stable aromatics. The near-edge X-ray absorption technique was used by Iglesia and co-workers to characterize the Mo species on Mo/HZSM-5 samples treated under various conditions. They estimated that MoC_x clusters are ca. 0.6 nm in diameter and contain ca. 10 Mo atoms. MoC_x clusters of this size are likely to reside in the zeolite channels.

In their recent study on the bifunctionality of Mo/HZSM-5 catalysts, Xu, Bao, and co-workers [49] investigated the effect of the $\text{Mo}/[\text{H}^+]$ ratio per unit cell on the catalytic performance of Mo/HZSM-5 catalysts with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios and Mo loadings. It is interesting to note that the exchange between the Mo species and the Brønsted acid sites was negligible when the parent HZSM-5 had a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio as high as 250 (see Fig. 2). In other words, the driving force behind the migration of the Mo species into the zeolite channels strongly depends on the Brønsted acid sites. On the other hand, the optimum $\text{Mo}/[\text{H}^+]$ ratio per unit cell of the active precursors in the Mo/HZSM-5

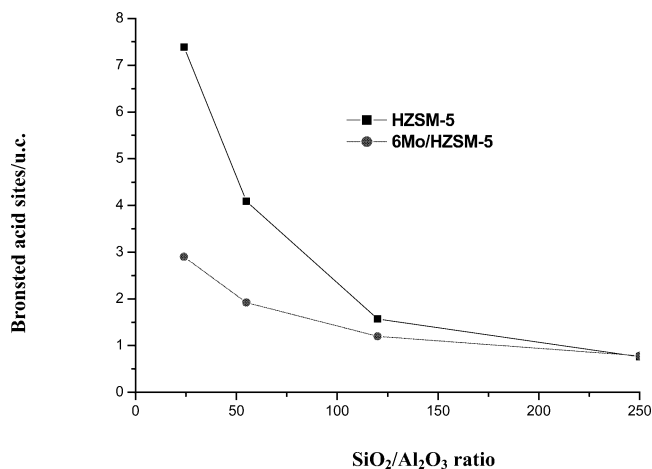


Fig. 2. Variation of the Brønsted acid sites per unit cell of HZSM-5 and 6Mo/HZSM-5 catalysts with the increase of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios estimated from ^1H MAS NMR spectra.

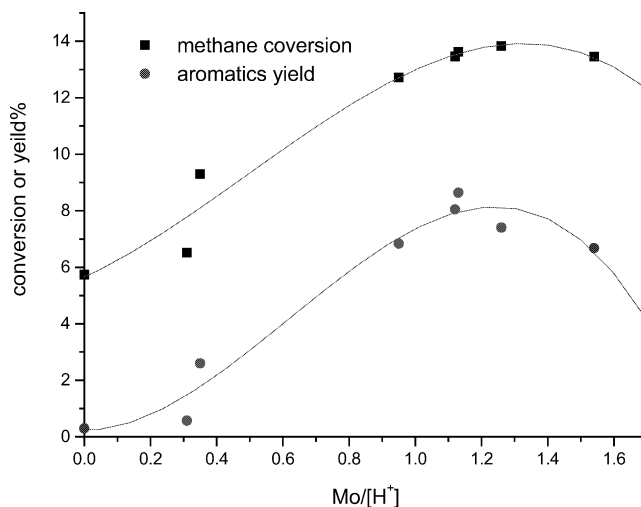


Fig. 3. Dependences of methane conversion and aromatics yield on the $\text{Mo}/[\text{H}^+]$ ratios. The $\text{Mo}/[\text{H}^+]$ ratios were adjusted through (i) 6 wt% Mo/HZSM-5 catalysts prepared using HZSM-5 with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios and (ii) Mo/HZSM-5 catalysts with different Mo loadings but using HZSM-5 with a fixed $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 55.

catalysts for MDA, estimated by ^1H MAS NMR and XRF, was found to be around 1 when the $\text{Mo}/[\text{H}^+]$ ratio per unit cell was adjusted by altering either the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio or the Mo loading, as shown in Fig. 3. This implies that a synergistic effect between the Mo species and the Brønsted acid sites probably features the bifunctionality of the Mo/HZSM-5 catalyst. Only with this $\text{Mo}/[\text{H}^+]$ ratio per unit cell can the Mo species cooperate with the Brønsted acid sites harmoniously to first activate the CH_4 and then transform the intermediates into aromatics.

4. Carbonaceous deposits: characterization and their roles in MDA

Heavy carbonaceous deposits are formed during MDA, which present a major obstacle for a better understanding of the reaction and process development. Lunsford and co-workers [50] identified three different types of surface carbon species on a used Mo/HZSM-5 catalyst by using XPS. The authors denoted them as species A, B, and C. Species A, characterized by a C1s binding energy (BE) of 284.6 eV, can be attributed to graphiticlike carbon and is mainly present in the zeolite channels. Species B, with a C1s BE of 282.7 eV, comes from the carbidiclike carbon in Mo_2C and mainly locates on the outer surface of the zeolite. Species C, with a C1s BE of 283.2 eV, is a hydrogen-poor sp type or pregraphitic type of carbon. Species C is also mainly present on the outer surface of the zeolite, and its amount increases with increasing time on stream. The sp-type carbon (species C) gradually covers both the zeolite surface and the Mo_2C phase during MDA and is responsible for the deactivation of the Mo/HZSM-5 catalyst.

The chemical nature of the carbonaceous deposits was characterized on Mo/HZSM-5 and Mo/MCM-22 catalysts by temperature-programmed surface reaction (TPSR) of CH₄, temperature-programmed hydrogenation (TPH), temperature-programmed reaction of CO₂ (TPCO₂), temperature-programmed oxidation (TPO), and thermal-gravimetric analysis (TGA) [51–53]. There are at least three different kinds of cokes: carbidic carbon in molybdenum carbide, molybdenum-associated coke, and aromatic-type coke on acid sites. The TPO profiles of the coked 6% Mo/HZSM-5 catalyst after TPSR of CH₄ show two temperature peaks: one is at about 776 K and the other at about 865 K. Note that it is difficult to separate the burning-off peak of the carbidic carbon in molybdenum carbide with the burning-off peak of the molybdenum-associated coke in TPO experiments, but the authors do observe some weight increments due to the transformation of molybdenum carbides into molybdenum oxides in the TGA course of coked Mo/HZSM-5 catalysts. The succeeding TPH experiments of the coked 6% Mo/HZSM-5 catalyst after TPSR of CH₄ only resulted in the diminishing of the area of the high-temperature peak and had no effect on the area of the low-temperature peak. On the other hand, the TPO profiles of the coked catalyst, after succeeding TPCO₂ experiments, exhibited obvious reduction in the areas of both the high- and low-temperature peaks, particularly in the latter. The results suggest that H₂ might only react with the coke, which is burned off at high temperatures in the TPO experiment, while CO₂ can eliminate the carbonaceous deposits, which are burned off at both low and high temperatures. Either the procedure of TPH followed by TPCO₂ or the procedure of TPCO₂ followed by TPH, could only partially reduce the amount of coke on a coked 6% Mo/HZSM-5 catalyst [51].

Xu, Bao, and co-workers [54] also studied the effect of contact time on the catalytic performance of MDA on a 6% Mo/MCM-22 catalyst. The CH₄ conversion sharply increased when the contact time was less than 0.5 s g ml⁻¹ and then changed less rapidly with the contact time. This means that the MDA is severely inhibited by the products or intermediates. Since the yields of the products, such as C₂₊, C₆H₆, and C₁₀H₈, passed through the origin and displayed an increasing trend, whereas the yield of the carbonaceous deposits decreased with the contact time in the range of < 1.5 s g ml⁻¹, the implication is that the carbonaceous deposits are the initial products. C₂₊, C₆H₆, and C₁₀H₈ are the primary products formed in parallel and/or in succession with each other and/or are formed through the same reaction intermediate, i.e., the active carbon species, CH_x (x ≤ 2).

Therefore, the carbonaceous deposits created in MDA are in various forms and play different roles. First, Mo₂C and/or MoO_xC_y, which are possibly active species for CH₄ activation, are formed during the induction period. Second, the formation of the active intermediates, the CH_x species, follows the activation of CH₄ on Mo₂C and/or MoO_xC_y. The last one to be formed is coke, which leads to the deactivation of the catalyst. It is understandable that there

are some similarities between the carbonaceous species formed in MDA and those formed in the first step of the two-step process, since both reactions are carried out under nonoxidative conditions, and Mo₂C does show some precious-metal-like properties.

In spite of the fact that the reaction is thermodynamically unfavorable under pressurized conditions and that 10% CO₂ added to the feed totally suppresses the activity of the 2 wt% Mo/HZSM-5 catalyst [43], Ichikawa and co-workers found that an increase in CH₄ pressure and the addition of a small amount of CO and CO₂ (less than 3%) to the CH₄ feed enhanced catalyst stability in the reaction [55–57]. By increasing the CH₄ pressure, the formation rates of C₆H₆ and hydrocarbons could be moderately increased. This kind of pressure relationship may be connected to a sufficient supply of H₂ from CH₄ and a suitable concentration of surface carbon species CH_x for the formation of aromatics products. Furthermore, the authors claimed that the addition of CO and CO₂ to the CH₄ feed (less than 3%) led to a remarkable increase in the stability of the catalyst. By using a ¹³CO and CH₄ mixture as the feed to conduct the reaction, the authors suggested that CO dissociated on the Mo sites to form the active carbon species CH_x. The dissociated oxygen species [O] from CO might react with the surface inert carbon species to regenerate CO, resulting in the suppression of coke formation on the catalyst. This type of effect on catalyst stability, due to the addition of CO and CO₂, can be extended to the Co–Mo/HZSM-5, Fe–Mo/HZSM-5, and Re/HZSM-5 catalysts [58,59].

Another effective way of enhancing the activity and increasing the stability of the Mo/HZSM-5 catalysts is to adjust the Brønsted acid sites and their distribution on/in the parent zeolites. Recently, it was reported that treatment of the parent zeolite by steam dealumination, dealumination by acid solutions, or silanization with large-size Si-containing molecules could all greatly depress the rate of coke formation and improve the durability of Mo/HZSM-5 and Mo/MCM-22 catalysts. Lin and co-workers [60,61] demonstrated that significant improvements could be realized on a Mo catalyst supported on predealuminated HZSM-5 (by steam treatment). 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. Yu et al. [62] discovered that even a simple pretreatment of the parent HZSM-5 with N₂ at 773 K for 2 h could remarkably diminish the concentration of the Brønsted acid sites, thus markedly increasing the selectivity to C₆H₆ and the durability of the catalyst during MDA. These results imply that although the Brønsted acid sites are necessary, excess Brønsted acid sites are detrimental for the reaction, since severe coke formation will occur on them.

Iglesia and co-workers [63] claimed that selective silanation of external acid sites on HZSM-5 by using large organosilane molecules could decrease the content of acid sites as well as the number of MoO_x species retained at the external surface, which was regarded as a key factor

for coke formation during MDA. On samples prepared using silica-modified HZSM-5, acid sites, MoO_x precursors, and active MoC_x species formed during the CH_4 reaction at 950 K were found to predominately reside within the zeolite channels, where spatial constraints could inhibit the bimolecular chain-growth pathways. Consequently, the formation rate of hydrocarbons on a 4% Mo/silica-modified HZSM-5 increased by about 30% in comparison with that on a 4% Mo/HZSM-5.

5. Perspective: challenges and opportunities

Zeolite catalysts modified with TMI are becoming a new kind of catalyst system in heterogeneous catalysis, owing to the continual development of new zeolite materials and the new demand for green chemistry. The MDA reaction on Mo/HZSM-5 catalysts is also a typical example involving TMI-modified zeolite catalysts. Consequently, more-detailed, fundamental knowledge of the TMI-modified zeolite catalysts, particularly Mo/HZSM-5 catalysts, is necessary for solving many of the problems we are facing. The TMI species may reside in different locations and in various forms in a TMI-modified zeolite catalyst. They might exist as isolated ions in framework positions (isomorphously substituted) or in cationic forms in exchangeable sites or in binuclear and oligonuclear complex in extraframework positions, as oxide in nanoparticles < 2 nm in size, or as large oxide particles in a wide distribution located at the surface of the zeolite crystals [64]. Having control over the distribution of the TMI species on/in the zeolite and over their particle size is certainly an important way to influence the catalyst's activity and selectivity. In addition, the controlled activation of the C–H bond of methane and the formation of the C–C bond have been extremely important and common topics in transition metal chemistry and methane chemistry, as well as in homogeneous and heterogeneous catalysis. In fact, transition metal centers play crucial roles in the recent development of promising catalytic systems for C–H activation reactions in homogeneous catalysis, and considerable mechanistic insight has been gained. Labinger and Bercaw recently reviewed this topic in a publication [65]. Therefore, it may be appropriate to utilize to the increasing knowledge in the fields of transition metal chemistry and homogeneous catalysis gained at the molecular level when attempting to understand the nature and mechanism of the MDA reaction over the Mo/HZSM-5 catalysts.

Second, more definite experimental information is needed to understand the nature of the MDA reaction and its mechanisms at the molecular level. Solymosi et al. [66,67] studied the formation and reaction of CH_3 , CH_2 , and C_2H_5 species to gain more insight into the reaction mechanism by employing their corresponding halogenated hydrocarbons on a $\text{Mo}_2\text{C}/\text{Mo}(111)$ surface. The results demonstrated that the main products of the initially adsorbed CH_3 generated from CH_3I on Mo_2C were H_2 , CH_4 , and C_2H_4 , while the

coupling of CH_3 to C_2H_6 was not observed. Meanwhile, the CH_2 species introduced from CH_2I_2 were easily self-hydrogenated to CH_4 and dimerized into C_2H_4 . TPD measurements confirmed that coupling of the CH_2 species to C_2H_4 species was a more favorable step on Mo_2C than on precious metals such as Rh(111) and Pt(111). Therefore, it was suggested that Mo_2C is the active component for methane activation and dimerization to C_2H_4 , and aromatization occurred, catalyzed by protonic acid sites, through the oligomerization/cyclization reactions of C_2H_4 . However, Mériaudeau and co-workers [68–70] challenged this bifunctional description of the reaction mechanism and suggested a monofunctional mechanism, with C_2H_2 formed from CH_4 on highly dispersed Mo_2C as the primary product. Moreover, C_6H_6 was also formed from C_2H_2 over Mo_2C . These authors claimed that based on their results of the reactions of CH_4 , C_2H_2 , and C_2H_4 over acidic HZSM-5, nonacidic $\text{Mo}_2\text{C}/\text{SiO}_2$ and $\text{Mo}_2\text{C}/\text{HZSM-5}$ catalysts, and H^+ ions almost completely removed after the induction period following CH_4 reaction at 623 K, the H^+ sites are not a prerequisite for C_2H_2 or C_2H_4 aromatization. On the other hand, Derouane-Abd Hamid and co-workers [71,72] noticed that two molybdenum carbide phases existed: $\beta\text{-Mo}_2\text{C}$ in a hexagonally close-pack structure, and $\alpha\text{-MoC}_{1-x}$ in a face-centered cubic structure. The authors showed that the $\alpha\text{-MoC}_{1-x}$ species was more effective than the $\beta\text{-Mo}_2\text{C}$ species for MDA, demonstrating a higher activity, selectivity, and stability. Unfortunately, most of the research teams prepared their Mo/HZSM-5 catalysts with a $\beta\text{-Mo}_2\text{C}$ phase during the reaction. The work of Liverpool's group was recently repeated in our group. Figures 4A and 4B illustrate that the catalytic performances of MDA over the catalyst prepared by reduction of $\text{MoO}_3/\text{HZSM-5}$ with only H_2 at about 623 K for 6 h are similar to that from those pretreated with a mixture of $\text{H}_2/n\text{-C}_4\text{H}_{10}$ at 623 K for 24 h.

Third, Iglesia et al. [73] pointed out that there are two bifunctional pathways: concerted bifunctional pathways and sequential bifunctional pathways. In general, concerted bifunctional pathways require sites to coexist within molecular distances, which is often the case in homogeneous and enzymatic catalysis. In heterogeneous catalysis, however, concerted interaction may be prevented by the fixed and inappropriate location of the sites in question, but rapid transfer of intermediates via surface or gas-phase diffusion leads to kinetic coupling between distant sites and, thus, to a sequential bifunctional pathway. For example, the sequential bifunctional pathways are well accepted for dehydroaromatization of light alkanes (LHDA) on Zn- and/or Ga-modified HZSM-5 catalysts. However, a concrete description of the sequential bifunctional pathway is still up for debate. It is generally accepted that the Ga species take part in all dehydrogenation reactions, such as the dehydrogenation of propane into propene and the transformation of alkenes into dienes and finally into aromatics, as involved in the propane aromatization process [74]. In contrast, Iglesia et al. simultaneously measured the rates of C–H activation,

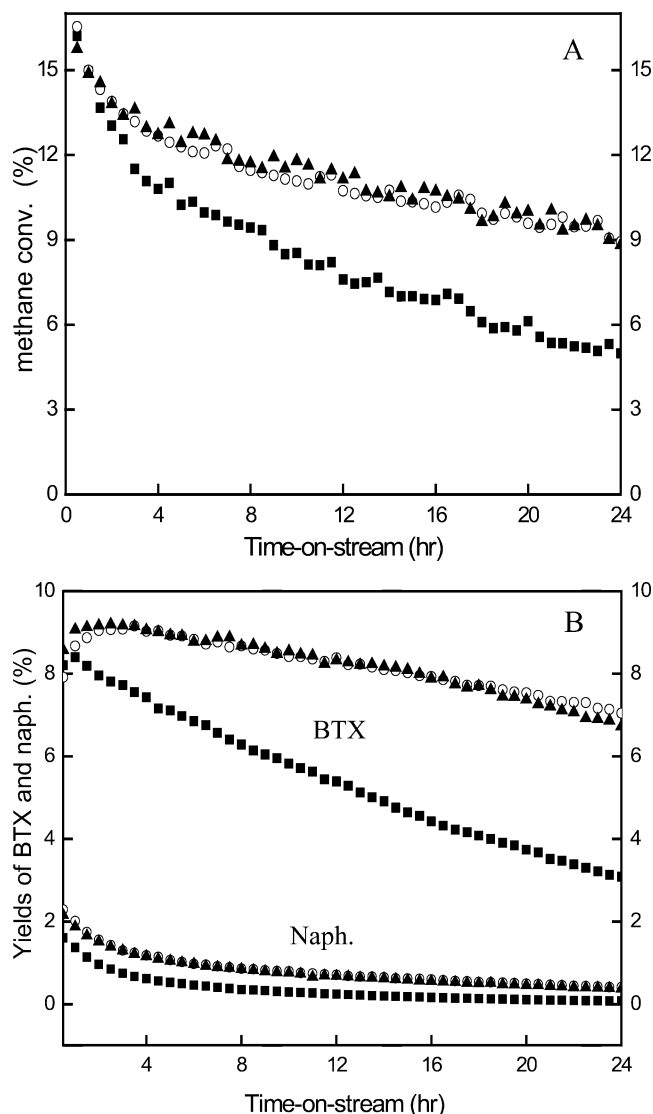


Fig. 4. A comparison of the catalytic performances of 6% Mo/HZSM-5 catalysts pretreated with different modes: (A) methane conversion, (B) the yields of BTX and naphthalene. ■, Pretreated with CH₄; ○, pretreated with H₂; ▲, pretreated with H₂/n-C₄H₁₀.

recombinative hydrogen desorption, and propane dehydrogenation by using isotopic redistribution and chemical conversion data obtained from C₃H₈/C₃D₈ and D₂/C₃H₈ mixtures. The authors pointed out that the activation of the C–H bond in propane predominantly occurs on the Brønsted acid sites, and the Zn and/or Ga cations play a role in the recombination of hydrogen adatoms formed during the C–H activation [73].

Due to the similarities between the MDA and the LHDA (both processes use HZSM-5 as the support, a certain TMI is necessary (Zn or Ga for LHDA and Mo, W, or Re for MDA), both reactions regard olefin as their intermediate product, and the activation and dehydrogenation of alkane concerned is the rate-determining step), the MDA can be regarded as an extension of the LHDA. Until now, the general description of the MDA reaction on Mo/HZSM-5

catalysts has followed the sequential bifunctional pathway and has been quite similar to those of the LHDA. Methane is first activated and dehydrogenated into CH_x, which will oligomerize into C₂ species on Mo₂C and/or MoO_xC_y species on the external surface and/or in the zeolite channels, then it oligomerizes further and cyclizes into aromatics on the Brønsted acid sites. Lin and co-workers carried out a comparative FT-IR study on the interaction of CH₄ with silica, alumina, and HZSM-5 [75]. The results demonstrated that OH groups played a very important role in CH₄ adsorption. When an interaction between the OH groups and CH₄ took place, the band shift of the OH groups varied and the strength of the interaction decreased in accordance with the order of their acidities (Si–OH–Al > Al–OH > Si–OH). The authors considered the possibility that CH₄ is activated by interacting with a proton to form an intermediate CH₅⁺, which would be decomposed to CH₃⁺, leading to a heterolytic cleavage of a C–H bond of CH₄. Therefore, the MDA reaction may require dehydrogenation and chain-growth steps that occur on Brønsted acid sites, aided by hydrogen desorption sites provided by MoC_x species.

Fourth, coupling the MDA reaction with other reactions and/or techniques is perhaps the most plausible way to make methane conversion under nonoxidative conditions a commercially applicable process. As mentioned above, dehydrogenative coupling of methane, particularly with a mixture of CH₄ and H₂ under the assistance of plasma, has already made great progress. Recently, Heintze and Magureanu reported the conversion of CH₄ to aromatics in pulsed microwave plasma at atmospheric pressure in the presence of a heterogeneous catalyst [76]. The CH₄ conversion could reach 60–70% if average input powers were higher than 200 W. The main product under the experimental conditions was C₂ hydrocarbons. Since the aromatics could be observed only after initial carbon formation, the authors suggested that the solid carbon could catalyze methane aromatization. Studies to couple the MDA reaction with the membrane separation technique are already under way by several research groups. Based on thermodynamic calculations, it was estimated that if half of the H₂ produced during MDA at 973 K could be removed, the corresponding CH₄ conversion would increase from about 10 to 66% [77]. However, preliminary reports on this approach are not very optimistic. In one case, the H₂ transport rates were too low to match the hydrogen formation rate in the MDA reaction [77]. In another case, it was reported that if the reaction was carried out in a membrane catalytic reactor, because of the continuous withdrawal of the coproduced H₂, catalyst deactivation was more pronounced than in a fixed-bed reactor [78].

We mentioned in Section 4 that adjusting the Brønsted acid sites and their distribution is an effective way to enhance the activity and increase the stability of the Mo/HZSM-5 catalysts. In reference to other catalytic reactions involving acid sites, there is still room left to fine-tune both the acid

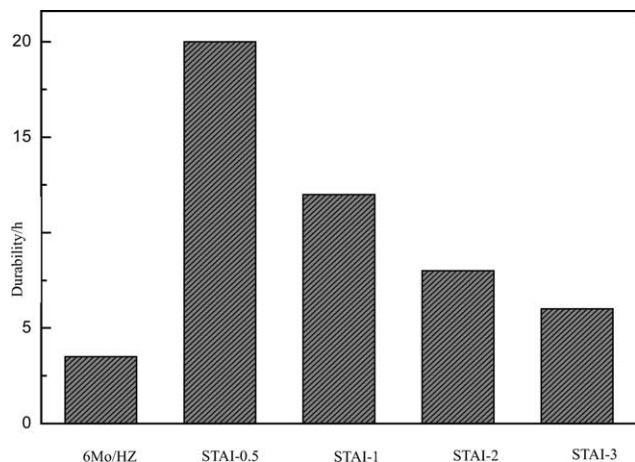


Fig. 5. Durabilities of various 6% Mo/HZSM-5 catalysts before the yield of benzene dropped to 4.6%. STAI-*t* means that the 6% Mo/HZSM-5 catalysts were treated with steam for different times (in h).

amount and acid strength distribution of the Brønsted acid sites, so that they can be made to better match the active species, such as in the case of MoC_x species for MDA. For example, the driving force for the Mo species to move into the HZSM-5 zeolite channels and the interaction between the Mo species and the Brønsted acid sites are almost exponentially related to the number of Brønsted acid sites per unit cell [49]. Therefore, the effect of dealumination of HZSM-5 zeolites may be compensated for at the expense of the driving force of Mo species moving into the channels. We recently studied the effect of dealumination of the Mo/HZSM-5 catalysts by steam treatment on the catalytic performances of MDA. The results illustrated in Fig. 5 show that it is also an efficient procedure for enhancing the activity and stability of Mo/HZSM-5 catalysts.

6. Concluding remarks

As we mentioned above, hydrogen energy will inevitably replace fossil fuel energy in the near future. Therefore, the direct conversion of CH₄ under nonoxidative conditions has an intrinsic merit for production of H₂ and/or for H₂ production accompanied by basic chemicals. The development of methane dehydroaromatization is a potentially important process for hydrogen production, accompanied by aromatics. Considerable effort has been devoted developing active and selective catalysts and understanding the bifunctionality of Mo/HZSM-5 catalysts and the nature of carbonaceous deposits formed during the reaction. However, neither new active and selective catalysts nor a thorough understanding of the mechanism of the reaction has been achieved. In any case, our understanding of the direct conversion of CH₄ under nonoxidative conditions, particularly methane dehydroaromatization, has increased a great deal. Ongoing research in this area, in conjunction with the advancement in heterogeneous and homogeneous catalysis, transition metal chemistry, chemical engineering, and materials science, will

certainly enhance our knowledge of direct activation and conversion of methane and lead to the development of an efficient, clean, profitable, and applicable process.

Acknowledgments

Financial support from the Ministry of Science and Technology of China, the Natural Science Foundation of China, the Chinese Academy of Sciences, and the BP-China Joint Research Center is gratefully acknowledged.

References

- [1] J.H. Lunsford, *Stud. Surf. Sci. Catal.* 81 (1993) 1.
- [2] K. Tanabe, Y. Teng, T. Takemoto, E. Suzuki, M.A. Banares, M.A. Pena, J.L.G. Fierro, *Catal. Rev.* 44 (2002) 1.
- [3] G.A. Olah, Y. Halpern, J. Shen, Y.K. Mo, *J. Am. Chem. Soc.* 93 (1971) 1251; G.A. Olah, J.A. Olah, *J. Am. Chem. Soc.* 93 (1971) 1256.
- [4] R.A. Periana, D.J. Taube, E.R. Evitt, D.G. Loffler, P.R. Wentreck, G. Voss, T. Masuda, *Science* 259 (1993) 340; R.A. Periana, D.J. Taube, S. Gamble, H. Taube, T. Satoh, H. Fujii, *Science* 280 (1998) 560.
- [5] M. Belgued, P. Pareja, A. Amariglio, H. Amariglio, *Nature* 352 (1991) 789.
- [6] T. Koerts, M.T.A.G. Deelen, R.A. van Santon, *J. Chem. Soc. Chem. Commun.* (1991) 1281.
- [7] P. Pareja, A. Amariglio, M. Belgued, H. Amariglio, *Catal. Today* 21 (1994) 423.
- [8] H. Amariglio, P. Pareja, A. Amariglio, *Catal. Today* 25 (1995) 113.
- [9] H. Amariglio, M. Belgued, P. Pareja, A. Amariglio, *Catal. Lett.* 31 (1995) 19.
- [10] M. Belgued, A. Amariglio, P. Pareja, H. Amariglio, *J. Catal.* 159 (1996) 441; M. Belgued, A. Amariglio, P. Pareja, H. Amariglio, *J. Catal.* 159 (1996) 449.
- [11] M. Belgued, A. Amariglio, L. Lefort, P. Pareja, H. Amariglio, *J. Catal.* 161 (1996) 282.
- [12] A. Amariglio, M. Belgued, P. Pareja, H. Amariglio, *J. Catal.* 177 (1998) 113; H. Amariglio, M. Belgued, P. Pareja, A. Amariglio, *J. Catal.* 177 (1998) 121.
- [13] T. Koerts, M.T.A.G. Deelen, R.A. van Santon, *J. Catal.* 138 (1992) 101.
- [14] T. Koerts, R.A. van Santon, *J. Mol. Catal.* 74 (1992) 185.
- [15] T. Koerts, P.A. Leclercq, R.A. van Santon, *J. Am. Chem. Soc.* 114 (1992) 7272.
- [16] F. Solymosi, A. Erdohelyi, J. Cserenyi, A. Felvegi, *J. Catal.* 147 (1994) 272.
- [17] F. Solymosi, J. Cserenyi, *Catal. Lett.* 34 (1995) 343.
- [18] L. Guzzi, K.V. Sarma, L. Borko, *J. Catal.* 167 (1997) 495.
- [19] L. Guzzi, K.V. Sarma, L. Borko, *Catal. Lett.* 39 (1996) 43.
- [20] J.N. Carstens, A.T. Bell, *J. Catal.* 161 (1996) 423.
- [21] M. Wu, Q. Xu, D.W. Goodman, *J. Phys. Chem.* 98 (1994) 5104.
- [22] E. Marceau, J.-M. Tatibouet, M. Che, J. Saint-Just, *J. Catal.* 183 (1999) 384.
- [23] L. Guzzi, L. Borko, Zs. Koppány, I. Kiricsi, *Stud. Surf. Sci. Catal.* 119 (1998) 295.
- [24] L. Guzzi, L. Borko, *Catal. Today* 64 (2001) 91.
- [25] M.C.J. Bradford, *Catal. Lett.* 66 (2000) 113.
- [26] H.L. Mitchell III, R.H. Wanyhorne, US Patent 4,239,658, 1980.
- [27] T. Kurosaka, H. Matsuhashi, K. Arata, *J. Catal.* 179 (1998) 28.

- [28] S. Kado, Y. Sekine, K. Fujimoto, *Chem. Commun.* (1999) 2485.
- [29] A. Zhu, W. Gong, X. Zhang, B. Zhang, *Sci. China* 43 (2000) 208.
- [30] K. Thanyachotpaiboon, S. Chavadej, T.A. Caldwell, L.L. Lobban, R.G. Mallinson, *React. Kinet. Catal.* 44 (1998) 2252.
- [31] K. Onoe, A. Fujie, T. Yamaguchi, Y. Hatano, *Fuel* 76 (1997) 281.
- [32] Y. Xu, Z. Tian, Z. Xu, A. Zhu, L. Lin, *Stud. Surf. Sci. Catal.* 136 (2001) 75.
- [33] O.V. Bragin, T.V. Vasina, A.V. Preobrazhenskii, Kh.M. Minachev, *I. Ser. Khim.* 3 (1989) 750.
- [34] T. Inui, Y. Ishihara, K. Kamachoi, H. Matsuda, *Stud. Surf. Sci. Catal.* 49 (1989) 1183.
- [35] L. Wang, L. Tao, M. Xie, G. Xu, J. Huang, Y. Xu, *Catal. Lett.* 21 (1993) 35;
Y. Xu, S. Liu, L. Wang, M. Xie, X. Guo, *Catal. Lett.* 30 (1995) 135.
- [36] Y. Xu, L. Lin, *Appl. Catal. A* 188 (1999) 53.
- [37] Y. Shu, M. Ichikawa, *Catal. Today* 71 (2001) 55.
- [38] S. Liu, L. Wang, R. Onishi, M. Ichikawa, *J. Catal.* 181 (1999) 175.
- [39] D. Ma, W. Zhang, Y. Shu, Y. Xu, X. Bao, *Catal. Lett.* 66 (2000) 155.
- [40] F. Solymosi, A. Erdohelyi, A. Szoke, *Catal. Lett.* 32 (1995) 43.
- [41] A. Szoke, F. Solymosi, *Appl. Catal. A* 142 (1996) 361.
- [42] F. Solymosi, J. Cserenyi, A. Szoke, T. Bansagi, A. Dszko, *J. Catal.* 165 (1997) 150.
- [43] D. Wang, J.H. Lunsford, M.P. Rosynek, *Top. Catal.* 3 (1996) 289.
- [44] D. Wang, J.H. Lunsford, M.P. Rosynek, *J. Catal.* 169 (1997) 347.
- [45] D. Ma, Y. Shu, M. Cheng, Y. Xu, X. Bao, *J. Catal.* 194 (2000) 105.
- [46] D. Ma, Y. Shu, W. Zhang, X. Han, Y. Xu, X. Bao, *Angew. Chem. Int. Ed. Engl.* 39 (2000) 2928.
- [47] R.W. Borry III, Y.H. Kim, A. Huffsmith, J.A. Reimer, E. Iglesia, *J. Phys. Chem. B* 103 (1999) 5787.
- [48] W. Ding, S. Li, G.D. Meitzner, E. Iglesia, *J. Phys. Chem. B* 105 (2001) 506.
- [49] L. Su, Z. Yan, X. Liu, Y. Xu, X. Bao, *J. Nat. Gas Chem.* 11 (2002) 180.
- [50] B.M. Weckhuysen, M.P. Rosynek, J.H. Lunsford, *Catal. Lett.* 52 (1998) 31.
- [51] H. Liu, T. Li, B. Tian, Y. Xu, *Appl. Catal. A* 213 (2001) 103.
- [52] D. Ma, D. Wang, L. Su, Y. Shu, Y. Xu, X. Bao, *J. Catal.* 208 (2002) 260.
- [53] H. Liu, L. Su, H. Wang, W. Shen, X. Bao, Y. Xu, *Appl. Catal. A* 236 (2002) 263.
- [54] Y. Shu, D. Ma, L. Su, L. Xu, Y. Xu, X. Bao, *Stud. Surf. Sci. Catal.* 136 (2001) 27.
- [55] S. Liu, L. Wang, Q. Dong, R. Onishi, M. Ichikawa, *Stud. Surf. Sci. Catal.* 119 (1998) 241.
- [56] S. Liu, L. Wang, Q. Dong, R. Onishi, M. Ichikawa, *Chem. Commun.* (1998) 1217.
- [57] Y. Shu, R. Ohnishi, M. Ichikawa, *J. Catal.* 206 (2002) 134.
- [58] R. Onishi, S. Liu, Q. Dong, L. Wang, M. Ichikawa, *J. Catal.* 182 (1999) 92.
- [59] L. Wang, R. Ohnishi, M. Ichikawa, *J. Catal.* 190 (2000) 276.
- [60] Y. Lu, D. Ma, Z. Xu, Z. Tian, X. Bao, L. Lin, *Chem. Commun.* (2001) 2048.
- [61] D. Ma, Y. Lu, L. Su, Z. Xu, Z. Tian, Y. Xu, L. Lin, X. Bao, *J. Phys. Chem. B* 106 (2002) 8524.
- [62] L. Yu, Y. Song, F. Ye, C. Sun, Y. Fang, Z. Hao, Y. Xu, L. Lin, unpublished results.
- [63] W. Ding, G.D. Meitzner, E. Iglesia, *J. Catal.* 206 (2002) 14.
- [64] J. Perez-Ramirez, G. Mul, F. Kapteijin, J.A. Moulijn, A.R. Overweg, A. Domenech, A. Ribera, I.W.C.E. Arends, *J. Catal.* 207 (2002) 113.
- [65] J.A. Labinger, J.E. Bercaw, *Nature* 417 (2002) 507.
- [66] F. Solymosi, L. Bugyi, A. Oszko, *Catal. Lett.* 57 (1999) 103.
- [67] F. Solymosi, L. Bugyi, A. Oszko, I. Hovarth, *J. Catal.* 185 (1999) 160.
- [68] P. Mériaudeau, L.V. Tjep, V.T.T. Ha, C. Naccache, G. Szabo, *J. Mol. Catal. A* 144 (1999) 469.
- [69] P. Mériaudeau, V.T.T. Ha, L.V. Tjep, *Catal. Lett.* 64 (2000) 49.
- [70] V.T.T. Ha, L.V. Tjep, P. Mériaudeau, C. Naccache, *J. Mol. Catal. A* 181 (2002) 283.
- [71] C. Bouchy, I. Schmidt, J.R. Anderson, C.J.H. Jacobsen, E.G. Derouane, S.B. Derouane-Abd Hamid, *J. Mol. Catal. A* 163 (2000) 283.
- [72] S.B. Derouane-Abd Hamid, J.R. Anderson, I. Schmidt, C. Bouchy, C.J.H. Jacobsen, E.G. Derouane, *Catal. Today* 63 (2000) 461.
- [73] E. Iglesia, D.G. Barton, J.A. Biscardi, M.J.L. Gines, S.L. Soled, *Catal. Today* 38 (1997) 339.
- [74] A. Montes, G. Giannetto, *Appl. Catal. A* 197 (2000) 31.
- [75] L. Chen, L. Lin, Z. Xu, T. Zhang, D. Liang, *Catal. Lett.* 35 (1995) 245.
- [76] M. Heintze, M. Magureanu, *J. Catal.* 206 (2002) 91.
- [77] R.W. Borry III, E.C. Lu, Y.-H. Kim, E. Iglesia, *Stud. Surf. Sci. Catal.* 119 (1998) 403.
- [78] O. Rival, B.P.A. Grandjean, C. Guy, A. Sayari, F. Lrachi, *Ind. Eng. Chem. Res.* 40 (2001) 2212.