Microwave effects on the selective reduction of NO by CH_4 over an In–Fe_2O_3/HZSM-5 catalyst

Xiaodong Wang, Tao Zhang,* Changhai Xu, Xiaoying Sun, Dongbai Liang and Liwu Lin

State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China. E-mail: taozhang@ms.dicp.ac.cn

Received (in Cambridge, UK) 30th November 1999, Accepted 7th January 2000

Microwave effects have been shown to promote the activation of NO_x molecules in the process of selective reduction of NO by CH_4 over an In–Fe_2O_3/HZSM-5 catalyst and to enhance the water tolerance of this catalyst for NO reduction.

Microwave radiation technology has been applied in heterogeneous catalysis research in the last ten years.[1] The use of microwave radiation to stimulate catalytic reactions has provided some remarkable results.[2,3] However, the effects of microwave radiation on heterogeneous catalysis have not been clearly elucidated yet. Recently the selective catalytic reduction (SCR) of nitrogen oxides by hydrocarbons has received much attention as this process has the advantage of using a gas mixture very similar to that found in automobile exhausts. Since methane exists in nearly all combustion exhausts, the CH_4-SCR has attracted increasing interest, and various types of catalysts have been reported for this reaction.[4] We studied the selective catalytic reduction of NO with CH_4 in a microwave field.[5] An In–Fe_2O_3/HZSM-5 catalyst has been found to show high activity at low reaction temperatures. Here, we report on the microwave effects on this process.

The In–Fe_2O_3/HZSM-5 catalyst was prepared by impregnating a mechanical mixture of commercial pure Fe_2O_3 and HZSM-5 powders (SiO_2/Al_2O_3 = 25, supplied by Nankai University, China) with a required amount of an aqueous solution of $In(NO_3)_3$ (Tianjin No. 3 Reagent Plant, China). The samples were dried at 120 °C for 6 h and subsequently calcined in air at 700 °C for 6 h. The catalysts were denoted by the weight ratios of indium, iron oxide and HZSM-5 zeolite, for example, In–Fe_2O_3/HZSM-5(1 : 8 : 20) indicates In : Fe_2O_3 : HZSM-5 = 1 : 8 : 20 (weight ratio).

The SCR of NO by CH_4 was carried out in a quartz microcatalytic single-pass flow reactor. The feed gas contained 2500 ppm NO, 2000 ppm CH_4 and 4.0% O_2 (balance He); 3.3% H_2O was added to this feed gas when the water tolerance effect was investigated. Under standard reaction conditions, 60 ml min^{-1} of this mixture were fed over a catalyst loading of 500 mg, which results in a space velocity of 3600 h^{-1}. Product analyses were performed with a gas chromatograph and a NO_x analyzer. The catalytic activity was evaluated in terms of the conversion of NO_x to N_2.

The microwave reaction system consisted of a microwave generator, a rectangular waveguide, a circulator, a resonant cavity and a plunger. The microwave energy was supplied by a 200 W, 2.45 GHz microwave generator and the effective power for this experiment ranged from 10 to 50 W. The reactor was placed at the center of the single mode resonant cavity, which was parallel to the direction of the electric field. An IR thermometer and a thermocouple were employed to measure the reaction temperature of the catalyst bed in the microwave field, both of which have been proven to be relatively accurate methods.[3,6]

Fig. 1 shows the conversion of NO to N_2 as a function of temperature over In–Fe_2O_3/HZSM-5(1 : 8 : 20) and In/HZSM-5(1 : 20) catalysts in microwave and conventional reaction mode. Although In/HZSM-5 exhibited high activity for NO conversion, it was inactive when operated in the microwave mode (not shown in Fig. 1). Probably, this is associated with the fact that the In/HZSM-5 has poor microwave absorption ability. On the other hand, NO conversion was very high and even reached 100% over the In–Fe_2O_3/HZSM-5(1 : 8 : 20) catalyst. Obviously the Fe_2O_3 component in this catalyst was responsible for the good activity. This can be attributed to the fact that Fe_2O_3 is a good microwave medium, so that microwave energy can be effectively converted into the activation energy of the reacting molecules adsorbed on the catalyst.

It is worthwhile to note that although the In–Fe_2O_3/HZSM-5(1 : 8 : 20) catalyst also showed high NO reduction activity in the conventional reaction mode, the reaction temperature needed was much higher than that in the microwave reaction mode. The mechanism of microwave catalysis is, as yet, not clear. However, it can be rationalized that a direct interaction of microwaves with the catalyst bed would cause a strong coupling between the microwave and the absorbing materials in the catalyst. Since the molecules in the gas phase are transparent to microwaves, no interaction will take place between the microwaves and the gaseous molecules. Our TPD experiments on Fe_2O_3 also agree well with the report of Otto and Shelef[7] that Fe_2O_3 is a good material for NO_x adsorption. Thus, it is speculated that a coupling may also occur between microwaves and the adsorbed polar NO_x molecules *via* Fe_2O_3, which is not only a good NO_x adsorber but also a microwave absorber. It has been reported that NO_2 plays an important role in the SCR of NO by hydrocarbon,[8,9] so coupling between microwaves and NO_2 molecules may weaken the NO–O bond and promote their activation and, in turn, greatly facilitate the activation of CH_4 by NO_2. As a result, it is reasonable to speculate that the activation energy of NO reduction by CH_4 on the In–Fe_2O_3/HZSM-5(1 : 8 : 20) will be reduced, so that the microwave-radiated reactor can operate at a lower temperature than the conventional reactor. It should be noted that although the In–Fe_2O_3/HZSM-5 was inactive for the NO + CH_4 reaction in the conventional reaction mode (not shown in Fig. 1), the reaction took place over this catalyst in the microwave reaction mode and the highest NO

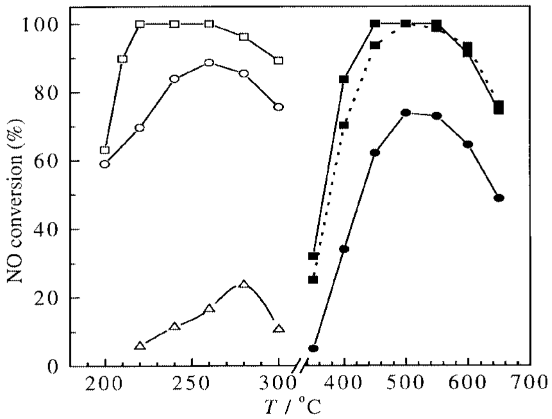

Fig. 1 NO conversions over In–Fe_2O_3/HZSM-5(1 : 8 : 20)(—) and In/HZSM-5(1 : 20)(----) in the microwave (open symbols) and conventional (filled symbols) reaction modes in the reaction systems NO + CH_4 + O_2 (squares), NO + CH_4 (triangles) and NO + CH_4 + O_2 + H_2O (circles).

conversion reached 23.6% (Fig. 1). This illustrates again that microwaves exhibit an effect on the activation of NO as the catalyst only chemisorbs NO_x.

The impact of H_2O on the NO conversion over the In–Fe_2O_3/HZSM-5(1:8:20) catalyst in both the conventional and the microwave reaction modes is also shown in Fig. 1. It is evident that the NO conversion suffered a more severe decrease in the conventional mode than in the microwave mode. As H_2O competes for the same adsorption sites as NO_x and inhibits the adsorption of the NO_x molecules, the catalyst will be deactivated in the presence of water vapor. However, H_2O is a strongly polar molecule and has a good microwave-absorbing ability, so that when H_2O molecules are adsorbed on the catalyst, they interact with the catalyst in the microwave field, leading to a strong coupling and resulting in the desorption of H_2O molecules from the adsorption sites, or in the weakening the adsorption of H_2O molecules on the catalytic surface. Therefore the microwave reaction mode provides the NO_x molecules with more adsorption sites than the conventional reaction mode when the feed contains water vapor. This suggests that microwave catalysis may lead to a new approach for the SCR of NO by hydrocarbons when dealing with feeds with high water content.

In conclusion, the In–Fe_2O_3/HZSM-5 catalyst shows some remarkable catalytic performances in the SCR of NO by CH_4 in a microwave field, indicating that microwaves have a beneficial effect on the activation of reacting molecules.

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Communication a909437g